

A Micro–mechanically Based Modeling of Double Network Hydrogels

Eine mikromechanisch basierte Modellierung von Doppelnetzwerk-Hydrogelen

Von der Fakultät für Maschinenwesen
der Rheinisch-Westfälischen Technischen Hochschule Aachen
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eines Doktors der Ingenieurwissenschaften
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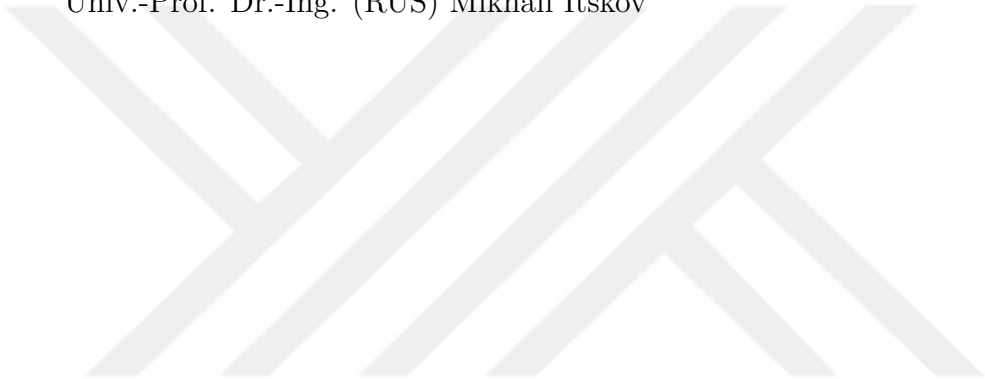
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Abstract

The present thesis deals with the constitutive modeling of double network hydrogels in –and after– the course of deformation. To this end, the thesis (i) studies the statistical mechanics of polymer chains and ideal chain models, (ii) introduces an evolution of the damage into the hyper-elastic model of the description of stress softening, (iii) characterizes yielding and necking instability, and (iv) demonstrates self-healing behavior.

In the introduction part, the entropic energy and entropic force of a single chain are derived based on Gaussian and non-Gaussian statistics. A hyper-elastic model is constituted in one-dimensional space. Using the method of integration over the unit sphere, one-dimensional strain energy of a hydrogel network is transferred to three-dimensions.

In the constitutive modeling of the stress softening phenomenon, the damage evolution concept is introduced. The double network hydrogel matrix is divided into polyelectrolyte and neutral polymer networks. A probability density function for the existence of a polymer chain in a polymer network is described based on Gaussian probability. The damage is defined as “permanent chain de-bonding” in a set of available chains.

A failure criterion is defined to describe yielding and necking in double network hydrogels. The force developed by a network in a particular direction is calculated based on the entropic force of a single chain and the number of active chains in a network. The double network hydrogel matrix is decomposed into three parts: clusters, chains between clusters and the neutral network. The failure criterion is applied to these parts. Sharp stress reduction and a plateau in the stress–stretch curve are represented.

The final element of the constitutive model is the description of the self-healing behavior of double network hydrogels after deformation. Said self-healing is related to the re-bonding of detached polymer chains. Internal kinetic energy and external energy sources are utilized in the re-bonding process. To model this, the double network hydrogel matrix is split into reversible and irreversible polymer networks. The number of re-bonded polymer chains is calculated using the Arrhenius equation and heat transfer equations. Lastly, reloading is described by taking re-bonded chains into account.

The model contains a small number of physically motivated material parameters. This thesis validates each modeling stage with experimental data regarding various double network hydrogels and achieves a high level of agreement between the model and experimental data.



Zusammenfassung

Die vorliegende Arbeit beschäftigt sich mit der konstitutiven Modellierung von Doppel-Netz Hydrogelen während und nach der Deformation. Zu diesem Zweck umfasst sie (i) das Studium der statistischen Mechanik von Polymerketten und idealer Polymerketten-Modelle, (ii) die Einführung eines Schadensmechanismus im hyperelastischen Modell zur Beschreibung von Spannungserweichung, (iii) die Charakterisierung der Nachgebens- und der Einschnürungsinstabilität und (iv) eine Beschreibung des Selbstheilungsverhaltens.

Im Einführungsteil werden, basierend auf sowohl gaußscher als auch nicht-gaußscher Verteilungsfunktionen, die entropische Energie und die entropische Kraft einer einzelnen Polymerkette hergeleitet. Ferner wird ein eindimensionales hyperelastisches Modell gegeben. Durch Integration über die Einheitssphäre wird die eindimensionale Formänderungsenergie eines Hydrogelnetzwerks auf drei Dimensionen übertragen.

In der konstitutiven Modellierung der Spannungserweichung wird ein Konzept der Schadensevolution eingeführt. Die Matrix von Doppel-Netz Hydrogelen wird in ein polyelektrolytes und neutrales Polymernetzwerk zerlegt. Eine Wahrscheinlichkeitsdichtefunktion für die Existenz einer Polymerkette in einem Polymernetzwerk wird auf Basis von gaußscher Wahrscheinlichkeit beschrieben. Der Schaden wird als die dauerhafte Polymerkettenablösung in einer Menge von verfügbaren Ketten definiert.

Ein Schadenskriterium wird definiert, um Nachgebens- und Einschnürungsinstabilität in Doppel-Netz Hydrogelen zu beschreiben. Die von einem Polymernetzwerk in eine bestimmte Richtung entwickelte Kraft wird auf der Basis der Entropiekraft einer einzelnen Kette und der Anzahl der aktiven Ketten in einem Polymernetzwerk berechnet. Die Matrix von Doppel-Netz Hydrogelen wird in drei Teile zerlegt: Cluster, Ketten zwischen den Clustern und das Neutralpolymernetzwerk. Das Schadenskriterium wird auf diese Teile angewendet. Dies ermöglicht scharfe Spitzen bei der Spannungsreduzierung und ein Plateau im Spannungs-Dehnungs-Diagramm.

Der letzte Teil der konstitutiven Modellierung ist die Beschreibung des Selbstheilungsverhaltens der Doppel-Netz Hydrogele nach der Verformung. Die Selbstheilung basiert auf dem Wiederverbinden freistehender Polymerket-

ten. Interne kinetische Energie und externe Energiequellen werden im Wiederbindungsprozess verwendet. Um dies zu modellieren wird die Matrix von Doppel-Netz Hydrogelen in ein reversibles und ein irreversibles Polymernetzwerk aufgeteilt. Die Anzahl der wiederverbundenen Polymerketten wird unter Verwendung der Arrhenius Gleichung und Wärmeleitungsgleichungen berechnet. Bei Wiederbelastung werden wiederverbundene Ketten berücksichtigt.

Das Modell enthält eine geringe Anzahl physikalisch motivierter Materialparameter. Alle Modellierungsschritte werden durch experimentelle Daten verschiedener Doppel-Netz Hydrogele validiert und eine gute Übereinstimmung zwischen dem Modell und den Daten wird erreicht.



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Aachen, September 2016

İsmail Doğan Külcü

Structure of the thesis

This thesis addresses the characterization of nonlinear inelastic behavior of double network hydrogels under/after deformation. There are a total of nine chapters, split into four parts, in addition to three appendices.

Part I begins with a short motivation expressing the significance of hydrogels and the need for a micro-mechanically motivated constitutive model. The following section consists of a brief introduction regarding hydrogels, tough hydrogel types, and mechanics of hydrogels.

Part II studies polymer physics and gives a brief overview of the concepts utilized in subsequent chapters. In Chapter 3, the mechanics of polymer chains are studied. The differences between Gaussian and non-Gaussian chains are depicted. Chapter 4 represents a hyper-elasticity model in a direction based on the entropic energy of Gaussian and non-Gaussian chains. For three-dimensional generalization a convenient numerical scheme is chosen among several numerical schemes of integration over the unit sphere.

The main contribution of the thesis is presented in Part III. In Chapter 5 a constitutive model for the stress softening phenomenon is established on the network decomposition concept and the continuum damage approach based on thermodynamic representation. A probability distribution of the polymer chain length is derived. The damage is described in the probability distribution by assuming the permanent rupture of polymer chains in their fully stretched state. In Chapter 6, the constitutive model of stress softening is extended to describe yielding and necking phenomena by considering a failure criterion of a network. A network is assumed to be destroyed when it starts to soften. Chapter 7 deals with the self-healing behavior of double network hydrogels. In a load-free double network hydrogel, it is assumed that re-bonding the detached reversible polymer chains results in self-healing. The number of re-bonded polymer chains is determined by the Arrhenius equation and heat transfer equations.

Part IV consists of the general conclusion, and appendices. Part II and III are supplemented by Appendices A and B. Appendix A summarizes the vector and tensor notation used in the thesis. Appendix B describes the kinematics and stress fields in the borders of continuum mechanics. Chapters are planned self-contained as far as possible. The nomenclature is provided

in Appendix C.



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*To my sister and my parents
Ahsen, Hasibe and Mehmet*



Part I

Introduction

1 Motivation

Hydrogels are excessively fluid absorptive polymers made up of chemically and/or physically cross-linked polymer networks. Due to their high water content, bio-compatibility and stimuli-sensitive polymer structure, they are utilized in a number of fields (i.e. tissue engineering, bio-medical, food, agriculture, cosmetic industries, etc.) and show promise in an even wider range of applications. The growing importance of hydrogels in regenerative medicine is due to the fact that living cells can survive in a hydrogel matrix. Despite the structural advantages of hydrogels for many industrial fields, conventional hydrogels suffer from a mechanical weakness that limits the large scale usage of hydrogels in particular applications that require load-bearing materials.

Engineering materials are mostly subjected to small or large deformation and expected to bear the load. For instance, a cartilage cannot be defined as hard tissue -unlike bones- and yet it carries a significant load. As a result, cartilage is one of the most damaged parts of the body, often necessitating surgery in middle-aged people. Cartilage has limited healing capacity, as cartilage cells, or chondrocytes, are bound in lacunae that do not exist in the damaged areas. The repair of cartilage requires a substrate in which chondrocytes can survive. In general, hydrogels are convenient environment for the enrichment and reproduction of cells. However, the mechanical weakness of hydrogels renders them unusable in cartilage defects. The mechanical issue persists in the implementation of hydrogels in other fields, for example, in use as conductors, gaskets, pharmaceutical component, and a substrate for hard and soft tissues. To become more useful in these context, hydrogels must be toughened.

The toughening of engineering materials can be performed in several ways, such as homogenization of the structure, supplementation with fillers, an use of sacrificial bonds. Many studies have been carried out over the last decade regarding hydrogel toughening, and tough hydrogel types have been produced as elastomeric gels. The mechanical properties of such gels are comparable to cartilage or industrial rubbers. Among tough hydrogel types, double network hydrogels are the toughest class of hydrogels due to high stiffness and the ability to dissipate large amounts of energy under deformation. However,

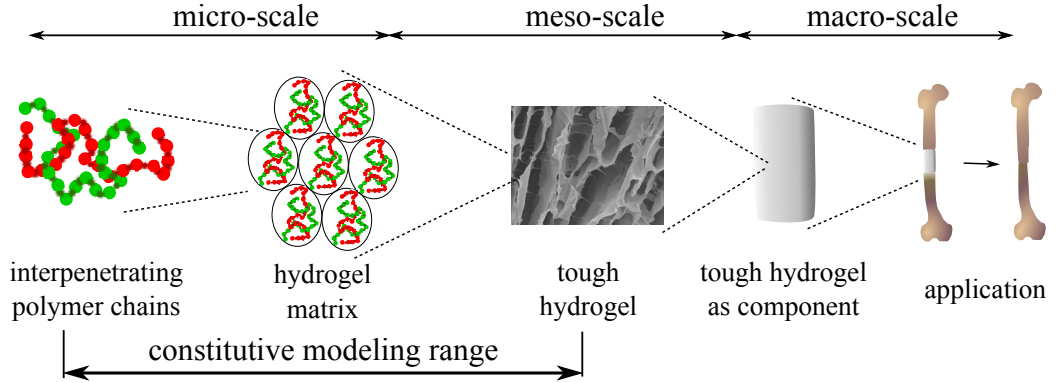


Figure 1.1: Schematic view of modeling range.

double network hydrogels exhibits non-linear inelastic behavior under large deformation showing stress softening, yielding and necking. The description of the non-linear inelastic behavior of elastomers is very complicated and challenging. Nonetheless, exploring the possible applications of tough hydrogel through, the investigation of the mechanical behavior of double network hydrogels is appealing.

Until quite recently, one of most significant deficiencies of double network hydrogels was its lack of self-healing behavior. After deformation, double network hydrogels did not undergo self-recovery and was therefore permanently damaged. Exchanging irreversible covalent bonding with reversible ionic bonds leads to self-healing behavior in the material. This improves the mechanical properties of the material with self-healing behavior induced by a heating process of the samples after deformation. The mechanical behavior of double network hydrogels even continues to exhibits the non-linear inelastic behaviors after the healing process.

The characterization of the mechanical behavior of double network hydrogels during and after its deformation in micro-scale is important to the material's real applications, and to enhance the mechanical properties with inverse engineering methods. However, to the best of our knowledge, micro-mechanical modeling of double network hydrogels has not yet been carried out.

The current thesis studies the micromechanics of double network hydrogels to close this gap in knowledge. The aim of this study is to develop a generalized micro-mechanically motivated constitutive model based on the continuum damage approach for double network hydrogels subjected to large deformation and subsequent shown self-healing. The model begins with the mechanics of polymer chains in micro-scale, and extrapolates it to the macro-

scale using the well-established concept of integration over the unit sphere (see Fig. 1.1). The modeling is planned stepwise, starting with a description of the stress softening and then adding the descriptions for yielding, necking and self-healing, gradually and respectively (see Table 1.1)

Table 1.1: Hydrogels to be studied in the thesis and their anticipated mechanical features

	Material	Mechanical properties
1	PAMPS/PAAm DN gel of 4% mol cross-linking in PAMPS	stress softening
2	Micro-gel reinforced PNI-PAm/PAAm DN gel	stress softening + yielding
3	PAMPS/PAAm of DN gel 2% mol cross-linking in PAMPS	stress softening + yielding + necking
4	Alginate/PAAm DN gel	self-healing

2 State of the art

2.1 Hydrogels

Hydrogels are polymeric gels that cross-link via physical and/or chemical cross-linkers. They are known for their extraordinarily absorptive, stimuli-sensitive and bio-compatible polymer structure. Hydrogels are important players in fields ranging from electronics to biology and from cosmetics to the food industry. In particular, the diffusible structure of hydrogels that permits the dissemination of cell nutrients in the matrix makes hydrogels one of the most vital materials for biological applications in near future. Therefore, the role of hydrogels in biology, in particular regenerative medicine as a substrate of damaged tissues, is expected to become more prominent [123].

One of the first biomedical investigations regarding hydrogel was reported after the development of poly(2-hydroxyethyl methacrylate) (PHEMA) as a contact lens material [138]. Polymethyl methacrylate (MMA), vinyl pyrrolidone (VP), metacrylate acid (MAA) -and their combinations- have been used as contact lens components [132]. Recently, use of polyvinyl alcohol (PVA) has become more common in contact lenses due to its better tension and elongation response compared to other contact lens materials. Subsequent applications have targeted hard-to-heal wounds, especially burn dressings due to the compatibility of hydrogels with dry and sloughy elements of a wound [14]. Applications of natural hydrogel, i.e. collagen, can be found as a component of wound dress in [23, 148].

Hydrogels -or "intelligent gels" - and their stimuli sensitivity can also be useful pharmaceutical applications [85]. Variation of swelling behavior due to their response to stimuli lies behind their main role in pharmacy. Such a property may lead to the prevention of symptoms resulting from late intervention. Thus, timely interference may be possible for terminal diseases, e.g. diabetic, asthma, etc. [115].

The latest statistical data demonstrates the need for a material that can be used as a substrate for artificial and regenerated tissues increases [114, 123]. Its similarities to soft tissues make hydrogel a convenient environment for cell immobilization; thus, hydrogels have been an apparently appealing component in tissue engineering. Lutolf et al. [92] proposed matrix enzyme-

sensitive hydrogel which reacts to matrix metalloproteinase (MMPs) a critical enzyme in cell behaviors such as cell proliferation, migration (adhesion/dispersion), and host defense. They expressed that such synthetic material can be exploited for use in bone regeneration and demonstrated the efficacy of their development in healing rat calvarial defect. Bakshi et al. [8] targeted the development of an artificial material that can be used for spinal cord injury. They implanted a non-biodegradable hydrogel, either PHEMA or PHEMA, synthesized in brain-derived neurotrophic factor (BDNF), which is one of the key proteins for a rat's central nervous system. The results of their proposal and observations meant that within 4 weeks, PHEMA had been adjusted for human use, and the cellular response against artificial material was eliminated, thus readying for use as a scaffold for spinal cord injury. Belkas et al. [12] reported that PHEMA-MMA hydrogel synthesized for nerve conduits maintained its structural integrity for up to 8 weeks and some of hydrogel tubes only experienced downfall at 16 weeks. Correspondingly, they reported that the material would be re-designed according to collapse-by-time, even though they worked well until the structural failure. Williams et al. [139] noted the applicability of polyethylene glycol (PEG)-based hydrogels as a scaffold for mesenchymal stem cells (MSCs) which are placed in bone, cartilage, and fate cells. Yasuda et al. [149] based their proposal on double network hydrogel that had similar mechanical properties to cartilage, and showed that in 4 weeks rabbit cartilage could be regenerated. Slaughter et al. [123], Hoffmann [65], Jen et al. [79], Peppas et al. [114] are some of the excellent reviews that can be consulted for more information about biomedical and regenerative medicine applications for hydrogels. Numerous studies have also recently shown that hydrogels can be used several fields with differing aims, such as their use as conductors in soft electronic devices, components in cosmetics and food, and as seals or gaskets [24].

2.2 Hydrogel compositions

Hydrogels can be synthesized from different resources, hence the categorization of hydrogels as natural, synthetic, and hybrid hydrogels, based on their composition.

- *Natural hydrogels* are formed from biological sources such as collagen, fibrin, and alginate. Depending on origin and usage aim, natural hydrogels are able to provide different kind of physical and chemical properties for several biomedical applications due to their biodegradability and low toxicity. For example, cell encapsulation [79], wound healing

[23], and drug delivery [85] can be achieved using natural hydrogels. Among the natural hydrogels, collagen is the most known and studied due to its status as a key protein for the mammalian cell and the lack of chemical modification necessary for the derivation of collagen [65].

- *Synthetic hydrogels*, first synthesized to handle the problems resulting from the usage of plastics in body [138], can be produced using various chemical methods depending on the required properties, e.g. orthogonal step-growth cross-linking, and chain-growth. The main advantages of synthetic hydrogels are its easy to modify chemical structure and the ability to synthesize different hydrogels by, for example, changing the cross-linking density or molar ratio of component. Polyhydroxyethyl-methacrylate (PHEMA), polyvinyl alcohol (PVA), polyethylene glycol (PEG), polyacrylamide (PAAm) are the most widely studied and used synthetic hydrogels types [49].
- *Hybrid hydrogels* are the combinations of synthetic hydrogels and biological assets for the purpose of specifying the necessary properties, for example PAAm-alginate [126], PEG-peptides [22].

2.3 Tough hydrogels

Materials are toughened using different methods, such as adding fillers, inserting sacrificial bonds into the system, or homogenizing the structure. These methods have been utilized to toughen hydrogels over the last decade and they lead hydrogels to exhibit excellent mechanical features comparable to industrial-filled rubbers and load-bearing tissues (see Fig. 2.1). Tough hydrogels can be characterized under the compositions of synthetic and/or hybrid hydrogels as natural hydrogels are mechanically weak. Descriptions of some tough hydrogel types follow.

2.3.1 Nano-composite gel

Nano-composite gel (NC gel), which consists of organic polymer chains and inorganic clays, was developed by Haraguchi and Takehisa [60] (see Fig. 2.2-a). The inorganic clays are absorbent and play a crucial role as multifunctional cross-linkers. The number and type of inorganic clays are directly influential on the mechanical properties of the NC gel [59]. Depending on the types and numbers of components, NC gel shows hysteresis and yielding behaviors [58].

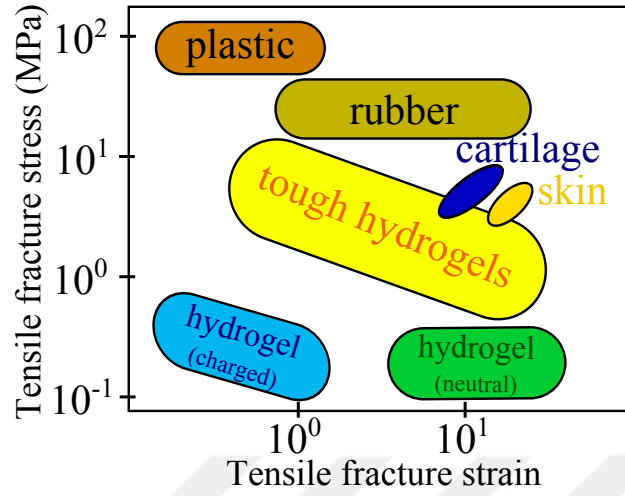


Figure 2.1: Comparison of tough hydrogels against conventional ones and the load-bearing tissues/materials [52, 88]

2.3.2 Slide-ring gel

Slide-ring gel (SR gel) was used by Okamura and Ito [112], and shows 100 kPa stress and 1100% elongation without defect. SR gel is proposed to occur as a polyrotaxane (PR) structure that is mainly based on the concept of a nearly homogeneous polymer matrix (see Fig. 2.2-b). The idea is proposed by De Gennes [37] in the mathematical form. In the concept, PR is a dumb-bell shaped structure where a polymer chain threads into a cyclodextrine (CD) molecule and the ends of the chain are covered by bulky ends [83]. CD molecules are bonded to each other chemically and provide a pulley effect. Furthermore, there is no connection between polymer chains [74]. Due to cyclic and movable CD molecules that are physical cross-linkers, stress localizations are prevented and thus, improved mechanical properties are observed. According to experimental results, SR gel has elastic behavior under tension and shows neither hysteresis nor yielding behaviors [96].

2.3.3 Tetra-PEG hydrogel

Creating a well-defined network structure, such as that observed in SR gels or in gels synthesized by γ -radiation, is an effective method of toughening hydrogels. Homogenization of physical cross-linking is relatively easy but as the cross-linking occurs randomly, the procedure cannot be strictly controlled. Sakai et al. [121, 48, 95] produced a gel consisting of tetrahydroxyl-

terminated polyethylene glycol (THPEG) and tetraamine-terminated polyethylene glycol (TAPEG), which have symmetric tetrahedron-like structure (see Fig. 2.2-c). When the macro-monomers are stoichiometrically used, entanglements in the polymer structure are almost absent and topological defects are prevented [3]. Therefore, mechanical properties are enhanced. The tetra-PEG gel behaves as an elastic network and hysteresis under cyclic loading is negligible, similar to SR gels [113].

2.3.4 Double network hydrogel

Double network hydrogel (DN gel) is developed by Gong et al.[53] and consists of highly cross-linked polyelectrolyte and loosely cross-linked neutral polymer networks (see Fig. 2.2-d). The toughening mechanism of DN gels is based on the sacrificial bond concept. The polyelectrolyte network acts role as a sacrificial network and serves as "skeleton" of the hydrogel matrix. The neutral network covers its polyelectrolyte counterpart and holds the structure together. To synthesize tough DN gel, the molar ratio of neutral to polyelectrolyte network must be around 20 [103]. The coupling between these polymer network can be controlled during the synthesizing procedure [105]. A connected DN gel (*c*-DN gel) is one in which chemical reactions appear between the DN gel networks. Truly independent DN gel (*t*-DN gel) is a DN gel synthesized in such a way that the chemical reactions between polymer networks are restricted and prevented.

In conventional DN gels polyelectrolyte network is a continuous network and is covalently cross-linked. Nonetheless, it is possible to produce DN gels by changing the shape and/or cross-linking type of polyelectrolyte network that leads to different mechanical properties. For example, micro-gel reinforced DN gel is produced in such way that the polyelectrolyte network is formed as "micro-gels" and dispersed throughout the neutral network [68]. In micro-gel reinforced DN gels, the energy dissipation under loading is more effective than in conventional DN gels.

To our knowledge, the best mechanical response among tough hydrogels in terms of stiffening and the toughening is observed in DN gel [52]. The DN gel may exhibit 17.2 MPa comprehension stress, 1 kJ/m² fracture stress, and up to 1500% elongation with 90% water content. In addition, the DN gel shows non-linear, inelastic behavior similar to that observed in filled-rubbers and soft tissues. Under quasi-static cyclic loading stress softening, yielding and necking behaviors are observed. Per these mechanical features, it has the closest mechanical properties and behaviors to load-bearing tissues like

cartilage of any of the tough hydrogels [106].

In this study we gradually deal with the mechanical behavior of DN gels under and after deformation. Chapter 5, 6, and 7 are mainly involved with non-linear inelastic behavior of DN gels whereas the mechanics of DN gels are discussed in the following section.

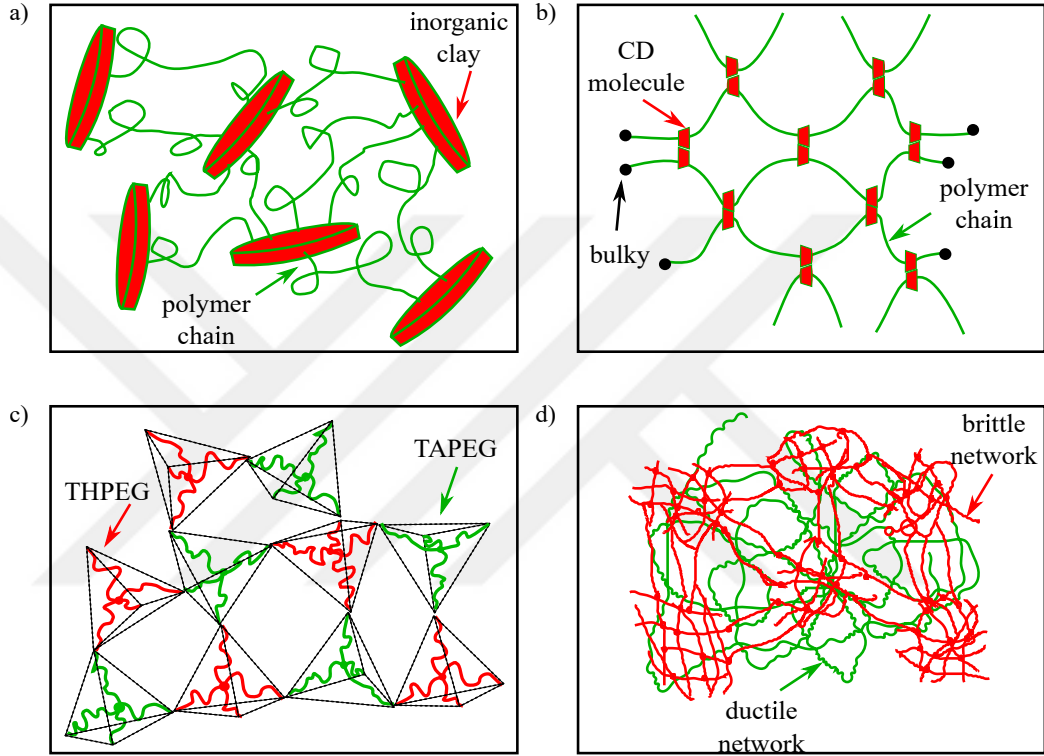


Figure 2.2: Schematic view of tough hydrogels. a) Topological gels. b) Nanocomposite gel. c) Tetra-PEG gel. d) Double network hydrogel.

2.4 Mechanics of hydrogels

2.4.1 Swelling

Since hydrogels were known as mechanically weak polymers with high water content until the last decade, the first investigations of hydrogels from the mechanical point of view was mainly related to their swelling and deswelling behaviors. The Flory-Huggins mixing model [72, 46] is widely utilized in the field of swelling mechanics of polymers to explore the interaction between the polymer network and the solvent. Applying the lattice model to the matrix in

which each segment occupies a lattice site, Flory and Huggins independently derived a mathematical model for polymer solutions that takes into account the molecular size of polymer segments in the entropy of polymer-liquid mixture. Although many assumptions are made in the Flory-Huggins mixing model, such as assuming an invariable polymer molecules size, neglecting the inter-changeability of polymers and solvents in lattice, and a homogenous mixture of polymer and solution, the model generates utilitarian approach to clarify the experimental results.

In particular, Tanaka and Fillmore [129] performed one of the first studies in swelling mechanics of gels. They studied the kinetics of the gel swelling in a fluid using the equation of motion of the gel network. This demonstrated the diffusion coefficient using the characteristic time of swelling. Recently, swelling, deswelling and diffusion-deformation aspect of hydrogels have been studied extensively by numerous research groups [90, 26, 66, 28, 29, 7, 41].

During the synthesizing process a DN gel absorbs water and is saturated. If the damaged DN gel is placed in a water, it may absorb more water due to micro-structural damage [106]. However, during the experimental tests used to validate the model in Part III, the DN gel is not placed in a water under and after deformation, and does not experience further swelling. Additionally, under deformation the DN gel does not exude water and the water content remains unchanged [5]. Therefore, it should be noted that the swelling behavior of DN gels is not studied in the context of this paper.

2.4.2 Tensile behavior

Nonlinearity and incompressibility

Tough hydrogels are highly extensible materials which can handle up to 2200% strain values [126] before rupture. Although some of tough hydrogel types, such as SR gels, exceptionally shows linear-elastic behavior under tension, majority of tough hydrogels exhibit S - and J -shaped non-linear behavior under large deformation as observed in rubbers. The reason for such non-linear behavior is still not sufficiently imaginable. Nonetheless, the increase of the alignment of the polymer chains along the loading direction and accordingly increase of the number of chains responding to the deformation might lead to such behaviors.

In addition, water has high degree of incompressibility, and DN gels have a water content 90%. Furthermore, due to trapped water the DN gel matrix, the DN gel can be assumed as an incompressible material in terms of

modeling.

Stress softening

Under quasi-static cyclic large deformations tough hydrogels show the stress softening similar to one observed in filled rubber-like materials, so called the Mullins effect. The stress softening is the difference between loading and the unloading curves, which shows the energy dissipation in the material during the deformation. The energy dissipation of tough hydrogels, in particular DN gels, is more than 80% that is remarkably higher than filled rubbers [106]. Since the hydrogel matrix is mainly made up of water media, viscoelastic properties may be thought to be negligible. Therefore, the rupture of the cross-linkers may be shown as the reason for the stress softening phenomenon in the tough hydrogels [137, 106]. For more details, please refer to Chapter 5.

Yielding and necking instability

Yielding is a phenomenon caused by localized deformation. The yielded material is able to bear loads and dissipate more energy than non-yielding materials, exhibiting less (if any) stiffening under quasi-static loading. It is therefore observed in tough materials such as tough hydrogels. From mechanical characterization point of view, yielding behavior is essential. It is investigated in details regarding DN gels in Chapter 6.

Necking is observed as an instability in a small region of the material. In tough hydrogels, particularly DN gels, during the necking nearly constant nominal stress is observed. Further, when the small region of the material where the instability is observed is spread over the sample, the hardening is observed.

Self-healing

Self-healing behavior is defined as the ability to recover after deformation. Self-healing in tough hydrogels is mainly related to the reversible cross-linking procedure. For example; such behavior is observed where polymer chains are ionically linked to each other [126] or to clays [60]. However, tough hydrogels containing only covalent bonds does not show any healing behavior [137].

2.5 The complexity in modeling inelastic behavior of tough hydrogels

Constitutive modeling of elastomers is characterized by inelastic, temperature- and rate-dependent non-linear response. Although, elastomers have been extensively studied for more than 70 years, a consensus has not yet been reached as to the source of their mechanical response due to their complicated structure. Therefore, the first difficulty in the modeling of elastomeric tough hydrogels is establishing that the source of their mechanical behavior is plausible. Furthermore, tough hydrogels are relatively new materials, and more experimental investigation is necessary to understand their behavior under deformation. Another difficulty is the lack of experimental data, which leads to interpretation of their behavior with respect to other elastomer types that are studied more, such as filled rubbers.

Aside from these difficulties, the investigation of such materials requires interdisciplinary studies, and therefore, many fields, such as physics, statistical mechanics, and chemistry must melt into the same pot.



Part II

Polymer physics

3 Polymers and polymer chains

The mechanical investigation of polymers in micro-scale begins with the mechanics of a single polymer chain. To develop a micro-mechanical constitutive model for a class of polymers, we consider the statistical mechanics of a polymer chain as a critical point. In this chapter, we first discuss polymers, polymer types and polymerization methods. Then, we look into the mechanics of polymer chains based on Gaussian and non-Gaussian statistics. The free energy function of a single chain is also derived. For further, the classical polymer physics textbooks by Treloar [133] and by Rubinstein and Colby [120] are referred.

3.1 Polymers

A polymer is a macromolecule that consists of subunits, called monomers. Monomers are attached with covalent bonds to make polymer chains. Due to their broad range of features, polymers play a significant role in almost every aspects of life. For example, DNA and polyisoprene are both polymers, yet they display remarkably different physical and chemical properties. DNA is an important biological structure with a fundamental role in living things. Polyisoprene, also known as rubber, is a tough and highly extensible material with many applications in industry.

Polymers are commonly characterized into classes of thermoplastics, elastomers, and thermosets.

- *Thermoplastics* are a class of polymers that generally have high molecular weight. They may have crystalline, semi-crystalline, and amorphous structure due to their melting and critical temperatures. Their viscosity decreases when external heat is applied, and the curing process in which chemical bonds do not take place is reversible. Thermoplastics are therefore re-moldable.
- *Elastomers* are wide-meshed cross-linked polymers that are extensible and generally tough. The cross-linking density of elastomers significantly influences their extensibility and toughness. Under load, poly-

mer chains disentangle; however, after removal of the load, they relax and re-entangle due to their viscoelastic properties.

- *Thermosets* are tight-meshed cross-linked polymers that utilize irreversible chemical bonding in their curing process. Due to their highly cross-linked structure, remelting is prevented, which makes thermosets convenient for applications that require heat resistance and chemical stability.

The structure of polymers are generated by polymerization processes. The polymerization process varies due to the different kind of reaction mechanisms. Step-growth and chain-growth polymerization are the most significant mechanisms in polymerization techniques.

- *Step-growth polymerization* is made by stepwise intermolecular reactions between functional groups of reactants. Monomers react with dimer, trimer, or oligomer that have the same reactivity potential. This type of polymerization entails a repetitive condensation reaction, and proceeds by a rather small increase of the molecular weight of the polymers. To produce high molecular weight through this polymerization method, high conversion is necessary.
- *Chain-growth polymerization* is a kinetic chain reaction, and the process requires external source, such as energy or a catalyst, to activate the polymerization. Monomers react only with active centers of a growing chain, but not with each other. The active center may be a free radical, anion, or cation. A free radical is an atom, molecule, or ion that contains unpaired valency atoms. A variety of alkenes or dienes are polymerized by the free radical polymerization method. Ionic polymerization due to an anion or a cation takes place due to an ionic intermediate, and is generated by anionic or cationic initiators depending on the nature of the involved ions.
- *Copolymerization* is a process where two or more monomers are polymerized together. This may be considered a branch of both the step-growth and the chain-growth polymerization.

The molecular weight of a polymer on the extent of conversion of monomers is the significant difference between step-growth and chain-growth polymerization [109]. Chain-growth polymerization synthesizes homo-chain polymers, whereas step-growth polymerization produces hetero-chain polymers. Thermosets are generally formed by the step-growth method, while thermoplastics are generated by the chain-growth method.

The degree of polymerization characterizes the molar mass of a polymer, and is described as the number of monomers in a polymer structure. The molar mass and molar mass distribution are significant parameters of the mechanical and chemical properties of polymers. These parameters identify the size of polymer chains, which influences the melting point, density, crystallinity, tensile strength and extensibility of polymers [94]. Due to its importance, identification of polymer chains in the field of polymer physics is carried out extensively in the literature.

3.2 Polymer chains

A polymer chain is generated by repeating sub-units during the polymerization process and designating features of the polymer with size distribution. Long polymer chains build stronger materials than short chains due to the number of interactions between chains in the polymer matrix. Thus, the polymers (i.e. rubbers, tough hydrogels, etc.) are investigated in the mechanics of long polymer chains. However, chain conformations are complicated in the polymer matrix as the entanglement of long chains leads to many physical and chemical reactions.

3.2.1 Polymer chain conformations

Many correlations of polymer chains and segments exist within polymer chains due to complex structure of polymers. Therefore, many refinements must be carried out even for very simple models. In the literature several ideal chain models that exclude interactions between chain segments have been developed, such as freely jointed chain, freely rotating chain and worm-like chain models. This paper utilizes the freely jointed chain model (FJC) for its simplicity. The FJC model which is made up of n number of segments, each of fixed length, where the angle at each bond linking the segments is “free”.

In the FJC model, each chain may have different linking directions, and consequently different end-to-end directions. Thus, the average end-to-end distance r of an isotropic assemblage in a polymer chain with n segments ($n - 1$ bonds) is zero,

$$r_{n-1} = 0. \quad (3.1)$$

The simplest non-zero term is the mean-square end-to-end distance of chains,

$$\begin{aligned}
 r_{n-1}^2 &= r_{n-1} \cdot r_{n-1} = \sum_{i=1}^{n-1} r_i \cdot \sum_{j=1}^{n-1} r_j = \sum_{i=1}^{n-1} \sum_{j=1}^{n-1} r_i \cdot r_j \\
 &= \sum_{i=1}^{n-1} \sum_{j=1}^{n-1} l^2 \cos \theta_{ij},
 \end{aligned} \tag{3.2}$$

where l is the length of the bond between two consecutive segments, i and j denote different directions and θ_{ij} is the angle between the directions i and j (see Fig.3.1) [120].

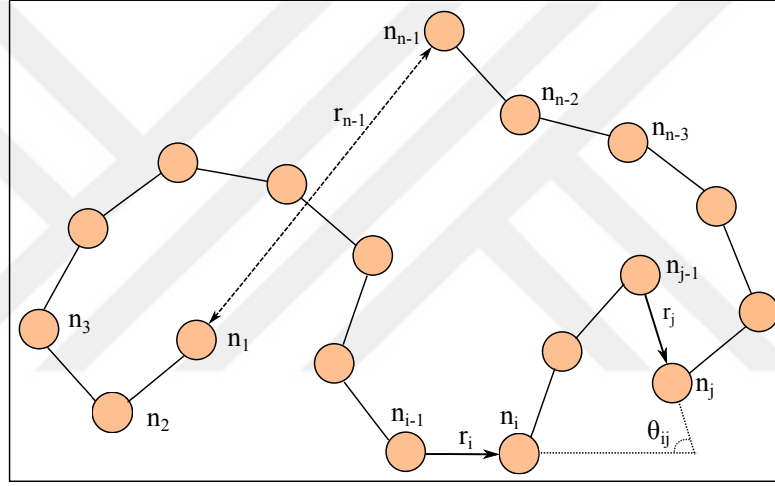


Figure 3.1: A polymer chain with n segments

Due to the uncorrelated directions of the neighboring bonds along the chain in the FJC model,

$$\cos \theta_{ij} = 0 \quad (i \neq j). \tag{3.3}$$

Therefore,

$$r_{n-1}^2 = (n-1)l^2. \tag{3.4}$$

The Flory's characteristic ratio is defined as the ratio of the number of bonds in a chain to the normalized mean square end-to-end distance of a chain, and is represented by

$$C_{n-1} = \frac{(n-1)l^2}{r_{n-1}^2}. \tag{3.5}$$

The characteristic ration is 1 for FJC model [45].

3.2.2 Gaussian chain

Distribution of end-to-end vectors based on Gaussian statistics

The mean square end-to-end distance of a polymer network is not sufficient to describe the properties of polymer chains, although it helps us to look into polymer network structure at first glance. Therefore, to look into more details, we focus on the probability density function of the end-to-end distance of a polymer chain in a network.

In one dimension, the number of possible bond conformations along the chain is 2^n . Furthermore, the probability $p(\frac{r}{l})$ is represented with the discrete binomial coefficients. The probability tends to 0 when the chain is fully stretched, and has the most disordered while $r_{n-1} \ll (n-1)l^2$. The Gaussian theory is sufficient for the representation of the end-to-end length distribution of a chain, if infinitesimal deformations are applied to the adequately long chain due to the fact that the behavior of a chain is linear up to $(r/l) < 0.2$, and conformations of chains can be assumed as isotropic.

For a very long chain ($n \rightarrow \infty$), the probability density function based on Gaussian statistics in a one-dimensional space is written

$$p(n, \bar{r}_x) d\bar{r}_x = \sqrt{\frac{3}{2\pi n l^2}} \exp\left(-\frac{3}{2n} \bar{r}_x^2\right) d\bar{r}_x, \quad (3.6)$$

where $\bar{r} = r/l$ and denotes the relative end-to-end distance of a chain. Eq. 3.6 can be generalized to 3D as

$$r^2 = r_x^2 + r_y^2 + r_z^2. \quad (3.7)$$

Thus, probability density per unit volume is represented

$$\begin{aligned} p(n, \bar{r}) d\bar{r}_x d\bar{r}_y d\bar{r}_z &= p(n, \bar{r}) d\bar{r} \\ &= \left(\sqrt{\frac{3}{2\pi n l^2}}\right)^3 \exp\left(-\frac{3}{2n} \bar{r}^2\right) d\bar{r}. \end{aligned} \quad (3.8)$$

In this case, the appropriate coordinate system is spherical coordinates (see [133]). Accordingly, the probability density in spherical coordinates is written as

$$p(n, \bar{r}) 4\pi r^2 dr = \left(\sqrt{\frac{3}{2\pi n l^2}}\right)^3 \exp\left(-\frac{3}{2n} \bar{r}^2\right) 4\pi r^2 dr \quad (3.9)$$

The free energies of polymer chains

The polymer chains are described using entropy rather than strain applied. The entropy is defined with Boltzmann's equation as

$$S = k \ln \Omega, \quad (3.10)$$

where k is a Boltzmann constant and Ω is number of conformations which is proportional to $p(n, \bar{r})$. Accordingly, due to the second law of thermodynamics, the Helmholtz free energy is written as

$$\psi = \mathcal{W} - TS, \quad (3.11)$$

where $\mathcal{W}$ is the energy of an ideal chain in an unperturbed state. For the Gaussian chain, Eq. 3.11 is

$$\begin{aligned} \psi_g &\approx -Tk \ln(p(n, \bar{r})) \\ &\approx \frac{3}{2}kT \frac{\bar{r}^2}{n}. \end{aligned} \quad (3.12)$$

The Helmholtz free energy is equal to the work done by the deformation. Thus, ψ can be defined using force and length as

$$d\psi = fdr - \mathcal{P}dV, \quad (3.13)$$

where f , $\mathcal{P}$ and V are the force applied to the system, pressure and volume, respectively. Considering the incompressibility condition ($dV = 0$), the chain force f is therefore shown for the Gaussian chain as

$$f_g = \frac{d\psi}{d\bar{r}} = \frac{3}{l}kT \frac{\bar{r}}{n}. \quad (3.14)$$

3.2.3 non-Gaussian chain

In the statistical treatment of chains using the Gaussian theory, the end-to-end distance is assumed to be very small in comparison to the fully stretched state. Therefore, this theory is used under very moderate deformations, and is adequate from the calculation point of view. However, polymers, in particular tough hydrogels, are subjected to large deformation, which can go up to 2000% strain, and Gaussian statistics is therefore not valid for such materials. Hence, we consider FJC model based in non-Gaussian theory, which takes into account the finite extensibility of a chain, and sufficiently describes the large deformations in polymers.

The inverse Langevin approximation

Non-Gaussian chain theory, also so-called the Langevin chain model, is based on the approximation of the inverse Langevin equation. The Langevin function is the simplified form of the Brillouin function that is developed to investigate the behavior of paramagnetic materials and the dielectric properties of insulators. The Langevin function is defined analytically as

$$\mathcal{L}(x) = \coth(x) - \frac{1}{x}. \quad (3.15)$$

The inverse Langevin function is utilized in statistical network models to describe the behavior of rubber-like materials under large deformations [54, 51, 33]. However, it is not possible to write a closed form of the inverse Langevin function. Therefore, in literature many numerical solutions can be found for the inverse Langevin function based on Taylor series expansion and rational approximation [133, 30, 116, 77, 78, 32]. Some of these solutions are as follows:

a) Treloar [133]:

$$\mathcal{L}^{-1}(y) = \frac{3y}{1 - \left(\frac{3}{5}y^2 + \frac{36}{175}y^4 + \frac{108}{875}y^6\right)}. \quad (3.16)$$

b) Cohen [30]:

$$\mathcal{L}^{-1}(y) = y \frac{3 - y^2}{1 - y^2}. \quad (3.17)$$

c) Puso [116]:

$$\mathcal{L}^{-1}(y) = \frac{3y}{1 - y^3}. \quad (3.18)$$

d) Darabi and Itskov [32]:

$$\mathcal{L}^{-1}(y) = y \frac{y^2 - 3y + 3}{1 - y}. \quad (3.19)$$

In our constitutive model, the Puso approximation [116] is used for the inverse Langevin function.

Distribution of end-to-end vectors based on non-Gaussian statistics

In 1942 a non-Gaussian probability density function based on the inverse Langevin approximation for a statistical network model was proposed by Kuhn and Gr  n [87] as

$$p(n, \bar{r}) = \frac{c}{l^3} \left(\frac{\sin \beta}{\beta} \right)^n \exp(-\beta \bar{r}), \quad (3.20)$$

where c is the normalization factor and β is calculated implicitly by the inverse Langevin approximation as

$$\beta = \mathcal{L}^{-1} \left(\frac{\bar{r}}{n} \right). \quad (3.21)$$

Using the Stirling's approximation ($\ln n! = n \ln n - n$), the logarithmic form of the probability density function is represented as

$$\ln p(n, \bar{r}) = \text{constant} - n \left(\frac{\bar{r}}{n} \beta + \ln \frac{\beta}{\sinh \beta} \right). \quad (3.22)$$

The free energies of polymer chains

The entropy can be written using Eq. 3.22 as

$$S = k \ln p(n, \bar{r}) = \text{constant} - kn \left(\frac{\bar{r}}{n} \beta + \ln \frac{\beta}{\sinh \beta} \right). \quad (3.23)$$

Accordingly, the Helmholtz free energy is shown as

$$\begin{aligned} \psi_{ng} &= \mathcal{W} - TS \\ &= kTn \left(\frac{\bar{r}}{n} \beta + \ln \frac{\beta}{\sinh \beta} \right). \end{aligned} \quad (3.24)$$

The chain force of a non-Gaussian chain is represented using Eq. 3.13 and incompressibility condition as

$$f_{ng} = \frac{\partial \psi}{\partial \bar{r}} = \left(\frac{KT}{l} \right) \mathcal{L}^{-1} \left(\frac{\bar{r}}{n} \right). \quad (3.25)$$

4 Full network models

Like elastomers, DN gels consist of polymer chains and have the ability to undergo large strain and exhibit nonlinear deformations [53, 146]. Therefore, the rubber elasticity is a physically meaningful way to understand and describe the elastic behavior of the polymer network in hydrogels. In the present chapter hyper-elastic ideal network models are presented using FJC based on Gaussian and non-Gaussian statistics. The results are then compared against experimental data shown in [146].

4.1 Introduction

The most significant feature of rubber-like materials is their ability to undergo large deformation without rupture. “Rubber elasticity” and “viscoelasticity” are two main elements useful to the investigation of the behavior of such materials. Due to deformation response of tough hydrogels, in particular DN gels, the rubber elasticity and viscoelasticity appear as an appropriate start to describe the behavior of DN gels. However, as DN gels are predominantly elastic and more than 90% of DN gel matrix is water, viscoelastic effects under tensile loading in such material with this media is inappreciable in comparison to the rubber elasticity. To this end, we will focus on rubber elasticity in order to characterize mechanics of DN gels.

In literature, many hyperelastic isotropic models have been proposed such as three-chain, four-chain, and eight-chain models. The advantage of these models is that they do not require any numerical integration. Therefore, these are very useful models where only hyperelastic behavior of rubber-like materials is being studied.

The three-chain model was first proposed by Wang and Guth [135], and describes the deformation of the polymer network with the affine deformation of three independent sets of chains parallel to the principle directions. The four-chain model was introduced by Flory and Rehner [47]. The four chains are at the corner of a regular tetrahedron and linked at the center of tetrahedron. The eight-chain model was developed by Arruda and Boyce [6]. In their model, the chains are located along the diagonals of a unit cube, and linked each other at the center of the cube. In general, most hyperelastic

models capture uniaxial deformation quite well, but do not account for pure shear and equibiaxial tensile deformations. An excellent review of hyperelastic models for rubber-like materials are given in Boyce and Arruda [16] and in the rubber elasticity textbook by Treloar [133].

4.2 Mechanics of a hyperelastic polymer network

Let us assume a purely elastic polymer network in which polymer chains are subjected to affine deformation. In this case, the deformation gradient in micro-scale $\mathbf{F}_m$ that is applied to the polymer chains is written as

$$\mathbf{F}_m = \mathbf{F} \quad (4.1)$$

where $\mathbf{F}$ is the deformation gradient applied on the macro-scale. The stretch χ applied to a network in the direction $\mathbf{d}$ is obtained by the right Cauchy-Green tensor $\mathbf{C}$ as

$$\begin{aligned} \chi^{\mathbf{d}} &= \sqrt{\mathbf{d} \mathbf{C} \mathbf{d}} \\ &= \sqrt{\mathbf{d} \mathbf{F}^T \mathbf{F} \mathbf{d}} = \sqrt{\mathbf{d} \mathbf{F}_m^T \mathbf{F}_m \mathbf{d}} \\ &= \lambda^{\mathbf{d}}, \end{aligned} \quad (4.2)$$

where $\lambda^{\mathbf{d}}$ is the micro-stretch applied in the direction $\mathbf{d}$. The change of the mean relative end-to-end distance is proportional to $\lambda^{\mathbf{d}}$. Thus, relative end-to-end distance in the current configuration is written as

$$\bar{r} = \lambda^{\mathbf{d}} \bar{r}_0, \quad (4.3)$$

where $\bar{r}_0$ is the mean relative end-to-end distance in the reference configuration. Hence, the energy of a single chain in the direction $\mathbf{d}$ is written as

$$\psi = \psi \left(n, \lambda^{\mathbf{d}} \bar{r}_0 \right). \quad (4.4)$$

Accordingly, the energy of a network in the direction $\mathbf{d}$ is represented as

$$\Psi = N \psi \left(n, \lambda^{\mathbf{d}} \bar{r}_0 \right), \quad (4.5)$$

where N is the active chain number in a network. From Eq. 3.12 and 3.24, energy of a network in the direction $\mathbf{d}$ is written based on the Gaussian and

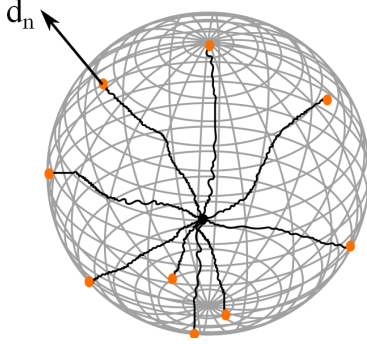


Figure 4.1: Illustration of the numerical integration over the unit sphere and integration directions

non-Gaussian statistics as

$$\Psi_g^d = N \frac{3}{2} k T n \left(\frac{d}{\chi} \bar{r}_0 \right)^2, \quad (4.6)$$

$$\Psi_{ng}^d = N k T n \left(\frac{d}{\chi} \bar{r}_0 \frac{1}{n} \mathcal{L}^{-1} \left(\frac{d}{\chi} \bar{r}_0 \frac{1}{n} \right) + \ln \frac{\mathcal{L}^{-1} \left(\frac{d}{\chi} \bar{r}_0 \frac{1}{n} \right)}{\sinh \mathcal{L}^{-1} \left(\frac{d}{\chi} \bar{r}_0 \frac{1}{n} \right)} \right), \quad (4.7)$$

where subscripts $\bullet_g$ and $\bullet_{ng}$ represents the Gaussian and non-Gaussian statistics.

4.2.1 Three-dimensional generalization using integration over the unit sphere

To generalize the one-dimensional energy of a purely elastic network to the three-dimensional space, the numerical integration over the unit sphere concept is used in present thesis (see Fig. 4.1). The numerical integration over the unit (micro) sphere enables us to generalize almost any one-dimensional model to three dimensions and, for this reason, represents a very powerful tool for constitutive modeling. However, as with any numerical procedure, the micro-sphere model is characterized by inherent errors. Moreover, it disturbs the initial material symmetry of the underlying model. Verron [134] recently suggested that the numerical integration scheme may cause enormous deviation from analytical solutions and must be chosen very carefully. Nevertheless, complicated micro-sphere constitutive equations demand the use of an integration scheme.

The numerical scheme by Bažant and Oh [11], in particular the numerical scheme with 21 points for the half-unit sphere, is widely utilized by the majority of studies. Heo and Xu [63] proposed a symmetric cubature formulae.

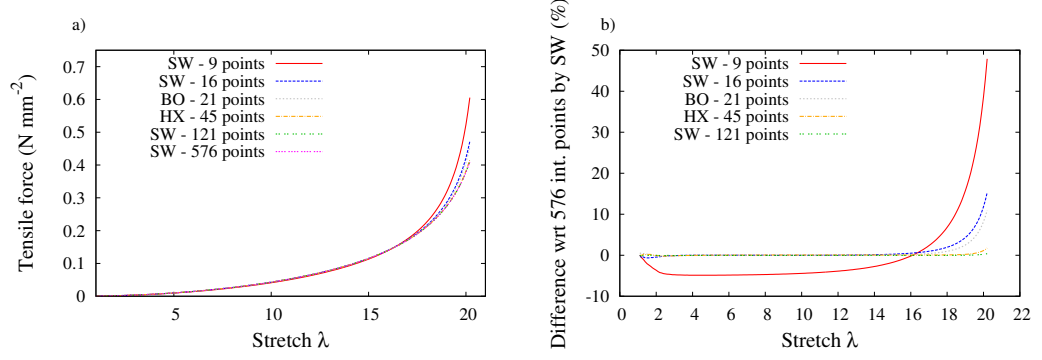


Figure 4.2: a) Comparison of the numerical schemes. SW: Sloan and Womersley [141], BO: Bažant and Oh[11], HX: Heo and Xu [63], b) Difference of the numerical schemes in percentage with respect to SW 576 integration points.

Ehret et al. [42] emphasized in their comparative study that the numerical scheme of Heo and Xu [63] with 45 integration points is the optimal scheme among several numerical schemes considering the accuracy and preservability of the initial material symmetry. Far from the field of rubber elasticity, Sloan and Womersley [124] developed an approximation on the sphere for the investigation of the earth's gravitational potential. Later, they proposed a method of extremal systems of points on the unit [125]. The points and weights of this study are available in [141].

Different numerical integration schemes are compared via the chain force derived using non-Gaussian statistics in Fig. 4.2-a. As expected in the linear part of the deformation all schemes matched. However, the numerical schemes with a fewer number of integration points deviated great deal in the non-linear part. Therefore, considering accuracy of schemes and computational costs (see Fig. 4.2-b), the numerical scheme of Bažant and Oh with 21 integration points for a half-unit sphere [11] was chosen for the numerical integration calculations in consecutive sections and chapters (see Table. 4.1).

The three-dimensional energy of a network is written by integrating Eq. 4.5 over the unit sphere S as

$$\Psi = \frac{1}{4\pi} \int_S \Psi \, d\mathbf{u}. \quad (4.8)$$

Table 4.1: The numerical scheme of Bažant and Oh [11] with 21 integration points for a half-unit sphere

i	x_i	y_i	z_i	ω_i
1	1	0	0	0.026521424
2	0	1	0	0.026521424
3	0	0	1	0.026521424
4	0.707106781187	0.707106781187	0	0.0199301476312
5	0.707106781187	-0.707106781187	0	0.0199301476312
6	0.707106781187	0	0.707106781187	0.0199301476312
7	0.707106781187	0	-0.707106781187	0.0199301476312
8	0	0.707106781187	0.707106781187	0.0199301476312
9	0	0.707106781187	-0.707106781187	0.0199301476312
10	0.387907304067	0.387907304067	0.836095596749	0.0250712367487
11	0.387907304067	0.387907304067	-0.836095596749	0.0250712367487
12	0.387907304067	-0.387907304067	0.836095596749	0.0250712367487
13	0.387907304067	-0.387907304067	-0.836095596749	0.0250712367487
14	0.387907304067	0.836095596749	0.387907304067	0.0250712367487
15	0.387907304067	0.836095596749	-0.387907304067	0.0250712367487
16	0.387907304067	-0.836095596749	0.387907304067	0.0250712367487
17	0.387907304067	-0.836095596749	-0.387907304067	0.0250712367487
18	0.836095596749	0.387907304067	0.387907304067	0.0250712367487
19	0.836095596749	0.387907304067	-0.387907304067	0.0250712367487
20	0.836095596749	-0.387907304067	0.387907304067	0.0250712367487
21	0.836095596749	-0.387907304067	-0.387907304067	0.0250712367487

Eq. 4.8 is carried out numerically as

$$\Psi = \sum_{i=1}^{21} \omega_i \Psi_{\mathbf{d}_i}, \quad (4.9)$$

where $\mathbf{d}_i = x_i \mathbf{e}^1 + y_i \mathbf{e}^2 + z_i \mathbf{e}^3$ in the orthonormal basis.

4.2.2 Constitutive equation for the ideal chain model

Considering the affine deformation $\left(\frac{\mathbf{d}_i}{\chi} = \frac{\mathbf{d}_i}{\lambda}\right)$, the first Piola Kirchoff stress tensor is written based on incompressibility condition as

$$\begin{aligned}\mathbf{P} &= \frac{\partial \Psi(\mathbf{F})}{\partial \mathbf{F}} - p\mathbf{F}^T \\ &= N \sum_{i=1}^{21} \omega_i \frac{\partial \psi(n, \bar{r}_0 \frac{\mathbf{d}_i}{\chi})}{\partial \frac{\mathbf{d}_i}{\chi}} \frac{\partial \frac{\mathbf{d}_i}{\chi}}{\partial \frac{\mathbf{d}_i}{\chi}} \frac{1}{2 \frac{\mathbf{d}_i}{\chi}} \frac{\partial \mathbf{C}(\mathbf{d}_i \otimes \mathbf{d}_i)}{\partial \mathbf{F}} - p\mathbf{F}^T\end{aligned}\quad (4.10)$$

where

$$\frac{\partial \psi(n, \bar{r}_0 \frac{\mathbf{d}_i}{\chi})}{\partial \frac{\mathbf{d}_i}{\chi}} = f \quad (\text{see Eq. 3.13}) \quad (4.11)$$

and

$$\begin{aligned}\frac{\partial \mathbf{C}(\mathbf{d}_i \otimes \mathbf{d}_i)}{\partial \mathbf{F}} &= \frac{\partial \mathbf{F}^T \mathbf{F}(\mathbf{d}_i \otimes \mathbf{d}_i)}{\partial \mathbf{F}} \\ &= 2\mathbf{F}(\mathbf{d}_i \otimes \mathbf{d}_i).\end{aligned}\quad (4.12)$$

Finally, the first Piola–Kirchoff stress tensor for the chains based on Gaussian $\bullet_g$ and non-Gaussian $\bullet_{ng}$ statistics are expressed as

$$\begin{aligned}\mathbf{P}_g &= f_g \sum_{i=1}^{21} \omega_i \mathbf{F}(\mathbf{d}_i \otimes \mathbf{d}_i) - p\mathbf{F}^T \\ &= 3NkT \frac{\bar{r}}{nl} \sum_{i=1}^{21} \omega_i \mathbf{F}(\mathbf{d}_i \otimes \mathbf{d}_i) - p\mathbf{F}^T,\end{aligned}\quad (4.13)$$

$$\begin{aligned}\mathbf{P}_{ng} &= f_{ng} \sum_{i=1}^{21} \omega_i \mathbf{F}(\mathbf{d}_i \otimes \mathbf{d}_i) - p\mathbf{F}^T \\ &= \left(\frac{KT}{l}\right) \mathcal{L}^{-1}\left(\frac{\bar{r}}{n}\right) \sum_{i=1}^{21} \omega_i \frac{1}{\frac{\mathbf{d}_i}{\chi}} \mathbf{F}(\mathbf{d}_i \otimes \mathbf{d}_i) - p\mathbf{F}^T\end{aligned}\quad (4.14)$$

4.2.3 Application of the ideal chain model to double network hydrogels

The model is compared to the experimental data of DN gel shown in [146]. The DN gel consists of poly(2,2'-disulfonyl-4,4'-benzidine terephthalamide)

and polyacrylamide, and is subjected to tensile loading of up to 20 stretch values. At high stretch values, the material shows highly non-linear behavior. Therefore, the non-Gaussian chain model for the behavior of such materials is more appropriate than the Gaussian chain model (see Fig. 4.3).

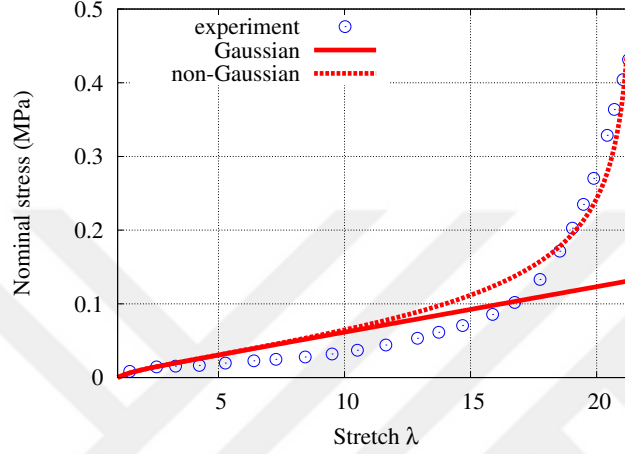


Figure 4.3: Comparison of hyperelastic models against the experimental data of the DN gel shown [146]. $NkT = 3.2 \cdot 10^{-7}$, $\bar{r} = 11$, $n = 240$ and $l = 200$ nm.

4.3 Concluding remarks

In the present chapter, derivations of the classical Gaussian and non-Gaussian chain models in a direction have been shown. To consider all possible directions, the appropriate numerical integration scheme for a unit sphere was chosen. Finally, the Gaussian and non-Gaussian chain ideal models have been compared against experimental data of a highly extensible DN gel. As expected, both chain models were able to predict the behavior of said DN gel using less numerical integration points in the linear part. However, the non-Gaussian chain model provides a better approximation with a relatively high number of numerical integration points in the non-linear part. It should be noted that this chapter is presented for the sake of completeness of the modeling approach. Our contribution is represented in the following chapters.



Part III

Constitutive modeling

5 Stress softening in double network hydrogels

In this chapter, DN gel stress softening phenomena is investigated. Firstly, the industry standard for stress softening in rubbers and DN gels is briefly explained. Then, the network decomposition concept is applied, and the probability distribution of existence of a polymer chain for DN gel networks is obtained. Network re-orientation based on the network alteration concept is explained, and the constitutive equation is then developed for the DN gel matrix. Finally, the results are validated against experimental data for a DN gel.

5.1 Introduction

In general, elastomeric materials exhibit linear behavior under small deformations, whereas highly non-linear behavior is observed under large deformations. Some of elastomeric materials, such as filled-rubbers, also show the stress softening phenomenon under cyclic loading. The stress softening is the energy dissipated during loading, which results in the deviation between loading and unloading curves. The stress softening phenomenon was first investigated in filled rubbers by Mullins and his coworkers [101, 99, 100], and is known as the “Mullins effect”.

The Mullins effect is one of most studied phenomena in the field of rubbers. In the literature many constitutive models have been developed to describe this behavior (see [40]). Mullins and Tobin [101, 102] decomposed the rubber matrix into a soft and hard phase. The soft phase is responsible for the rubber’s elasticity, whereas the hard phase describes its stiffness. During deformation the hard phase is transformed to the soft phase. Following this approach, Qi and Boyce [117] developed an isotropic model using a scalar damage parameter. Wineman and Rajagopal [140] constituted an evolution equation based on Neo-Hookean material law, in which the governing equation describes the damage process in micro-structure. De Tommasi et al. [38] utilized the two-phase approach by considering the breakage of molecular bonds and chain rupturing from the work of Wineman and Rajagopal [140]. Ogden and Roxburg [110] proposed a phenomenological model based on pseudo elasticity. Elías-Zúñiga and Beatty [153, 43] enhanced the Ogden–Roxburgh

model by adding a damage function and applying it to the Gaussian and the non-Gaussian chain models shown in the chapter 4.

Cantournet et al. [25] related slipping and sliding of chains on another to the Mullins effect and obtained the reasonable predictions for stress softening. Bueche [20, 21] considered the stress softening to be a result of chain rupture. Another method of modeling stress softening is built on the idea of Bueche [20, 21], which is the continuum damage approach based on thermodynamic representation [122, 54]. Following the idea of Bueche [20], Govindjee and Simo [54, 55] decomposed the rubber matrix into crosslink-to-crosslink and particle-to-particle networks. The deformation history is based on the maximum stretch applied to a polymer matrix where the damage appears in the particle-to-particle polymer network. The pure rubber network is assumed to be elastic and undamaged. Miehe and coworkers [98, 97, 51] extended this idea by applying the strain amplification concept to the tube model of Kaliska and Henrich [62] to obtain anisotropy. Instead of the three-chain model used in the model of Govindjee and Simo [54], they generalized the strain energy function using a numerical integration scheme with 21 points per half-unit sphere. Diani et al. [39] proposed a model based on the network alteration concept [93], which defines the material directions. The model is able to describe stress softening, residual stretch after deformation, and anisotropy. Dargazany and Itskov [34] proposed a model based on the decomposition of the polymer matrix into two parts as shown in the model of Govindjee and Simo [54] and the network alteration theory [93]. The de-bonding of polymer chains from the filler surface is assumed to be the reason for the damage during deformation. The model is able to predict stress softening, residual stretch appearing after the cyclic loading, and the strain-induced anisotropy. Further, the model is extended to describe hysteresis, which is the difference between the unloading and the reloading curves [35]. In this study, the damage and the healing of filler agglomerates [86] are taken into account to describe hysteresis.

Although many studies have been carried out to define and describe the Mullins effect, the reason for this phenomenon in elastomers is still nebulous.

In general, one does not expect hydrogels to show the Mullins effect-like behavior due to their mechanically weak and brittle structure. Nonetheless, after the development of tough hydrogel types, Webber et al. [137] have shown that a double network hydrogel, which is made up of polyelectrolyte PAMPS and neutral PAAm polymer networks, shows remarkable stress softening under the deformation (see Fig. 5.1). However, unlike elastomers, re-loading curves match the previous unloading curve, which implies that af-

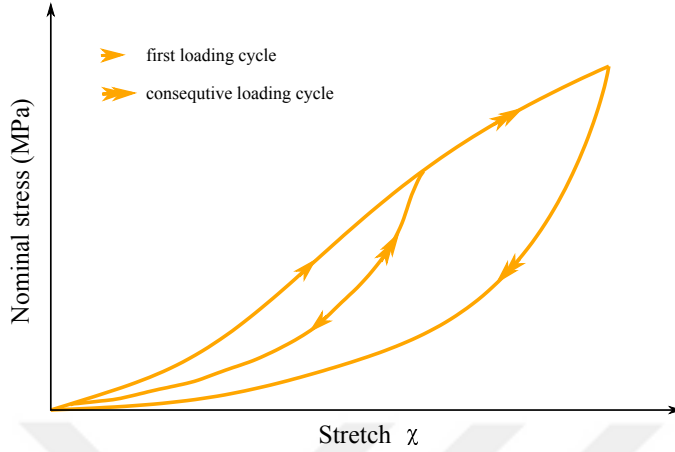


Figure 5.1: The schematic view of stress softening observed in DN gels

ter the loading cycle, the material does not heal itself [137]. Understanding the source of such behaviors in these exceptional materials is very important to the creation of new designs with these materials using inverse engineering techniques and fulfills the required properties for applications. This is what self-healing behavior in the material.

The stiffness of PAMPS/PAAm DN gel is similar to the stiffness of the polyelectrolyte PAMPS network, and the stress softening is observed after the stretch $\chi > 1.4$. This stress softening is similar to the damage observed in single PAMPS network [137]. During the deformation, decrease of the stiffness has also shown the similar behavior with the single PAMPS network. The damage is thus often associated with the damage in PAMPS network, whereas PAAm network is like sticky solvent keeps the structure together. To illustrate, one might think the polyelectrolyte network as the skeleton of the material, whereas the neutral one is the filling.

The DN gel contains ca. 90% water with no filler inside. Therefore, the damage may appear as the rupture of cross-links [137, 130]. Consequently, first hydrogel models attributed the stress softening and the damage only to the highly cross-linked polyelectrolyte network [130, 17]. The undeformed network was assumed to be linear elastic whereas the elasticity modulus decreases due to the nucleation and propagation of multiple cracks. In a further model [136], the high fracture energy, the Mullins effect, and yielding of a DN hydrogel were described on the basis of the Ogden-Roxburgh pseudo-elasticity model [110]. Later, Zhao [152] proposed a model based on the Arruda-Boyce eight chain model [6] and the network alteration concept [93] for interpenetrating polymer networks (IPN). The IPN matrix decomposed

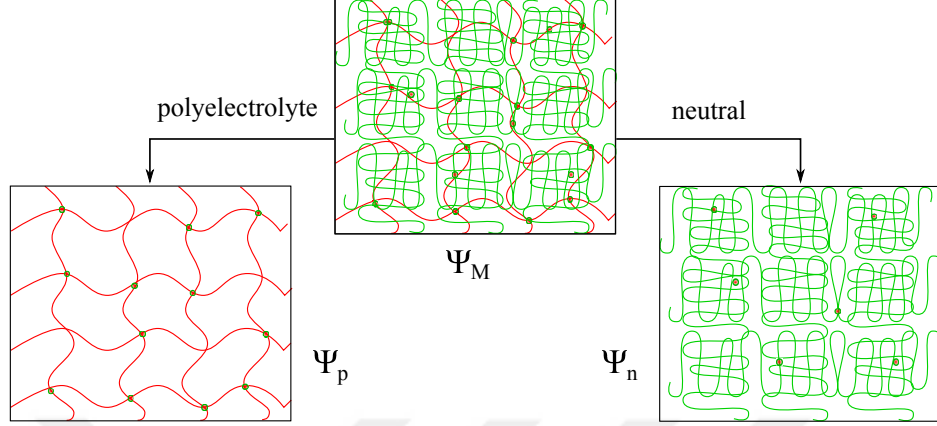


Figure 5.2: Micro-structure of a DN hydrogel (PAMPS/PAAm of 4% mol cross-linking in PAMPS) characterized by stress softening: illustration of the network decomposition

into long and short chain networks. The damage is assumed to appear with respect to the chain length. The model is validated with the experimental data shown in [137].

5.2 Modeling

The modeling is based on the continuum damage approach. In the modeling, the damage is considered as the de-bonding of cross-links. The energy dissipation observed as stress softening is assumed to be the result of the energy used to de-bond cross-links. Also, chain de-bonding is considered to be permanent, and de-bonded chains do not contribute to the stress.

5.2.1 The first network decomposition

A DN gel matrix consists up of two different types of polymer networks. We assume that the sample is t-DN gel [106] and the interaction between these polymer networks is prevented. Therefore, the polymer matrix is decomposed into two parts: polyelectrolyte and neutral network (see Fig. 5.2). Then, the energy of a DN gel matrix Ψ_M is considered to be the total energy of polymer networks in the DN gel matrix as

$$\Psi_M = \Psi_p + \Psi_n, \quad (5.1)$$

where subscripts $\bullet_p$ and $\bullet_n$ represent the polyelectrolyte and neutral networks, respectively. Considering the number of active chains in a network N , the energy of DN gel matrix is rewritten as

$$\Psi_M = N_p \psi_p + N_n \psi_n, \quad (5.2)$$

where ψ is given in Eq. 3.24. Further, by integrating over the set of available chain D_A , the strain energy of chains in a particular direction $\mathbf{d}$ is formulated as

$$\Psi_M^{\mathbf{d}} = \int_{D_A^p} N_p \psi_p^{\mathbf{d}} dn + \int_{D_A^n} N_n \psi_n^{\mathbf{d}} dn, \quad (5.3)$$

where superscripts $\bullet^p$ and $\bullet^n$ represent the polyelectrolyte and neutral networks, respectively.

5.2.2 Probability density of a chain existence in a network and the chain de-bonding

The modeling of stress softening in DN gels is initially described with the chain orientation in one-dimensional space. The chain de-bonding is therefore assumed to appear with respect to the chain length, proceeding from the shortest chain to longer chains [50, 33]. Also, due to permanent de-bonding of chains, N reduces during deformation. The probability density function of the chain existence for a network over D_A is consequently needed in order to consider the change of N , and describe the damage evolution in the polymer matrix (see Fig. 5.3).

D_A is written as

$$D_A = \{n | n_{min} \lambda \leq n \leq n_{max}\}, \quad (5.4)$$

where n_{min} and n_{max} represent the minimum and maximum segment numbers, respectively. The latter one is taken as a material parameter. The shortest chain length is equal to the relative end-to-end distance of a chain. However, the entropic energy tends to infinity, if the chain is considered to be fully stretched. To prevent such singularity, an effective strength of a chain between two cross-linkers f^{eff} is introduced as

$$f^{eff}(n, \lambda \bar{r}) = \frac{kT}{l} \mathcal{L}^{-1} \left(\frac{\bar{r}}{n} \right). \quad (5.5)$$

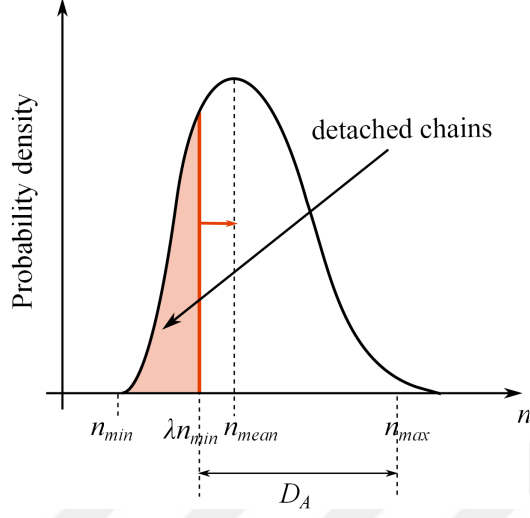


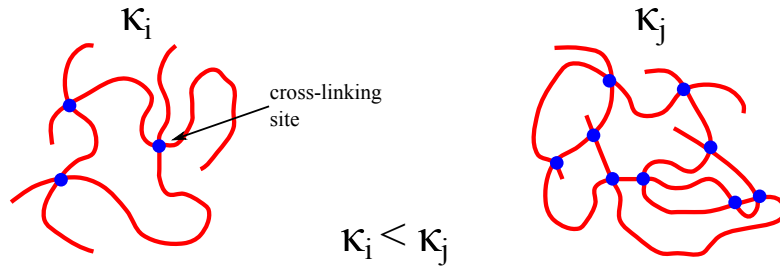
Figure 5.3: Schematic view of the probability density

Thus, the shortest available chain over D_A written as

$$n_{min} = n_{min}^{eff}(\lambda) = \frac{\lambda \bar{r}}{\mathcal{L}\left(\frac{f^{eff}_l}{KT}\right)}. \quad (5.6)$$

$\left[\mathcal{L}\left(\frac{f^{eff}_l}{KT}\right)\right]^{-1}$ is considered as a material parameter, and represented by ν . ν is the sliding ratio [55, 54, 33], and is related to the energy dissipation due to chain de-bonding. In the case where ν tends to 1, the increase of the energy dissipation leads to infinity. To this end, ν is said to be > 1 in the calculations. Finally, the shortest chain length over D_A is expressed as

$$n_{min} = \nu \bar{r} \lambda. \quad (5.7)$$

Figure 5.4: Illustration for κ of a network

A Gaussian probability density function is sufficient, if the chain distribution is assumed to occur randomly in a polymer network. To this end, the probability density function for the existence of a polymer chain in a polymer

network is formulated as

$$\tilde{P}(n, \bar{r}) = \Delta \sqrt{\frac{3}{2n\pi l^2}} \exp\left(-\frac{3\bar{r}^2}{2n}\right), \quad (5.8)$$

where Δ is length of cross-linking, l is the length of a segment. In literature, the adsorption site separation distribution is introduced to take into account the cross-linking density of a polymer network. Govindjee and Simo [54] proposed a Gaussian distribution for the adsorption site separation distribution. To determine the mean and width of the underlying distribution, the visual inspection of electron micrographs of the material was suggested. Instead, we use the material parameter κ to define the cross-linking density of a polymer network (see [21]), and reformulate Eq. 5.8 as

$$\tilde{P}(n, \bar{r}, \kappa) = \kappa \Delta \sqrt{\frac{3}{2n\pi l^2}} \exp\left(-\frac{3\bar{r}^2}{2n}\right), \quad (5.9)$$

where κ is the density of cross-linking site of a polymer network and proportional to the cross-linking density of the polymer network (see Fig. 5.4). Assuming $\Delta = l$ [21, 33], the probability density function for the existence of a polymer chain in polymer network can be rewritten as

$$\tilde{P}(n, \bar{r}, \kappa) = \kappa \sqrt{\frac{3}{2n\pi}} \exp\left(-\frac{3\bar{r}^2}{2n}\right). \quad (5.10)$$

Govindjee and Simo [54] considered that if a chain, which consists of i number of segments (n_i), is assumed to be cross-linked at i^{th} segments, the previous segments n_k ($k = 1, 2, \dots, i-1$) are never cross-linked. This can be described mathematically as

$$P(n, \bar{r}, \kappa) = \tilde{P}(n, \bar{r}, \kappa) \underbrace{\prod_{i=1}^{n-1} (1 - \tilde{P}(n, \bar{r}, \kappa))}_{\prod_{i=1}^{n-1} \left(1 - \kappa \sqrt{\frac{3}{2i\pi}} \exp\left(-\frac{3\bar{r}^2}{2i}\right)\right)}. \quad (5.11)$$

Thus, Eq. 5.11 is carried out as

$$\begin{aligned}
 P(n, \bar{r}, \kappa) &= \tilde{P}(n, \bar{r}, \kappa) \exp \left[\sum_{i=1}^{n-1} \ln \left(1 - \kappa \sqrt{-\frac{3}{2i\pi}} \exp \left(\frac{3\bar{r}^2}{2i} \right) \right) \right] \\
 &= \tilde{P}(n, \bar{r}, \kappa) \exp \left[\int_{i=1}^{n-1} \ln \left(1 - \kappa \sqrt{-\frac{3}{2i\pi}} \exp \left(-\frac{3\bar{r}^2}{2i} \right) \right) di \right] \\
 &\approx \tilde{P}(n, \bar{r}, \kappa) \exp \left[\int_{i=1}^{n-1} \kappa \sqrt{\frac{3}{2i\pi}} \exp \left(-\frac{3\bar{r}^2}{2i} \right) di \right]. \quad (5.12)
 \end{aligned}$$

Finally, the probability density function can be represented as (cf. [54, 33])

$$P(n, \bar{r}, \kappa) = \kappa \sqrt{\frac{6}{\pi n}} e^B, \quad (5.13)$$

where

$$B = -A - \kappa \sqrt{\frac{24}{\pi}} \left[\sqrt{An\pi} \left[\operatorname{erf}(\sqrt{A}) - \operatorname{erf}(\sqrt{An}) \right] + \sqrt{n} e^{-A} - e^{-An} \right], \quad (5.14)$$

$$A = \frac{3\bar{r}^2}{2n}. \quad (5.15)$$

The probability density function of the existence of a polymer chain in a polymer network contains three different variables: n , $\bar{r}$ and κ . The effect of these variables is shown in Fig. 5.5. $\bar{r}$ and κ influence the probability distribution inversely. The probability distribution spreads widely with the increase of $\bar{r}$, whereas the same behavior is observed with the decrease of κ . In other words, either increase of the cross-linking density or decrease of the relative mean end-to-end distance leads to the decrease of the mean chain length of a network (see Fig. 5.5a-b). In Fig. 5.5c-d, n and κ are taken as material parameters and the probability distribution is considered as the function of only $\bar{r}$. Hence, it is observed that the mean $\bar{r}$ is proportional to n , whereas it is inversely proportional to κ . The effect of these variables to the probability distribution is reasonable from polymer physics point of view. Eq. 5.13 is sufficient, and is therefore used in the modeling.

5.2.3 The network reorganization

In a polymer network, a chain may be linked from many points along its length. These links can be characterized as active and de-active cross-links

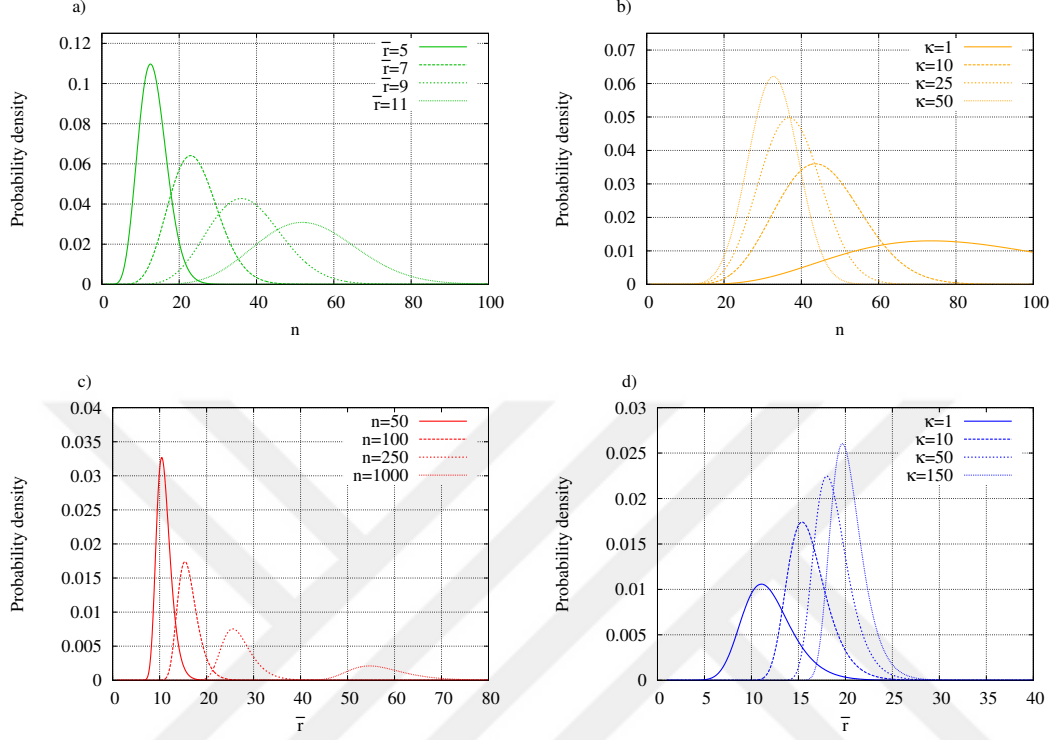


Figure 5.5: Schematic view of the probability distribution with different material parameters. a) $\kappa = 10$ b) $\bar{r} = 10$ c) $\kappa = 10$ d) $n = 100$.

(see Fig. 5.6). Under deformation active cross-links bear the load, whereas their de-active counterparts are load-free. The rupture of active cross-links actuates de-active cross-links. If a chain does not have any de-active bonds, the breakage of the last active cross-link causes dangling of the chain. Dangling chains are not able to bear load, and are assumed not to contribute to the stress.

As the number of active chains reduces during deformation, the following identity is written:

$$\int_{D_A\left(\frac{d}{\lambda}\right)} P(n, \bar{r}, \kappa) dn \leq 1. \quad (5.16)$$

To satisfy normalization condition, a normalization function $g\left(\frac{d}{\lambda_m}\right)$ is intro-

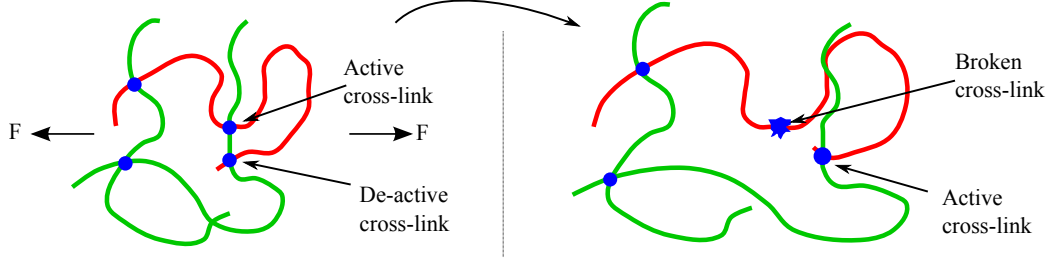


Figure 5.6: Illustration of active segment number in the probability distribution

duced as

$$g\left(\frac{d}{\lambda}\right) \int_{D_A\left(\frac{d}{\lambda}\right)} P(n, \bar{r}, \kappa) dn = 1. \quad (5.17)$$

Introducing the total number of active chains N_a in a network and the probability density distribution $g\left(\frac{d}{\lambda_m}\right) P(n, \bar{r}, \kappa)$, the number of fully stretched chains at a particular point in the deformed network is written as

$$N(n, \bar{r}, \kappa) = N_a g\left(\frac{d}{\lambda}\right) P(n, \bar{r}, \kappa) \quad (5.18)$$

$$= \tilde{N}\left(\frac{d}{\lambda}\right) P(n, \bar{r}, \kappa). \quad (5.19)$$

Marckmann et al. [93] proposed a network alteration theory for the complicated polymer structure. The idea is to assume constant active segment number in a network. Although the number of active chains during the deformation decreases, a chain containing de-active cross-links continues to contribute to the stress as the longer chain. In other words, more segments become active along the chain. Considering the decrease of the active number of chains and increase of the active segments proportional to each other, one may assume the active segment number in a polymer network remains constant under deformation as

$$\tilde{N}(\lambda_i)n(\lambda_i) = \tilde{N}(\lambda_j)n(\lambda_j) \quad (i \neq j). \quad (5.20)$$

Further, Chagnon et al. [27] extended the work considering the decrease of the number of active segments due to dangling chains. The approximation is carried out with an exponential function including two phenomenological constant. Therefore, the dangling of chains are neglected in the model, and the primarily proposed network alteration theory is used in the calculations.

The number of active segments at any deformation state is written as

$$\int_{D_A(\lambda_i)} \tilde{N}(\lambda_i) n P(n, \bar{r}, \kappa) dn = \int_{D_A(\lambda_j)} \tilde{N}(\lambda_j) n P(n, \bar{r}, \kappa) dn. \quad (5.21)$$

Let us assume an undeformed network ($i = 1$) as (see also Fig. 5.7)

$$\int_{D_A(\lambda_1)} \tilde{N}(\lambda_1) n P(n, \bar{r}, \kappa) dn = \int_{D_A(\lambda_j)} \tilde{N}(\lambda_j) n P(n, \bar{r}, \kappa) dn, \quad (5.22)$$

$$\tilde{N}(\lambda_j) = \frac{\tilde{N}(\lambda_1) \int_{D_A(\lambda_1)} n P(n, \bar{r}, \kappa) dn}{\int_{D_A(\lambda_j)} n P(n, \bar{r}, \kappa) dn}. \quad (5.23)$$

The nominator in Eq. 5.23 is shown as

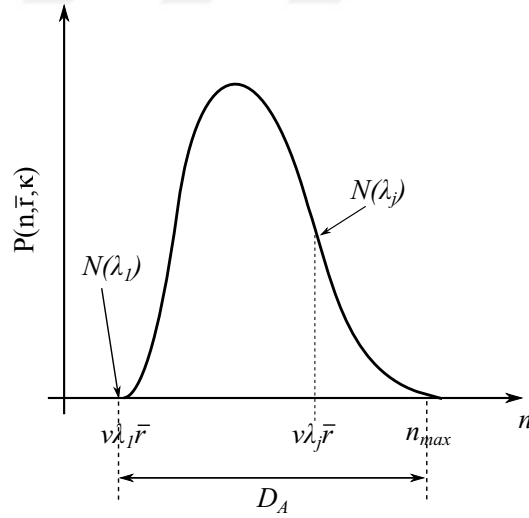


Figure 5.7: Illustration of bonding types in a polymer network

$$N_0 = \tilde{N}(\lambda_1) \int_{D_A(\lambda_1)} n P(n, \bar{r}, \kappa) dn, \quad (5.24)$$

where N_0 is the active chain number in the undeformed network. N_0 is calculated due to synthesizing process of the network as

$$N_0 = a \frac{N_A M}{n_{mean}}, \quad (5.25)$$

where N_A is Avagadro constant, M is molar ratio of the network, n_{mean} is the mean segment number that is obtained from the probability distribution (see also Fig. 5.3), and a is the active chain ratio in the network. Gong and co-workers [137, 106, 70] proposed an estimation for a due to the dissipated energy under cyclic loading. Due to synthesizing process the maximum number of cross-linking that may occur in the network is approximated. If one considers the dissipated energy as the result of the rupture of cross-links, the number of broken cross-linking is estimated.

Finally, the number of active chains at any point of the deformation is represented as

$$\tilde{N} \left(\frac{\mathbf{d}}{\lambda_j} \right) = N_0 \Phi \left(\frac{\mathbf{d}}{\lambda_j} \right), \quad (5.26)$$

where

$$\Phi \left(\frac{\mathbf{d}}{\lambda_j} \right) = \left(\int_{D_A \left(\frac{\mathbf{d}}{\lambda_j} \right)} n P(n, \bar{r}, \kappa) dn \right)^{-1}. \quad (5.27)$$

5.2.4 Final formulations for the stress softening

Let us assume the affine deformation for both networks as

$$\chi = \lambda. \quad (5.28)$$

Energy of a damaged network

The energy of a damaged chain in the direction $\mathbf{d}$ is written as

$$\psi_{\mathbf{d}} = \psi \left(n, \frac{\mathbf{d}}{\lambda} \bar{r} \right) \quad (5.29)$$

To calculate the free energy of the damaged network (Ψ), we take a relative end-to-end direction $\mathbf{d}$ and the number of active chains over D_A into account

as

$$\stackrel{d}{\Psi} = \int_{D_A\left(\stackrel{d}{\lambda}_m\right)} N(n, \bar{r}, \kappa) \psi\left(n, \stackrel{d}{\lambda} \bar{r}\right) \mathrm{d} n \quad (5.30)$$

$$= \int_{D_A\left(\stackrel{d}{\lambda}_m\right)} \tilde{N}\left(\stackrel{d}{\lambda}_m\right) P(n, \bar{r}, \kappa) \psi\left(n, \stackrel{d}{\lambda} \bar{r}\right) \mathrm{d} n, \quad (5.31)$$

where $\stackrel{d}{\lambda}_m$ is micro-stretch.

Substituting the Eq. 5.25 and 5.26 into 5.30, one can write the energy of a network in the direction $\mathbf{d}$ as

$$\stackrel{d}{\Psi} = a \frac{N_A M}{n_{mean}} \Phi\left(\stackrel{d}{\lambda}_m\right) \int_{D_A\left(\stackrel{d}{\lambda}_m\right)} P(n, \bar{r}, \kappa) \psi\left(n, \stackrel{d}{\lambda} \bar{r}\right) \mathrm{d} n \quad (5.32)$$

Generalization of the one-dimensional model to three-dimensions

As explained in chapter 4, the numerical integration scheme over the unit sphere is used to generalize the model from 1D to 3D. The numerical scheme of Bažant and Oh [11] is used (see Table 4.1). Thus, energy of the networks in 3D is written for polyelectrolyte and neutral networks as

$$\Psi = \frac{1}{4\pi} \int_S \stackrel{d}{\Psi}_{p,n} \mathrm{d} \stackrel{d}{u}, \quad (5.33)$$

$$= \sum_{i=1}^{21} \omega_i \stackrel{d_i}{\Psi}_{p,n}. \quad (5.34)$$

Thermodynamic consistency

The Clausius-Duhem inequality is a method to prove whether a constitutive equation satisfies the second law of thermodynamics in the system involving energy dissipation. Let us consider set of internal variables $\mathbf{\Omega}$ as shown in Section B.3. Since Eq. 5.32 contains only $\stackrel{d}{\lambda}_m$ as variable, $\mathbf{\Omega}$ is written as

$$\mathbf{\Omega} = \{\stackrel{d}{\lambda}_m: \mathbf{d} \in \mathbb{V} \wedge |\mathbf{d}| = 1\}. \quad (5.35)$$

Thus, 5.32 can be represented using the Clausius-Duhem inequality as

$$-\frac{\partial \Psi}{\partial \lambda_m} \cdot \left(\dot{\lambda}_m \right) \geq 0 \quad \forall \mathbf{d}. \quad (5.36)$$

During the loading $\dot{\lambda}_m > 0$. During unloading and reloading up to the maximum stretch applied in the primary loading $\dot{\lambda}_m = 0$. Thus,

$$-\frac{\partial \Psi}{\partial \lambda_m} \geq 0 \quad (5.37)$$

satisfies the Clausius-Duhem inequality for a damaged network in the DN gel matrix. Using the chain rule, Eq. 5.32 is adapted here as

$$\begin{aligned} & N_0 \frac{\partial \Phi \left(\dot{\lambda}_m \right)}{\partial \dot{\lambda}_m} \int_{D_A \left(\dot{\lambda}_m \right)} P(n, \bar{r}, \kappa) \psi \left(n, \dot{\lambda} \bar{r} \right) dn \\ & - N_0 \frac{\partial n_{min,d} \left(\dot{\lambda}_m \right)}{\partial \dot{\lambda}_m} \Phi \left(\dot{\lambda}_m \right) P(n_{min,d} \left(\dot{\lambda}_m \right), \bar{r}, \kappa) \psi \left(n_{min,d} \left(\dot{\lambda}_m \right), \dot{\lambda} \bar{r} \right) \leq 0, \end{aligned} \quad (5.38)$$

where

$$\frac{\partial \Phi \left(\dot{\lambda}_m \right)}{\partial \dot{\lambda}_m} = \frac{\partial n_{min,d} \left(\dot{\lambda}_m \right)}{\partial \dot{\lambda}_m} \frac{P(n_{min,d} \left(\dot{\lambda}_m \right), \bar{r}, \kappa) n_{min,d} \left(\dot{\lambda}_m \right)}{\left(\int_{D_A \left(\dot{\lambda}_m \right)} n P(n, \bar{r}, \kappa) dn \right)^2} \quad (5.39)$$

and $n_{min,d}$ is the minimum segment number in the deformed network and written as

$$n_{min,d} \left(\dot{\lambda}_m \right) = \nu \bar{r} \dot{\lambda}_m \quad (5.40)$$

Thus, Eq. 5.38 is represented as

$$n_{min,d} \left(\frac{\mathbf{d}}{\lambda_m} \right) \left(\int_{D_A \left(\frac{\mathbf{d}}{\lambda_m} \right)} P(n, \bar{r}, \kappa) \psi \left(n, \frac{\mathbf{d}}{\lambda} \bar{r} \right) dn \right) - \left(\Phi \left(\frac{\mathbf{d}}{\lambda_m} \right) \right)^{-1} \psi \left(n_{min,d} \left(\frac{\mathbf{d}}{\lambda_m} \right), \frac{\mathbf{d}}{\lambda} \bar{r} \right) \leq 0. \quad (5.41)$$

Eq. 5.41 holds under the condition shown in Eq. 5.16 as

$$n_{min,d} \left(\frac{\mathbf{d}}{\lambda_m} \right) < \left(\Phi \left(\frac{\mathbf{d}}{\lambda_m} \right) \right)^{-1} \quad (5.42)$$

and

$$\int_{D_A \left(\frac{\mathbf{d}}{\lambda_m} \right)} P(n, \bar{r}, \kappa) \psi \left(n, \frac{\mathbf{d}}{\lambda} \bar{r} \right) dn < \psi \left(n_{min,d} \left(\frac{\mathbf{d}}{\lambda_m} \right), \frac{\mathbf{d}}{\lambda} \bar{r} \right). \quad (5.43)$$

Constitutive equation

The first Piola-Kirchoff stress is written with respect to the incompressibility condition as,

$$\mathbf{P} = \frac{\partial \Psi_M}{\partial \mathbf{F}} = \frac{\partial \Psi_p}{\partial \mathbf{F}} + \frac{\partial \Psi_n}{\partial \mathbf{F}} - p \mathbf{F}^{-T}, \quad (5.44)$$

where p and $\mathbf{F}$ denote the arbitrary scalar parameter and the deformation gradient, respectively. Let us assume $\bar{r}$ and κ as material parameters and differ in the both networks. Finally, the first Piola-Kirchoff stress is written

as

$$\mathbf{P} = \sum_{i=1}^{21} \omega_i \left[\frac{\partial \Psi_p}{\partial \lambda} + \frac{\partial \Psi_n}{\partial \lambda} \right] \frac{1}{\lambda} \mathbf{F}(\mathbf{d}_i \otimes \mathbf{d}_i) - p \mathbf{F}^{-T} \quad (5.45)$$

$$= \sum_{i=1}^{21} \omega_i \left[N_p \binom{d}{\lambda_m} \int_{D_A^p \binom{d}{\lambda_m}} P(n, \bar{r}_p, \kappa_p) \frac{\partial \psi(n, x_p \bar{r}_p)}{\partial x_p} dn \right. \\ \left. + N_n \binom{d}{\lambda_m} \int_{D_A^n \binom{d}{\lambda_m}} P(n, \bar{r}_n, \kappa_n) \frac{\partial \psi(n, x_n \bar{r}_n)}{\partial x_n} dn \right] \frac{1}{\lambda} \mathbf{F}(\mathbf{d}_i \otimes \mathbf{d}_i) - p \mathbf{F}^{-T} \quad (5.46)$$

where x_p and x_n are replaced with $\frac{d_i}{\lambda}$ after the derivation.

5.2.5 Parameter study

The model contains 4 types of material parameters: n_{max} , ν , $\bar{r}$, κ . We first split these material parameters into two parts: matrix and network parameters. n_{max} and ν are taken as matrix parameters and assumed the same for the polyelectrolyte and neutral networks, whereas $\bar{r}$ and κ are network parameters, and are different for each network. Also, as mentioned above, κ is a material parameter depending on cross-linking density of the networks. To reduce the number of material parameters, and simplify the fitting procedure, one can determine the ratio of the cross-linking density of networks $\mathcal{C}$ from the synthesizing process of the DN gel. It is assumed that κ of the networks is proportional to $\mathcal{C}$ as

$$\kappa_p = \mathcal{C} \kappa_n. \quad (5.47)$$

The influence of material parameters on the modeling is shown in the Fig. 5.8. Decrease of the end-to-end distance stiffens the material, and the energy dissipation increases during the deformation. The same outcome appears if κ is increased. ν describes how close the breakage of the chain appears to the fully stretched state of a chain. If ν is 1, breakage appears at the fully stretch state and the entropic energy goes to infinity. Therefore, decrease of ν stiffens the material, and consequently energy dissipation increases. n_{max}

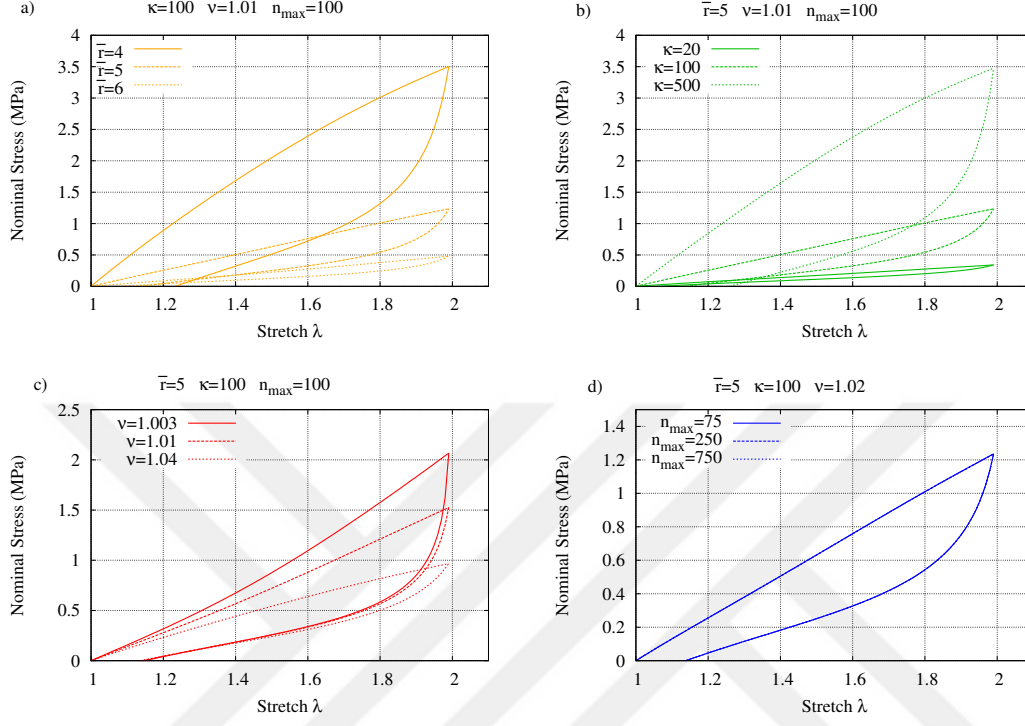


Figure 5.8: Influence of the material parameters on the modeling. Influence of a) $\bar{r}$ b) κ c) ν d) $n_{\max}$.

does not effect the result due to the fact that most of the broken chains are far from $n_{\max}$.

5.3 Validation

The DN gel consists of 1 mol AMPS of 4 mol% crosslinker and 2 mol acrylamide of 0.01 mol% cross-linker ($\mathcal{C} = 400$). Up to the complete failure of the DN gel sample, the fraction of the bonds remains below 1% (see [137]), consequently a must be chosen below 0.01. a is taken as 0.005 in the calculation. The molar ratio of the neutral network to its polyelectrolyte counterpart must be around 20 to produce a tough DN gel [53] ($M_p = 1$, $M_n = 20$). Due to the fact that the material is subjected to relatively small deformations (up to 71% strain), interactions between networks and the contribution of the neutral network to stress are negligible. To validate the model, the material parameters shown in 5.1 are used.

Fig. 5.9 describes the comparison of the model against experimental data

Table 5.1: Material parameters for DN gel showing softening

$\bar{r}_p$	$\bar{r}_n$	κ_p	n_{max}	ν
11.47	35	$5.57 \cdot 10^5$	83	1.034

shown in [137]. In the Fig. 5.9-a, two independent loading cycles are demonstrated. Using the material parameters given in 5.1, the model is able to predict these loading cycles. The Fig. 5.9-b exhibits the behavior of the individual networks in the modeling. The polyelectrolyte network is the main contributor to the stress. Due to loosely cross-linked and long-chain structure, the contribution of the neutral network to the stress is negligible. Finally, a high level of agreement between the model and experimental data is obtained.

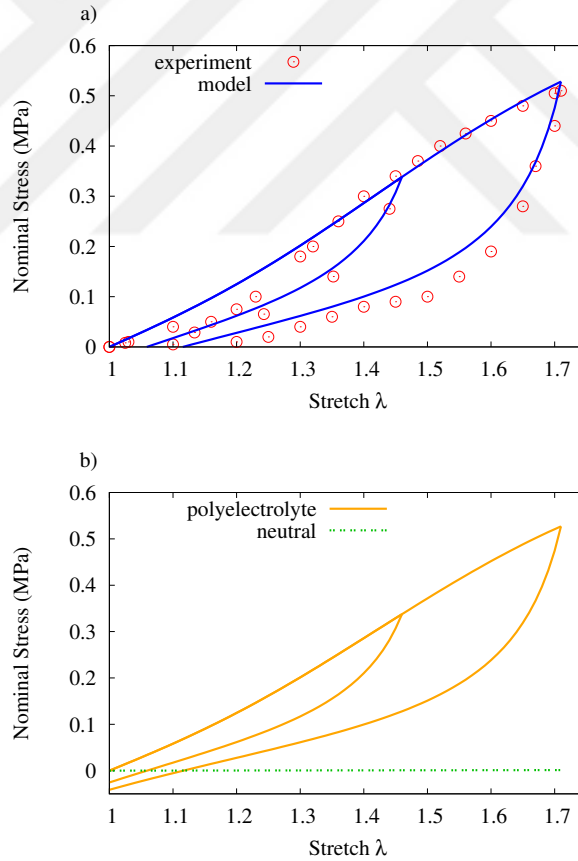


Figure 5.9: a) Comparison of the model against experimental data. b) Individual network behaviors in the modeling.

5.4 Concluding remarks

The present chapter described a model for the stress softening in double network hydrogels. A “continuum damaged approach” was applied in order to model non-linear inelastic behavior of DN gels. The polymer matrix is decomposed into parts due to the features of the polymer networks. The entropic energy based non-Gaussian statistics, Gaussian type probability density function and the network alteration were integrated in the modeling. To generalize the one-dimensional model, the concept of integration over the unit sphere was utilized. The model was validated with the experimental data and showed good agreement with experiments.

6 Yielding and Necking in double network hydrogels

The present chapter deals with the yielding phenomenon and necking instability observed in double network hydrogels (DN gels). In addition to the network decomposition concept based on the “continuum damage” approach shown in Chapter 5, a failure criterion is defined for a network and the strain reduction is included to describe the yielding and the necking instability. Finally, the results are validated against the experimental data of various DN gels.

6.1 Introduction

The yielding is a localized deformation of a material and it is an essential behavior that has to be identified and described to design any material. The yielding is usually associated with metals in engineering fields and is observed under small deformation due to the high stiffness of metals. Similar to metals, elastomeric polymers, in particular DN gels, show the yielding behavior as well under large deformation [91, 128].

The yielding phenomenon has various descriptions due to the stress-strain curve exhibited by real materials. For instance, the yielding point in metals, also named as the elastic limit is generally defined as the point where the material begins to deform plastically. Dislocations are initially locked by the solute atoms, hence the material is stiff and hyperelastic. Dislocations then move freely through the rupture of the interactions between solute atoms and dislocations, and then require less stress to deform. However, this description is not valid for polymers, in particular for DN gels due to the fact that DN gels show inelastic deformation before yielding as well [70]. Also, as 90% of the DN gel media is water [52], solute atoms may not be as effective as they are in metals.

In the following sections, the yielding point of a DN gel is defined as the transition of a linear stress-strain curve to a non-linear one. Thus, by looking into stress-strain diagram of the DN gel, the yielding point can generally be predicted at the point where the stiffness of the material is reduced, and the increase of the stress is non-existent [106] (or relatively less than the previous path [150]) (see Fig. 6.1). This behavior is similar to a phenomenon

called brittle-ductile transition (BDT) [2], which is investigated in the topic of elasto-plasticity.

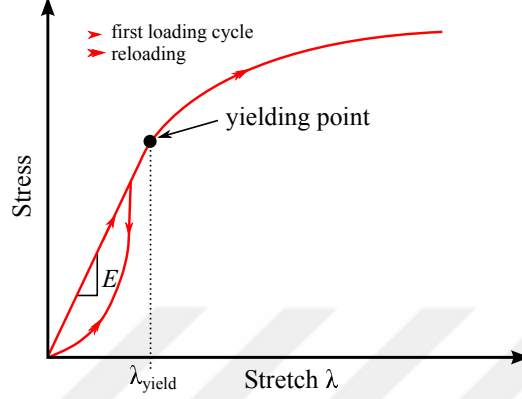


Figure 6.1: Stress-stretch curve of the yielding

In general, there are various factors influencing the BDT in polymers, and therefore the yielding point, such as molecular weight [18], temperature [9, 10], strain rate [80, 145], chemical interactions [143, 144, 80]. The BDT in polymers is mainly related to the interparticle distance [143]. Smaller interparticle distance leads higher yield stress and strain [81].

The BDT and the yielding point may be described by yielding criteria. In literature, the yield criteria are split into two parts due to the directional dependency of the material under deformation: isotropic and anisotropic yield criteria [82].

- Isotropic yield criteria in terms of principle stress $\sigma_1, \sigma_2, \sigma_3$
 - The *maximum principle stress theory* is proposed by Rankine and the simplest yielding criterion approach. The yielding occurs when the stress reaches the yield stress as

$$\max(\sigma_1, \sigma_2, \sigma_3) \leq \sigma_y. \quad (6.1)$$

- The *maximum principle strain theory* is proposed by St. Venant, and describes that the yielding appears when the maximum strain reaches the yielding strain as

$$\begin{aligned} \max(\sigma_1 - \nu(\sigma_2 + \sigma_3), \\ \sigma_2 - \nu(\sigma_1 + \sigma_3), \sigma_3 - \nu(\sigma_1 + \sigma_2)) \leq \sigma_y, \end{aligned} \quad (6.2)$$

where ν is Poisson's ratio.

- The *distortion energy theory* is known as Von Mises yield criterion. In the theory, the strain energy is decomposed into deviatoric (dev) and spherical (sph) parts as

$$\sigma = \text{dev}\sigma + \text{sph}\sigma, \quad (6.3)$$

where

$$\text{sph}\sigma = \frac{1}{3}\text{tr}(\sigma)\mathbf{I} = p\mathbf{I}, \quad (6.4)$$

$$\text{dev}\sigma = \sigma - \frac{1}{3}\text{tr}(\sigma)\mathbf{I} = \sigma - p\mathbf{I}, \quad (6.5)$$

p is the hydrostatic pressure and $\mathbf{I}$ is the identity tensor. Assuming that the material is characterized by pressure-independent plastic behavior, the criterion is written as

$$\frac{1}{6} \left((\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2 \right) \leq \tau_y^2. \quad (6.6)$$

Note that $\text{tr}(\text{dev}\sigma) = 0$, hence quadratic function is used.

- The *maximum shear stress theory* is also known as Tresca yield criterion, and assumes that the material yields when it exceeds the shear yield strength as

$$\tau = \frac{1}{2} \max(\sigma_1 - \sigma_2, \sigma_2 - \sigma_3, \sigma_3 - \sigma_1) \leq \tau_y \quad (6.7)$$

- *Total strain energy theory* proposes that yielding occurs when the total strain energy in the current configuration exceeds the the total strain energy in simple tension test as

$$\sigma_1^2 + \sigma_2^2 + \sigma_3^2 - 2\nu(\sigma_1\sigma_2 + \sigma_2\sigma_3 + \sigma_1\sigma_3) \leq \sigma_y^2. \quad (6.8)$$

- Mohr – Coulomb theory, Bresler Pister yield criterion, ..., etc.

- Anisotropic yield criteria in terms of principle stress $\sigma_1, \sigma_2, \sigma_3$

- The *generalized Hill yield criterion* [64] is generalized form of Von Mises yield criterion and written as

$$\begin{aligned} & A |\sigma_2 - \sigma_3|^k + B |\sigma_3 - \sigma_1|^k + C |\sigma_2 - \sigma_1|^k \\ & + D |2\sigma_1 - \sigma_2 - \sigma_3|^k + E |2\sigma_2 - \sigma_1 - \sigma_3|^k \\ & + F |2\sigma_3 - \sigma_2 - \sigma_1|^k \leq \sigma_y^k, \end{aligned} \quad (6.9)$$

where A, B, C, D, E, F and k material parameters.

- The *Hosford yield criterion* [67] is a generalization of the Von Mises yield criterion as

$$\frac{1}{2} |\sigma_2 - \sigma_3|^l + \frac{1}{2} |\sigma_3 - \sigma_1|^l + \frac{1}{2} |\sigma_2 - \sigma_1|^l \leq \sigma_y^l, \quad (6.10)$$

where l material parameter.

- Hill's quadratic yield criterion, The Caddell-Raghava-Atkins yield criterion, etc.

From a modeling point of view, the yielding behavior is investigated for metals [111, 1] and polymers [44, 15]. Estevez et al. [44] proposed a model to compare the crazing and shear yielding to identify the influence of these on the fracture toughness of glassy polymers. Richeton et al. [119, 118] investigated the influence of temperature and strain rate on the mechanical behavior of amorphous polymers. Boutaleb et al. [15] developed a micro-mechanical model for silica/polymer nanocomposites and applied their constitutive model to the finite element simulation. In the model, yielding is defined based on the classical Von Mises yield function and the model is able to predict the behavior of the material with different particles size and fractions.

In addition to the yielding, DN gels show the necking instability under tensile loading [106, 104, 107] (see Fig. 6.2). The stability of a material is characterized by a decrease of cross-sectional area due to Poisson's effect and strain hardening. The necking appears as an instability occurring due to the large number of strain localizations in a small region on the material and propagates along the specimen. The necking is generally associated with ductile materials. If a material is able to stabilize the necking region without failure, one can also observe the strain hardening after the necking part. The necking experimentally characterized using video-controlled tensile testing method by G'Sell et al. [57, 56] who express that the material is subjected to the plastic deformation in the necking region.

The modeling of necking instability has been an appealing challenge for the field of metal sheet forming to design materials with more complicated geometrical shapes [19, 31, 151]. In polymers, Tomita [131] proposed a model based on the eight chain model, the plastic shear rate developed by Argon [4] and a phenomenological function introducing entanglement of network chains. The model is able to predict the necking propagation indicated by the representative shear strain rate. To the best of our knowledge, there is no model predicting the necking instability in double network hydrogels available in current literature.

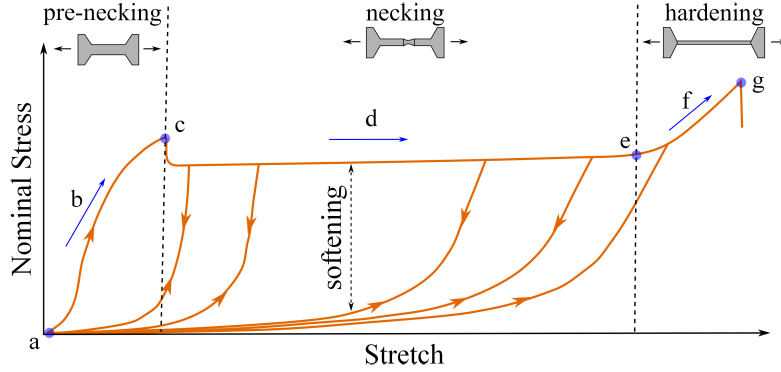


Figure 6.2: Schematic view of stress-stretch diagram of a DN gel exhibiting the necking instability

The deformation process in material showing necking usually splits into three parts: pre-necking, necking, and hardening (see also Fig. 6.2). The behavior of t -DN gels exhibiting necking instability in the these deformation stages is as follows [106]:

Pre-necking is the deformation stage where the material begins to deform. During pre-necking, the polyelectrolyte network deforms due to its charged and highly stretched structure. The polyelectrolyte network breaks into clusters and at the end of the pre-necking only clusters are left in this network. The neutral network does not respond to the deformation in pre-necking due to its sticky solvent-like structure. The inhomogeneous structure of the polyelectrolyte network is thought to be very important to the toughness of the material. Nakajima et al. [104] represented that if the polyelectrolyte network was produced with a homogenous structure via molecular stent method, the material undergoes a different fracture process. Thus, the amount of energy dissipation is reduces in the pre-necking, and yielding appears at higher strain values. To this end, it seems that inhomogeneity of the polyelectrolyte network is a key factor in the mechanical behavior of DN gel during pre-necking.

At the beginning of the necking, a sharp stress reduction is observed. During the necking clusters of the polyelectrolyte network respond to the deformation due to the load transferred by the neutral network chains, and split into smaller stiff splinters. Splinters are rigid and not damaged anymore. Due to the high strain values, the long and loosely cross-linked neutral network chains also stretch and contribute to the stress. In the necking stage, near-constant nominal stress is observed.

In the hardening stage, nominal stress increases. Hardening is presumed to

begin at the point when the material stabilizes itself, and the neutral network chains are oriented in the loading direction and are fully stretched.

6.2 Modeling

The modeling approach at this stage is built up on the description of the deformation stages in a DN gel with necking instability. In the model, in addition to stress softening, yielding and necking instability are also described by introducing a failure criterion for a network. Firstly, the damage is described as the chain de-bonding as explained in the stress softening model. The DN gel matrix is then decomposed into parts due to the deformation respond of polymer networks and polymer network parts, based on the concept of the network decomposition. A failure criterion is applied in order to introduce the yielding and the necking instability. Sharp stress reduction and stress plateau in stress/stretch diagram of the DN gel (see Fig. 6.2) are thus described.

6.2.1 Second network decomposition

As introduced in the stress softening model, the energy of a DN gel matrix is assumed as the total energy of the polyelectrolyte and the neutral networks. Although the DN gel consists of polyelectrolyte and neutral networks, the polyelectrolyte network contains parts responding to the deformation dissimilarly, which are clusters ($\bullet_{cc}$) and chain between clusters ($\bullet_c$) (see Fig. 6.3). To characterize the behavior of these parts during deformation, the polyelectrolyte network is therefore decomposed into two parts. Thus, the strain energy of a DN gel matrix (Ψ_M) is written as

$$\begin{aligned}\Psi_M &= \Psi_p + \Psi_n \\ &= \Psi_{cc} + \Psi_c + \Psi_n.\end{aligned}\tag{6.11}$$

6.2.2 Characterization of the yielding and the necking

In Chapter 5 the energy of a network in a particular direction is written by Eq. 5.32. To model the energy of a network in DN gel showing yielding and necking instability behavior, Eq. 5.32 is utilized due to the fact that

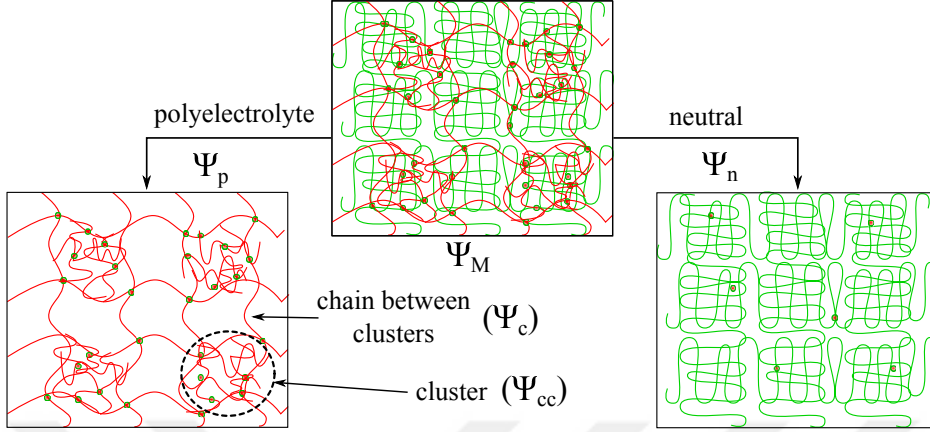


Figure 6.3: Micro-structure of a DN hydrogel (PAMPS/PAAm of 2% mol cross-linking in PAMPS) characterized by stress softening, yielding and necking instability: illustration of the network decomposition

the damage is assumed as the breakage of chain bonds, and the stress softening occurs in such materials as well. However, this consideration is not sufficient to explain the decrease of the stiffness that results the yielding and the necking instability inducing the sharp stress reduction at the end of the pre-necking.

As all chains between clusters are broken up to the end of pre-necking [106], the network of chains between clusters must be completely destroyed in the modeling. Furthermore, as the neutral network is expected to respond to the deformation progressively during the necking [130, 106], the contribution of the cluster network to stress must decrease in order to observe yielding exhibited as the stress plateau in the necking.

To describe these phenomena, a failure criterion is defined for networks of DN gels. The failure of a network due to the failure criterion causes sudden reduction in the stress, and the beginning of necking is thus described. The cluster network does not fail suddenly, unlike the network of chains between clusters. Hence, to introduce the failure of the cluster network incrementally, the cluster network split into sub-networks that have distinct mean relative end-to-end distances ranging from $\bar{r}_{cc,min}$ to $\bar{r}_{cc,max}$. Through different mean relative end-to-end distance of a network, the failure of the sub-cluster networks does not take place at the same time and appears gradually.

The number of active chains in a sub-cluster network $N_{0,cc,sub}$ is considered to be equal as

$$N_{0,cc} = \xi N_{0,cc,sub}, \quad (6.12)$$

where ξ is the number of sub-cluster network. The relative end-to-end distance of a sub-network is thus written as

$$\bar{r}_{cc,sub} = \bar{r}_{cc,min} + \frac{\bar{r}_{cc,max} - \bar{r}_{cc,min}}{\xi} i \quad (i = 1, 2, \dots, \xi). \quad (6.13)$$

Note that apart from $\bar{r}$ all other material parameters are assumed to be same for sub-cluster networks, and in calculations $\bar{r}_{cc,min}$ is taken as 1. Finally, the strain energy of the DN gel matrix is represented as

$$\Psi_M = \sum_{i=1}^{\xi} \Psi_{cc,sub,i} + \Psi_c + \Psi_n. \quad (6.14)$$

A failure criterion of a network

The force developed by a single chain reaches its critical value at the point where the de-bonding of the chain is assumed to appear. Therefore, using Eq. 3.25, the critical force of a network $\mathcal{F}$ in the direction $\mathbf{d}$ is written as

$$\begin{aligned} \frac{\mathbf{d}}{\mathcal{F}} \left(\frac{\mathbf{d}}{\lambda_m} \right) &= \int_{\nu \bar{r} \lambda_m}^{n_{max}} P(n, \bar{r}, \kappa) f(n, \bar{r} \frac{\mathbf{d}}{\lambda_m}) dn \\ &= \frac{KT}{l} \int_{\nu \bar{r} \lambda_m}^{n_{max}} P(n, \bar{r}, \kappa) \mathcal{L}^{-1} \left(\frac{\bar{r} \frac{\mathbf{d}}{\lambda_m}}{n} \right) dn \end{aligned} \quad (6.15)$$

where k is the number of chain directions. Accordingly, the force developed during the deformation in the entire network is written as

$$F = \sum_{i=1}^k \frac{\mathbf{d}_i}{\mathcal{F}}. \quad (6.16)$$

Considering Eq. 6.15 as a function of the stretch (see Fig. 6.4), one can state that the stiffness of the network increases up to a particular stretch point. After this point, which we further call as the 'critical stretch point', the network starts to soften. The critical stretch point λ_{cr} can be depicted as the extrema of Eq. 6.15 and characterized as

$$\frac{\partial \frac{\mathbf{d}}{\mathcal{F}}}{\partial \frac{\mathbf{d}}{\lambda}} = 0. \quad (6.17)$$

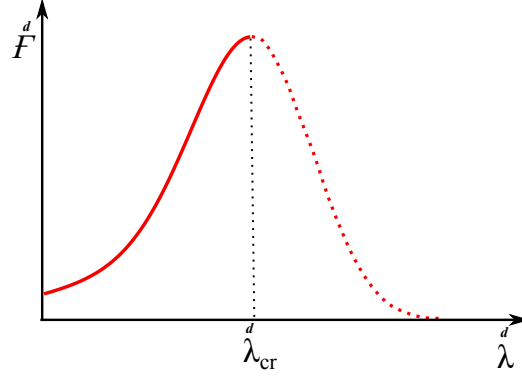


Figure 6.4: The schematic view of the critical force of a network in the direction $\mathbf{d}$.

λ_{cr} can be represented as the point where the stiffness of the network is zero. In the model, it is assumed that at λ_{cr} the chains of a network in the direction $\mathbf{d}$ is completely destroyed. Moreover, contribution of the network in the direction $\mathbf{d}$ is considered to be zero after λ_{cr}^d .

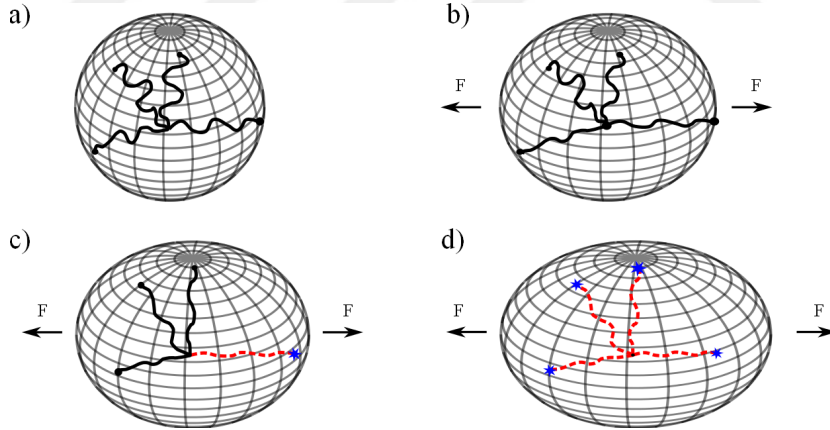


Figure 6.5: Illustration for the rupture of chains in a network. a) The virgin network. b) Deformation of the network. c) The rupture of the chains in a direction. d) the failure of a network.

In the numerical scheme for the integration of the unit sphere, the maximum load is carried by chains along the loading direction, which is also called the first principle direction. Therefore, chains along the first principle direction reach the failure point firstly (see Fig. 6.5). After the failure of a network chains in the principle direction, the force developed by de-bonded chains

must be carried by other directions as

$$F = \sum_{i=1}^k \frac{d_i}{\mathcal{F}} = \sum_{i=1}^{\check{k}} \frac{d_i}{\check{\mathcal{F}}}, \quad (6.18)$$

where $\check{k}$ and $\check{\mathcal{F}}$ are the number of active directions in the deformed network and the total force developed by different directions in a network containing destroyed chain directions, respectively. Also, it can be shown as $\check{k} \leq k$. This additional load coming from the destroyed directions influences active directions with respect to the directional coefficients, and leads them to pass over λ_{cr} suddenly. Therefore, active directions are also ruptured (see Fig. 6.6). The directional dependency of the failure of chains is related to the number of integration points in the numerical scheme of integration over the unit sphere. Increasing the number of points conduces to the failure of chain directions very close to each other. Due to this finding, one can conclude that if the principle direction is destroyed, the network can be assumed to be completely destroyed,

$$\frac{\partial \frac{d_1}{\mathcal{F}}}{\partial \lambda} = 0 \Rightarrow \frac{\partial F}{\partial \lambda} = 0. \quad (6.19)$$

Thus, the network does not contribute to the strain energy of the polymer matrix anymore, $\Psi = 0$. The sharp reduction in the stress/strain curve is correspondingly achieved.

Yielding appears when the stiffening of a network and the softening of another is balanced in the DN gel matrix. Therefore, yielding is assumed to start when the network containing sub-networks reaches the maximal stress, and then begins to soften. To this end, the maximal nominal stress of the network containing sub-networks is considered as the yielding point, and is written as

$$\mathbf{P}_y = \max \left(\sum_{i=1}^{\xi} \mathbf{P}_{sub,i} \right) = \max \left(\sum_{i=1}^{\xi} \frac{\partial \Psi_{cc,sub,i}}{\partial \mathbf{F}} \right), \quad (6.20)$$

where $\mathbf{P}_y$ and $\mathbf{P}_{sub}$ are the yielding stress and the nominal stress obtained by a sub network, respectively.

Non-affinity of cluster chains

Transition of macro-stretch χ to micro-stretch λ_m is a challenging topic for multi-scale modeling. Well-known approaches, e.g. affine deformation, strain

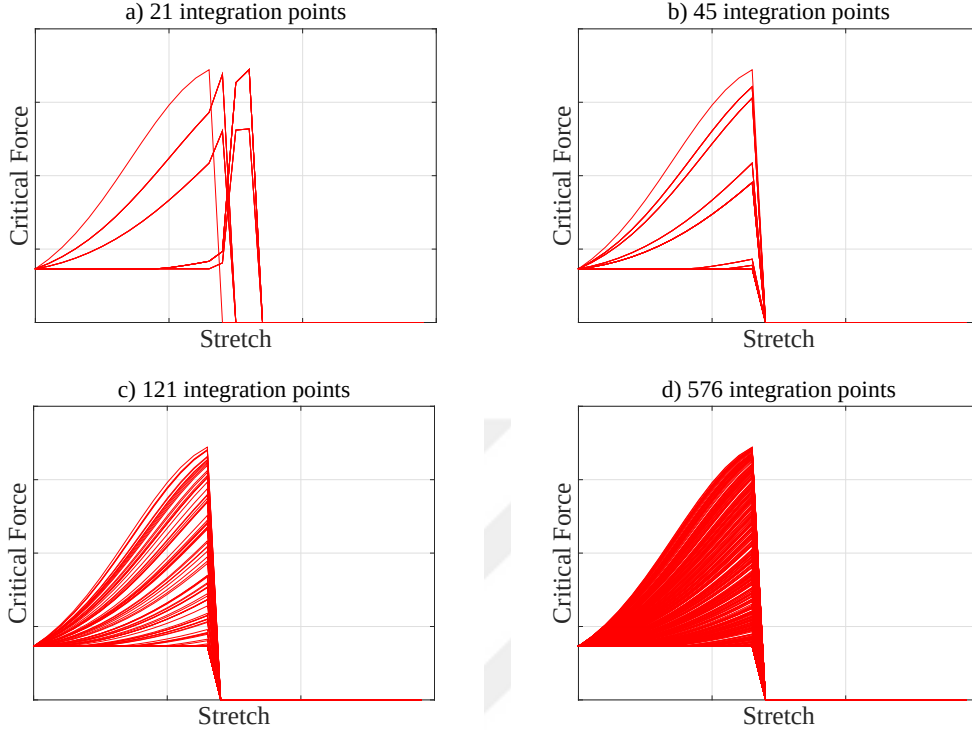


Figure 6.6: The failure of the directions. a) 21 integration points [11], b) 45 integration point [63], c) 121 integration points [141], d) 576 integration points [141].

amplification [61], are generally considered in constitutive models. In DN gels, the stretch obtained in a cluster-like structure is smaller than the stretch in other networks [68]. It is therefore not feasible to use affine deformation for all DN gel networks. As DN gels do not contain any filler and clusters cannot be taken as rigid, the strain amplification that is developed for materials filled by spherical rigid fillers is inappropriate.

Firstly, the DN gel matrix is idealized as illustrated in Fig. 6.7-b, and the affine deformation is assumed for the network of chains between clusters and the neutral network as

$$\chi = \lambda_{m,c} = \lambda_{m,n}. \quad (6.21)$$

Further, the ratio of the number of chains in a cluster to chains between two cluster is considered as

$$\mu = \frac{N_{0,cc}}{N_{0,c}}, \quad (6.22)$$

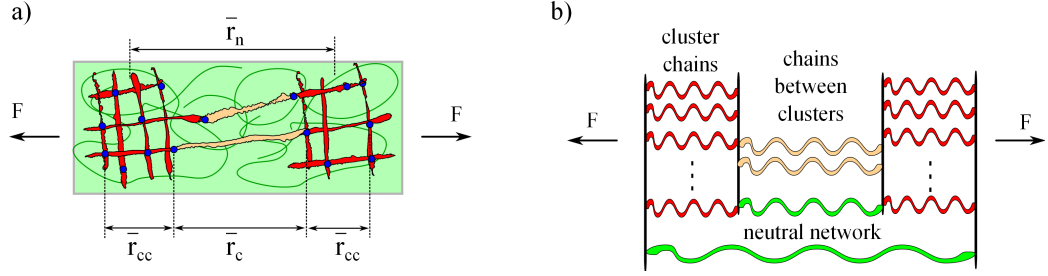


Figure 6.7: a) Schematic view of a DN gel. b) Idealized matrix of a DN gel

where μ is the stiffening ratio. The number of chains in a cluster is more than the number of chains between two clusters due to highly cross-linked structure. Therefore, as in spring systems, the stretch applied to a cluster network is taken inversely proportional to μ and the stretch applied to a cluster network is reduced as

$$\lambda_{m,cc} = \frac{\lambda_{m,c} - 1}{\mu} + 1 \quad (6.23)$$

$$= \frac{\chi - 1}{\mu} + 1. \quad (6.24)$$

Further, the relation between the number of polyelectrolyte network chains in clusters $N_{0,cc}$ and the number of active polyelectrolyte network chains between cluster $N_{0,c}$ is written using Eq. 6.22 and the total number of active chains in the polyelectrolyte network $N_{0,p}$ as

$$\begin{aligned} N_{0,p} &= N_{0,cc} + N_{0,c} \\ &= N_{0,cc} + \frac{1}{\mu} N_{0,cc}. \end{aligned} \quad (6.25)$$

Thus,

$$N_{0,cc} = \frac{\mu}{1 + \mu} N_{0,p}, \quad (6.26)$$

$$N_{0,c} = \frac{1}{1 + \mu} N_{0,p}. \quad (6.27)$$

6.2.3 Final formulations for the yielding and the necking with the stress softening

Generalization of the one-dimensional model to three dimensions

Using Eq. 6.11 and the integration scheme over the unit sphere with 21 points [11], the generalization of the model from $1D$ to $3D$ is carried out as

$$\Psi_M = \frac{1}{4\pi} \int_S \left(\sum_{i=1}^{\xi} \Psi_{sub,cc,i} + \Psi_c + \Psi_n \right) d\mathbf{u} \quad (6.28)$$

$$= \sum_j^{21} \omega_j \left(\sum_{i=1}^{\xi} \Psi_{sub,cc,i} + \Psi_c + \Psi_n \right). \quad (6.29)$$

Constitutive equation

The constitutive equation is developed by using the 'network decomposition', the 'network alteration', the 'stretch reduction concept', the failure and the yielding criteria.

The first Piola-Kirchoff stress is written considering the incompressibility condition as

$$\mathbf{P} = \frac{\partial \Psi_M}{\partial \mathbf{F}} = \frac{\sum_{i=1}^{\xi} \partial \Psi_{cc,sub,i}}{\partial \mathbf{F}} + \frac{\partial \Psi_c}{\partial \mathbf{F}} + \frac{\partial \Psi_n}{\partial \mathbf{F}} - p \mathbf{F}^{-T}. \quad (6.30)$$

Using Eq. 5.32 for networks with different material parameters, the first

Piola-Kirchoff stress of the DN gel matrix is formulated as

$$\mathbf{P} = \sum_{j=1}^{21} \omega_j \left[\frac{1}{\mu} \sum_{i=1}^{\xi} \frac{\partial \Psi_{cc,sub,i}}{\partial \frac{d_j}{\lambda}} + \frac{\partial \Psi_c}{\partial \frac{d_j}{\lambda}} + \frac{\partial \Psi_n}{\partial \frac{d_j}{\lambda}} \right] \frac{1}{\frac{d_j}{\chi}} \mathbf{F}(\mathbf{d}_j \otimes \mathbf{d}_j) - p \mathbf{F}^{-T} \quad (6.31)$$

$$\begin{aligned} &= \sum_{j=1}^{21} \omega_j \left[\frac{1}{\mu} \frac{N_{cc} \left(\frac{d_j}{\lambda_{m,cc}} \right)}{\xi} \sum_{i=1}^{\xi} \int_{D_A^{cc} \left(\frac{d_j}{\lambda_{m,cc}} \right)} P(n, \bar{r}_{cc,sub,i}, \kappa_{cc}) \frac{\partial \psi(n, x_{cc} \bar{r}_{cc,sub,i})}{\partial x_{cc}} dn \right. \\ &\quad + N_c \left(\frac{d_j}{\lambda_{m,c}} \right) \int_{D_A^c \left(\frac{d_j}{\lambda_{m,c}} \right)} P(n, \bar{r}_c, \kappa_c) \frac{\partial \psi(n, x_n \bar{r}_c)}{\partial x_n} dn \\ &\quad \left. + N_n \left(\frac{d_j}{\lambda_{m,n}} \right) \int_{D_A^n \left(\frac{d_j}{\lambda_{m,n}} \right)} P(n, \bar{r}_n, \kappa_n) \frac{\partial \psi(n, x_n \bar{r}_n)}{\partial x_n} dn \right] \\ &\quad \frac{1}{\frac{d_j}{\chi}} \mathbf{F}(\mathbf{d}_j \otimes \mathbf{d}_j) - p \mathbf{F}^{-T}, \end{aligned} \quad (6.32)$$

where where x_{cc} , x_c and x_n are replaced with $\frac{d_j}{\lambda_{m,cc}}$, $\frac{d_j}{\lambda_{m,c}}$ and $\frac{d_j}{\lambda_{m,n}}$ after the derivation, respectively.

Note that thermodynamic consistency shown in Chapter 5 is not disturbed here, since there is not any external energy that may disturb the first and the second laws of thermodynamics is inserted to the system in the present chapter.

6.2.4 Parameter study for the yielding and the failure criterion

In the addition to parameters introduced in the stress softening model ($\bar{r}$, κ , ν , and n_{max}), μ is also taken as a material parameter. The influence of material parameters on the stress-stretch behavior of a network, apart from

μ , is shown in Chapter 5. As the following, the influence of the material parameters on the failure and the yielding criteria are studied.

Firstly, the effect of the number of sub-cluster network is investigated. The path remains same for all number of sub-cluster networks. However, less number of sub-network causes sudden reductions in the stress-strain curve. Increasing the number of sub-cluster network ensures the smoothness of the curve (see Fig. 6.8). Nonetheless, to prevent the high computational time, the number of sub-cluster networks ξ should not be chosen very high. In the calculations, ξ is taken as 100.

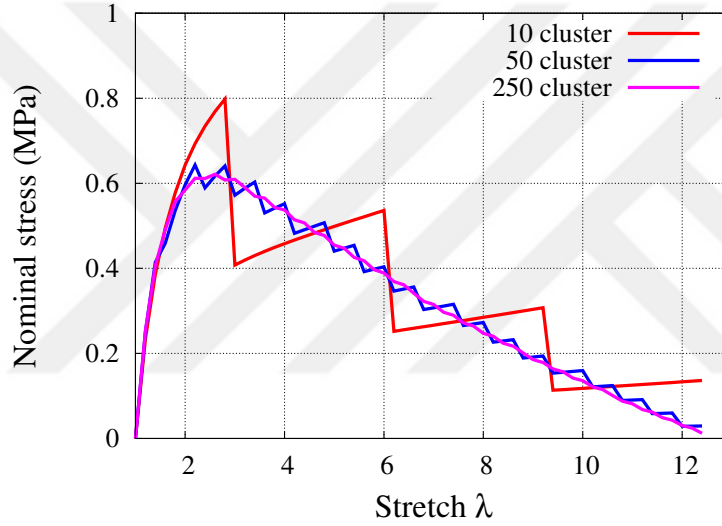


Figure 6.8: Influence of the number of sub-networks on the modeling

The failure point of a polymer network based on the failure criterion is effected by material parameters. The increase of $\bar{r}$ results in later failure of the network. As seen in Fig. 6.9-a, stress is not related to the failure point, and the failure point can be observed with small stress values. κ influences the failure point inversely with $\bar{r}$. Increase of the κ causes the failure point appearing afore (see Fig. 6.9-b). The increase of ν reduces the stretch point where the failure is observed (see Fig. 6.9). n_{max} does not affect the results as in the stress softening model, and it is not therefore demonstrated.

In the model, the yielding point is a result of softening of the network containing sub-networks. Keeping $\bar{r}_{cc,min} = 1$, the increment of $\bar{r}_{max,cc}$ leads the yielding point to appear at higher stretch points. In the stress softening model, the stress is inversely proportional to $\bar{r}$. However, if the failure criterion is taken into account, the stress is not necessarily inversely propor-

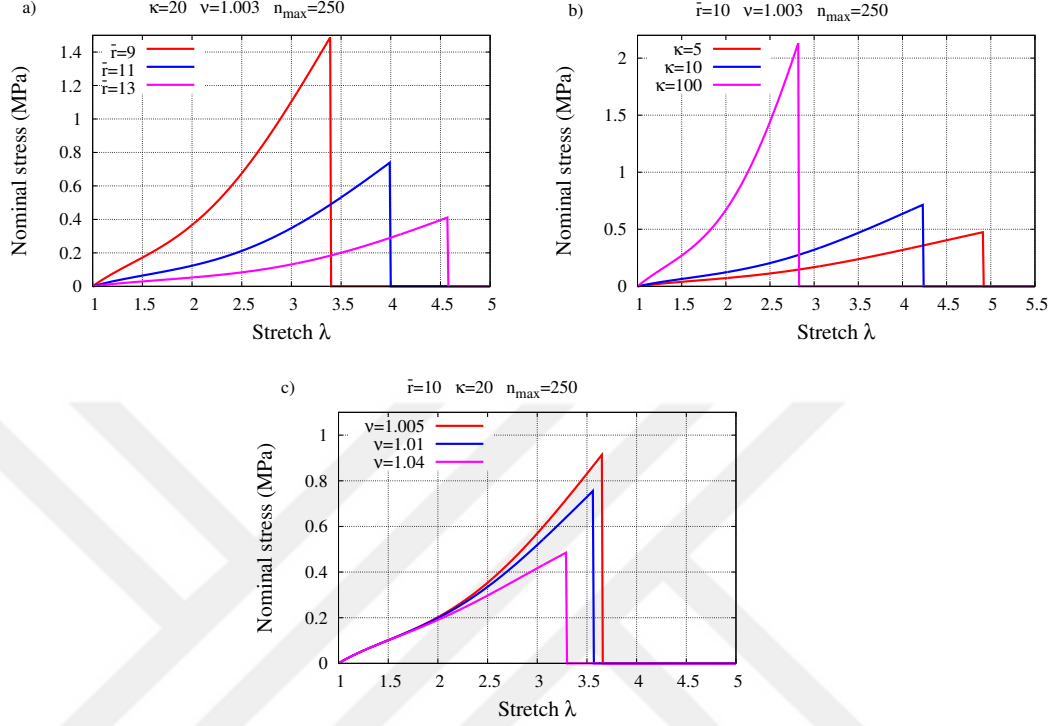


Figure 6.9: Influence of the material parameters on the failure point of a polymer network in the modeling. Influence of a) $\bar{r}$ b) κ c) ν .

tional to $\bar{r}$ (see Fig. 6.10–a). The stress is relative to κ , and the increase of κ conducts the yielding point to occur at smaller stretches. However, κ does not influence the yielding point very much. ν acts as κ on the regard of the yielding point, and increase of ν induces the decrease of the stretch point where the yielding begins to be observed. Nonetheless, the change on the yielding point with respect to the change of ν is rather small. μ plays a significant role in the complete failure of the network. The yielding point is also effected by the change of μ proportionally (see Fig. 6.10).

6.3 Validation

The model is validated with experimental data of various DN gel types.

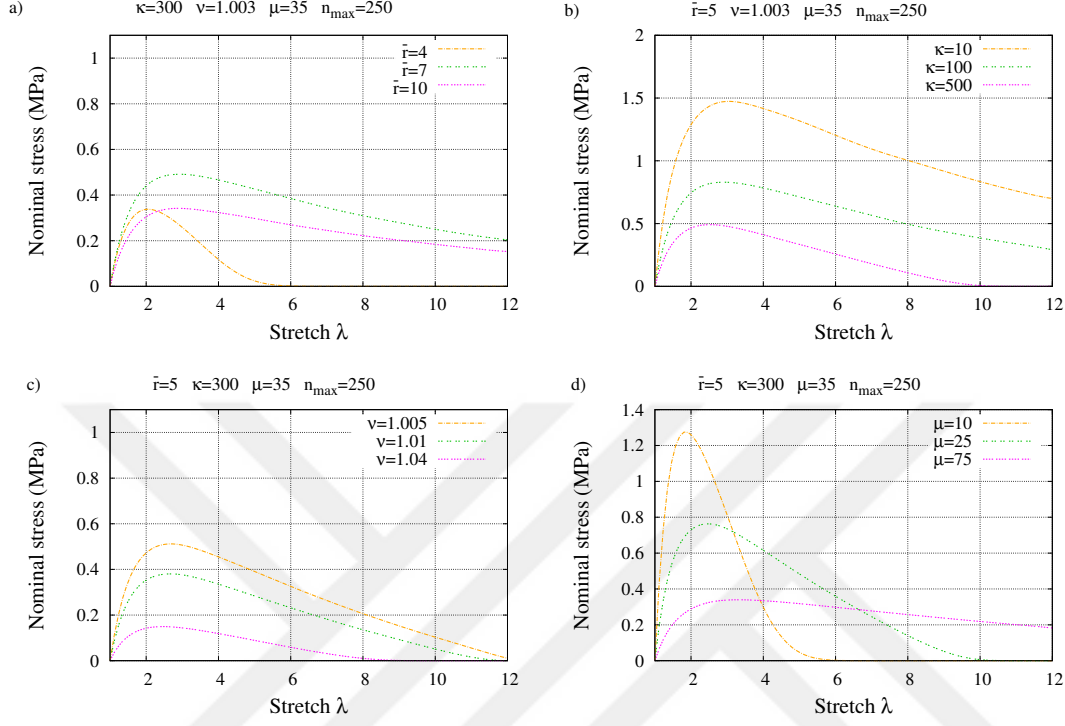


Figure 6.10: Influence of the material parameters on the yielding point of a polymer network containing 100 sub-networks in the modeling. Influence of a) $\bar{r}$ b) κ c) ν d) μ .

6.3.1 1. validation

Firstly, the model is compared against the experimental data of a DN gel exhibiting yielding and necking [106]. The DN gel consists of 1 mol AMPS of 2 mol% crosslinker and 2 mol acrylamide of 0.01 mol% cross-linker ($\mathcal{C} = 200$). Due to the relation between dissipated energy and the energy of broken bonds, 9% of all chains is assumed to be broken [106], and a is accordingly taken as 0.9. The molar ratio of the neutral to polyelectrolyte networks is 20. Therefore, M_p and M_n are taken as 1 and 20, respectively. Since the material is produced as t -DN gel, the interaction between the polymer networks are neglected. Values of material parameters used in the validation of the model are given in Table 6.1. The model is able to predict the experimental data including the necking instability (see Fig. 6.11). As mentioned above, the network of chains between clusters are destroyed completely at the end of pre-necking, and do not further contribute to the stress. The yielding point is observed where necking starts due to the maximal stress observed in the

Table 6.1: Material parameters for DN gel showing the yielding and the necking instability

$\bar{r}_c$	$\bar{r}_{cc,max}$	$\bar{r}_n$	κ_{cc}	κ_c	n_{max}	ν	μ
13	5.2	23.73	900	1500	425	1.007	7.98

network of clusters. The respond of the neutral network is considerable at the high stretch values, and significant contribution of the neutral network leads to hardening of the material right before the complete failure of the sample.

6.3.2 2. validation

The second validation of the model is performed using micro-gel reinforced DN gels. In micro-gel reinforced hydrogels, the polyelectrolyte network is shaped as micro-gels, which have the size of $5 - 7\mu m$ (see Fig. 6.12). The mechanical behavior of micro-gel reinforced DN gels shows nonlinear inelastic features under large deformation such as stress softening and the yielding behavior as the conventional DN gel described above [69, 70]. However, the necking phenomenon is not observed in such gels.

Micro-gels are like clusters, and play a role as multi-functional cross-linkers, whereas the neutral network retains the micro-gels. Micro-gels split into small stiffer splinters under the deformation. Thus, they can be assumed as a cluster network mentioned above. However, as there is no connection between micro-gels, there is not any network as the network of chains between clusters. The energy of the micro-gel reinforced DN gel is therefore assumed as the total energy of the micro-gels and the neutral network, and the influence of the chains between cluster may be neglected to model such DN gel. The macroscopic strain energy of the micro-gel reinforced DN gel is written as

$$\Psi_M = \Psi_{mg} + \Psi_n \quad (6.33)$$

where the subscript $\bullet_{mg}$ denotes the network of micro-gels. In the modeling the cluster network is replaced with the network of micro-gels, and the concept of sub-network is carried out for the micro-gel network as well.

The micro-gel reinforced hydrogel consists of 2 mol polyacrylamide (PAAm) containing 0.01 mol% crosslinker as the neutral network and 1 mole 2-acrylamido-2-methylpropanesulfonic sodium (NaAMPS) containing 4 mol% cross-linker as the polyelectrolyte network ($m_p = 1$, $m_n = 2$). Broken bonds in the micro-gels up to the end of deformation is estimated approximately

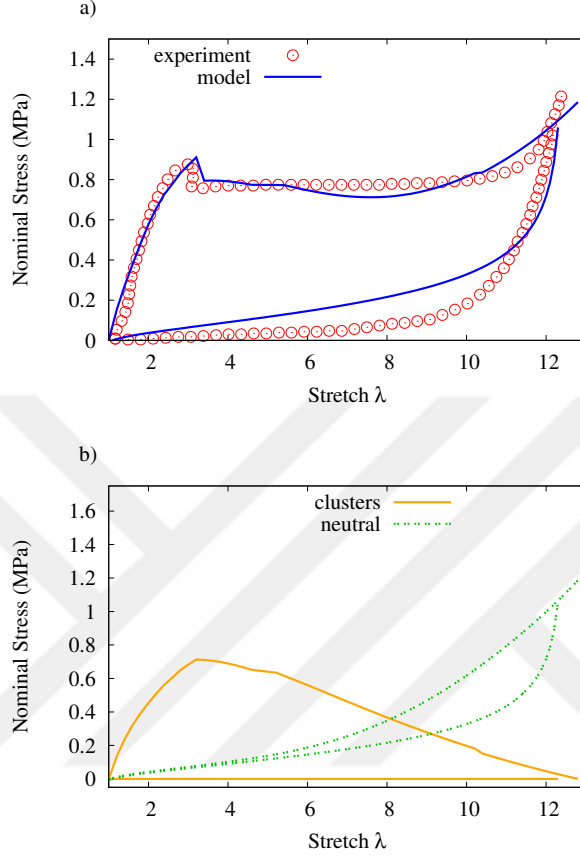


Figure 6.11: a) Comparison of the model against experimental data. b) Individual network behaviors in the modeling.

6.5% of all bonds ($a_p = a_n = 0.065$) [70]. It is assumed that the molar ratio of the neutral network to the polyelectrolyte one still remains 20 in this case ($M_p = 1$, $M_n = 20$). The material is produced with process of t -DN gel, consequently there is no interaction between networks. To fit the model, the material parameters shown in Table 6.2 is utilized. Since the network of chains between clusters are excluded, the model includes 7 material parameters for this material.

The yielding behavior is described as seen in Fig. 6.13-a, and the comparison of the model against experimental data shows good agreement. Fig. 6.13-b exhibits the behavior of the individual networks in the model. The yielding starts when the micro-gel network begins to soften. As the network of chains between clusters is not exist, the sharp stress reduction is not observed.

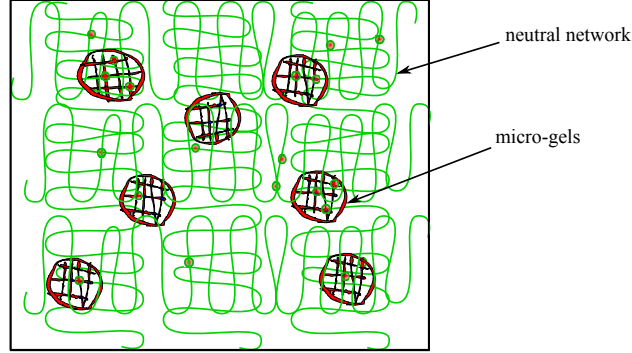


Figure 6.12: Influence of the number of sub-networks on the modeling

Table 6.2: Material parameters for DN gel showing the yielding and the necking instability

$\bar{r}_{cc,max}$	$\bar{r}_n$	κ_{cc}	κ_n	n_{max}	ν	μ
2.7	28.4	1000	50.3	600	1.01	10.8

6.4 Concluding remarks

In this chapter, a theory has been presented to describe the yielding and necking behavior of double network hydrogels when subjected to large deformation. Firstly, a failure criterion was defined for the chains in a particular direction in the network. Failure of the chains in this particular direction led to the complete failure of the network, and consequently the network was assumed not to contribute to the strain energy of the DN gel matrix. Thus, the stress reduction observed at the beginning of the necking was achieved.

Further, it was assumed that the yielding was the result of the balance between the stiffening of one network and the softening of another. Thus, one could observe nearly constant or *S*-shaped stress-stretch curves. The yielding phenomenon could be explained in light of a network containing cluster-like structures that split into sub-networks. Sub-networks were thought to have distinct mean end-to-end distances, which led them to fail at different deformation stages described by the failure criterion. Therefore, failures of sub-networks at different critical points softened the entire network in the stress-stretch curve whereas another network stiffened due to the high strain values. The yielding phenomenon was thusly observed in the DN gel matrix.

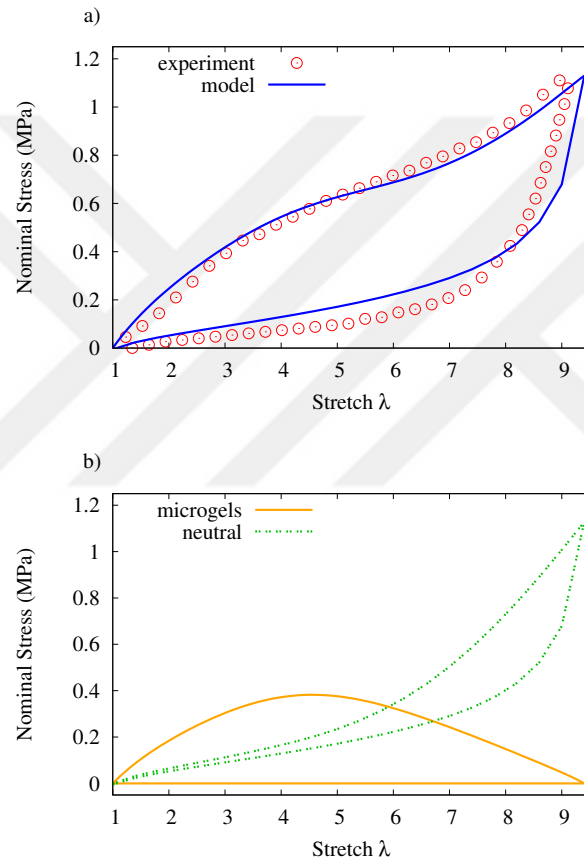


Figure 6.13: a) Comparison of the model against experimental data. b) Individual network behaviors in the modeling.

7 Self-healing in double network hydrogels

Chapter 7 considers the modeling of self-healing behavior in double network hydrogels. After deformation, DN gels are stored in a thermal chamber at different temperatures for different healing durations, and accordingly the material repairs itself. It is supposed that the source of self-healing behavior is reversible ionic bond interactions. To model self-healing, previously developed model in Chapter 5 are utilized to describe first loading cycle. It is then assumed that the activation energy needed to reattach the broken bond is provided by the internal kinetic energy and heat process after the deformation. The re-bonding energy is calculated based on heat transfer equations chemical reactions appearing between molecules. The number of re-bonded polymer chains is calculated, and the model is reloaded with re-bonded chains. Finally, the model is validated against experimental data.

7.1 Introduction

Damaged materials are conventionally repaired by gluing, welding, and patching. The ability to undertake repair without external intervention is an outstanding feature of natural materials, such as soft tissues. Such behavior is called "self-healing". Recent advances in materials science have demonstrated man-made materials that mimic the self-healing behavior of natural materials. Mechanisms of the self-healing behavior differ due to the structure of materials. Using a healing agent or altering the chemical structure to include reversible bonding are some ways to produce such materials [142, 13]. Although our understanding of the self-healing behavior has been enhanced due to recent improvements, physical and thermodynamic sources of these systems still give rise to many questions.

To demonstrate the self-healing ability of a DN gel, a DN gel sample was retested one week later after the first cyclic loading. As observed during the immediate second cyclic loading, the loading curve of retesting DN gel matches the previous unloading curves. This shows that conventional DN gels suffer a lack of self-healing behavior [137].

In polymers, healing a rupture of chain-linking is assumed to be the reattachment of chains (see Fig. 7.1). Reattachment of polymer chains may

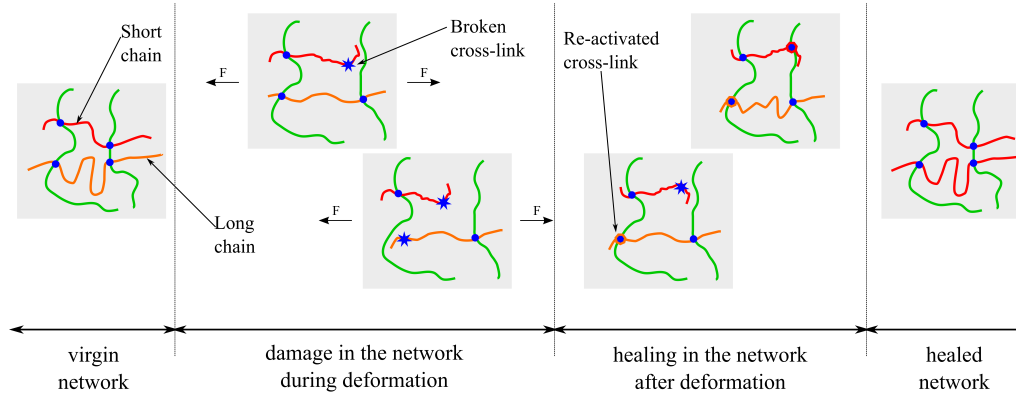


Figure 7.1: Illustration of the self healing behavior in polymers

be associated with covalent bonding, ionic reactions, or hydrogen-bonding [147]. Recently, Sun et al. [126] developed a hybrid tough hydrogel consisting of alginate and PAAm. Alginate-PAAm is synthesized according to the double network concept. In materials science, alginate is used as the polyelectrolyte network of a conventional DN gel. Unlike a polyelectrolyte network cross-linked by covalent bonds, alginate consists of ionic cross-links through divalent cations such as Ca^{+2} . Reactivating ionic bonds is simpler relative to their covalent counterpart reactivation due to the activation energy required for chemical reactions. Subsequent to deformation, when the alginate-PAAm hydrogel is resting and/or subjected to a heating process, the material exhibits self-healing behavior. The self-healing behavior of alginate-PAAm hydrogel is based upon the its internal kinetic energy and the energy supplied by the heating process. Increasing the heating temperature and the duration of resting leads to better mechanical properties in a self-healing material [126].

Alginate-PAAm DN gel provides crucial insight how to enhance the mechanical properties of a DN gel. As it potentially has an ability to heal itself autonomously, it can be used in applications requiring self-healing behavior in biology, medical, and engineering [149, 84, 36, 71]. It is therefore important to describe the behavior of this material after its healing process. Hui and Long [73] propose a model for an ionically cross-linked triblock copolymer hydrogel where ionic cross-linking is formed between the polyelectrolyte mid-blocks due to ionic interactions. Their model involves rate-independent recovery and is based upon the findings of Wang and Hong [136] mentioned in Chapter 5. Later, as an extension of [136], Long et al. [89] proposed a strain rate dependent phenomenological model for dual cross-linked self healing polyvinyl alcohol (PVA) hydrogels, which comprise dual cross-linkers and

was tough, though relatively weak, hydrogel.

7.2 Modeling

The modeling of the self-healing behavior is based on the reactivation of broken cross-links. In alginate-PAAm hydrogels, cluster-like structures do not appear during the deformation. Although DN self-healing hydrogels also demonstrate yielding behavior, it is pronounced to a smaller extent there and does not suffice for necking. Therefore, first loading cycle and stress softening is explained based on the idea shown in chapter 5. After cyclic loading and cyclic damage, alginate-PAAm hydrogel is stored at room or at a particular temperature in a thermal chamber for different durations, and material accordingly shows time and temperature dependent self-healing [126]. The self-healing behavior of alginate-PAAm hydrogel can be considered as a result of the internal kinetic energy and the energy supplied by heating process. Time and temperature dependency of the self healing is explained using heat transfer equations and the reaction rate based on molecular forces.

7.2.1 Third network decomposition

A DN gel showing self-healing behavior contains two types of cross-linking: reversible ionic and irreversible covalent cross-linking. Thus, the strain energy of such hydrogel matrix $\bullet_M$ can be investigated by the decomposition of the hydrogel matrix into reversible $\bullet_r$ and irreversible $\bullet_{ir}$ polymer networks as

$$\Psi_M = \Psi_r + \Psi_{ir}, \quad (7.1)$$

where Ψ is the strain energy function. Additionally, two different types of covalent bonds exist in the alginate-PAAm DN gel. One is cross-linking within PAAm network, whereas another is for cross-linking between alginate and PAAm networks. Thus, Eq. 7.1 is rewritten as

$$\Psi_M = \Psi_r + \Psi_{ir,n} + \Psi_{ir,int}, \quad (7.2)$$

where subscripts $\bullet_{ir,n}$ and $\bullet_{ir,int}$ represent the PAAm network and the interaction between alginate and PAAm networks, respectively.

Evolution equation based on the stress softening model

The first Piola-Kirchoff stress tensor of alginate-PAAm hydrogel is written using Eq. 7.2 as

$$\mathbf{P} = \frac{\partial \Psi_M}{\partial \mathbf{F}} = \frac{\partial \Psi_r}{\partial \mathbf{F}} + \frac{\partial \Psi_{ir,n}}{\partial \mathbf{F}} + \frac{\partial \Psi_{ir,int}}{\partial \mathbf{F}} - p\mathbf{F}^{-T} \quad (7.3)$$

Considering the affine deformation concept for polymer networks, and using Eq. 5.32 and integration over the unit sphere for the transition of the model from one-dimension to three dimensions, one can formulate the evolution equation for alginate-PAAm hydrogel as

$$\begin{aligned} \mathbf{P} &= \sum_{i=1}^{21} \omega_i \left[\frac{\partial \Psi_r}{\partial \frac{\mathbf{d}_i}{\lambda}} + \frac{\partial \Psi_{ir,n}}{\partial \frac{\mathbf{d}_i}{\lambda}} + \frac{\partial \Psi_{ir,int}}{\partial \frac{\mathbf{d}_i}{\lambda}} \right] \frac{1}{\frac{\mathbf{d}_i}{\lambda}} \mathbf{F}(\mathbf{d}_i \otimes \mathbf{d}_i) - p\mathbf{F}^{-T} \\ &= \sum_{i=1}^{21} \omega_i \left[N_r \left(\frac{\mathbf{d}}{\lambda_m} \right) \int_{D_A^r \left(\frac{\mathbf{d}}{\lambda_m} \right)} P(n, \bar{r}_r, \kappa_r) \frac{\partial \psi(n, \bar{r}_r, \lambda)}{\partial \lambda} \mathrm{d}n \right. \\ &\quad \left. + N_{ir,n} \left(\frac{\mathbf{d}}{\lambda_m} \right) \int_{D_A^{ir,n} \left(\frac{\mathbf{d}}{\lambda_m} \right)} P(n, \bar{r}_{ir,n}, \kappa_{ir,n}) \frac{\partial \psi(n, \bar{r}_{ir,n}, \lambda)}{\partial \lambda} \mathrm{d}n \right. \\ &\quad \left. + N_{ir,int} \left(\frac{\mathbf{d}}{\lambda_m} \right) \int_{D_A^{ir,int} \left(\frac{\mathbf{d}}{\lambda_m} \right)} P(n, \bar{r}_{ir,int}, \kappa_{ir,int}) \frac{\partial \psi(n, \bar{r}_{ir,int}, \lambda)}{\partial \lambda} \mathrm{d}n \right] \\ &\quad \frac{1}{\frac{\mathbf{d}_i}{\lambda}} \mathbf{F}(\mathbf{d}_i \otimes \mathbf{d}_i) - p\mathbf{F}^{-T}. \end{aligned} \quad (7.4)$$

7.2.2 Reactivation of broken bonds

The chemical process in which the reattachment of polymer chains appears requires an energy to start the chemical reaction, so-called "activation energy". The activation energy is the minimum energy to start the chemical reaction. External sources and/or the internal kinetic energy generate total energy that can be utilized to reactivate the broken cross-links. Therefore, the ratio of re-bonded cross-linking $\mathcal{K}$ due to external $\bullet_{ext}$ and internal $\bullet_{int}$

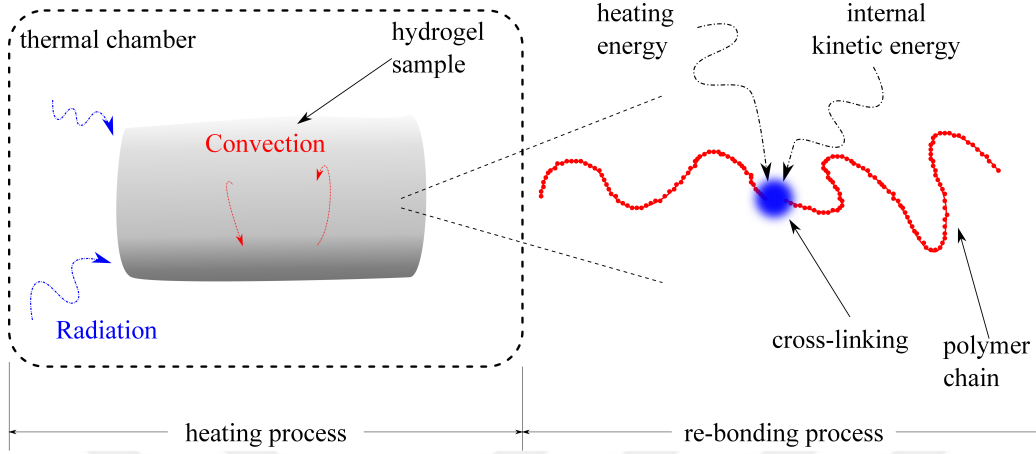


Figure 7.2: Illustration for the heating and the re-bonding processes

resources is written as

$$\mathcal{K}_M = \mathcal{K}_{ext} + \mathcal{K}_{int}. \quad (7.5)$$

External sources

External energy sources such as heat, light, a catalyst generally fasten chemical reactions. In the alginate-PAAM hydrogel the heating process is applied to the sample in a thermal chamber at different temperatures for different durations. In the modeling this process is addressed to be the reason for the different self-healing behavior of samples at different temperatures and different durations.

The heating process is taken as a heat transfer problem from oven at $T_\infty^\circ\text{C}$ to the sample at $T_0^\circ\text{C}$. The process is assumed as a convection and radiation (see fig. 7.2). Therefore, the temperature at time t is written as

$$\begin{aligned} U_{st} &= U_{conv} + U_{rad} \\ \rho V c \frac{dT}{dt} &= -(hA(T - T_\infty) + \epsilon \sigma_b (T^4 - T_\infty^4)), \end{aligned} \quad (7.6)$$

where ρ is mass density of the sample, V is the volume, h convectional is heat transfer rate, ϵ is the emissivity coefficient of the object and σ_b is the Stefan-Boltzmann constant. Change of the temperature with respect to time can be shown as in Fig. 7.3.

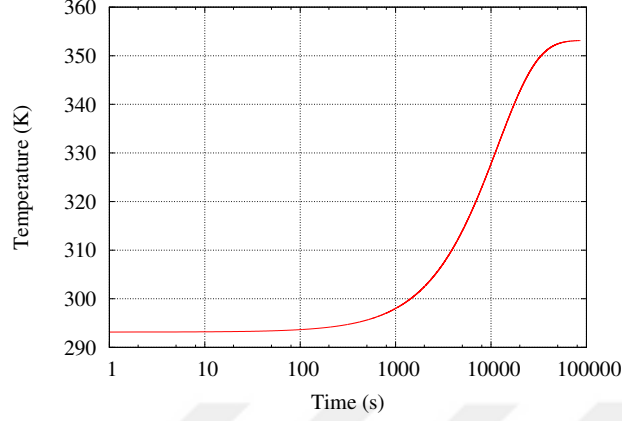


Figure 7.3: Temperature change with respect to time

The entire energy coming from the heat transfer is written as

$$U_{ht}(T, t) = \sum_{i=1}^{t_A} U_{st}(T(t_i)), \quad (7.7)$$

where t_A is the healing duration. Let us assume alginate-PAAm hydrogel is a closed system and $U_{ht}(T, t)$ is entirely used to re-bond the broken cross-linkers. Thus, the ratio of re-bonded cross-linking due to external sources can be written as

$$\mathcal{K}_{ext}(T) = \frac{U_{ht}(T, t)}{U_a} \quad (7.8)$$

where U_a is the activation energy.

Internal kinetic energy

Even though there is not any external source to prompt the chemical process, the chemical reaction occurs in the system due to inter-molecular forces. The thermal energy of molecules induces internal kinetic energy that is linked with the reaction kinetics of reactant molecules. The internal kinetic energy of system is associated with motions of molecules, and is related to the reaction rate of the chemical process. The chemical reaction rate k is defined by the Arrhenius equation that is based on collision theory as

$$k(T) = \mathcal{A}e^{-\frac{U_a}{RT}}, \quad (7.9)$$

where R , T and A are the gas constant, absolute temperature and the pre-exponential factor, respectively. Eq. 7.9 shows that higher the activation

energy, slower the chemical reaction is. If chemical reaction rate is known at different temperatures, one can calculate the activation energy as

$$U_a = \frac{R \ln \frac{k_j}{k_i}}{\frac{1}{T_i} - \frac{1}{T_j}}, \quad (7.10)$$

where subscripts $\bullet_i$ and $\bullet_j$ denotes the chemical reactions at different temperatures. Using Eq. 7.10, the activation energy for broken bond between the ionic divalent cation (Ca^{+2}) and the gluconate anion is found to be between 11 - 33.5 kJ due to experimental data of self-healing process of alginate-PAAm hydrogel shown in [126].

Pre-exponential factor $\mathcal{A}$, also known as the frequency factor, is based on the frequency of collisions between reactant molecules and written as

$$\mathcal{A} = Zp, \quad (7.11)$$

where Z and p denote collision factor and steric factor, respectively. $\mathcal{A}$ can be defined using Coats-Redfern, MacCallum-Tanner or Horowitz-Metzger methods. In literature, $\mathcal{A}$ is given for calcium oxalate in a wide range of values, that changes from $5.5 \cdot 10^5$ to $1.9 \cdot 10^{23}$ due to different heating rate [108].

Finally, one can define the reaction rate per unit mole using Eq.7.9 that leads to the number of reaction appears to reactivate broken cross-links. Let us assume all reactions lead to re-bonding of cross-linkers. Thus, the healing ratio of re-bonded cross-linkers $\mathcal{K}_{int,1}$ due to internal kinetic energy $U_{int,1}$ at time t is written as

$$\mathcal{K}_{int,1}(T, t) = \frac{1}{N_A} \sum_{i=1}^{t_A} k_i(T(t)), \quad (7.12)$$

where N_A is the Avogadro constant.

The material exhibits self-healing in an immediate consecutive loading. This is related to the energy potential of the sample. The energy potential of the sample $U_{int,2}$ at T_0 is written as

$$U_{int,2}(T) = mcT_0, \quad (7.13)$$

where m and c are the mass and specific heat capacity of the sample. Thus, the ratio of re-bonded cross-linkers due to internal energy stored $\mathcal{K}_{int,2}$ at temperature T is written as

$$\mathcal{K}_{int,2}(T) = \frac{U_{int,2}(T)}{U_a}. \quad (7.14)$$

Total re-bonded cross-linkers due to internal energy sources of the sample is represented as

$$\mathcal{K}_{int} = \mathcal{K}_{int,1} + \mathcal{K}_{int,2}. \quad (7.15)$$

Finally, using Eq. 7.8, 7.12 and 7.14, one can express the ratio of re-bonded cross-linkers as

$$\begin{aligned} \mathcal{K}_M(T, t) &= \mathcal{K}_{ext}(T, t) + \mathcal{K}_{int,1}(T, t) + \mathcal{K}_{int,2}(T) \\ &= \frac{1}{U_a} \left[\sum_{i=1}^{t_A} -(hA(T_i - T_\infty) + \epsilon\sigma_b(T_i^4 - T_\infty^4)) \right. \\ &\quad \left. + mcT_0 \right] + \frac{1}{N_A} \sum_{i=1}^t k_i(T). \end{aligned} \quad (7.16)$$

Time and temperature dependency of healing ratio ($\mathcal{K}_M$) is shown in Fig. 7.4. Increasing the healing time and/or temperature leads to high self-healing ratio.

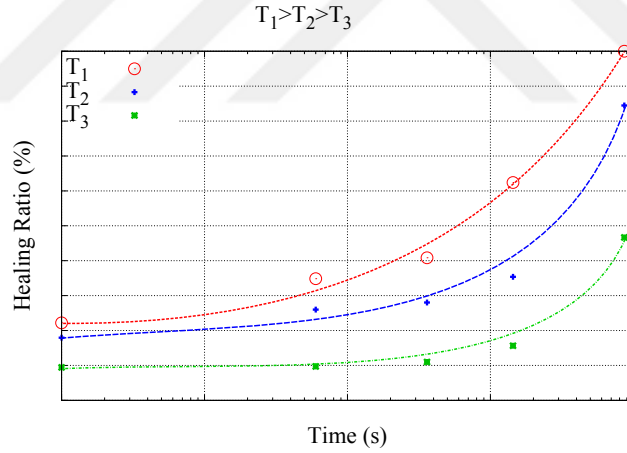


Figure 7.4: Healing ratio of reversible network at different temperatures for different durations

7.2.3 Conformation of polymer chains after healing

In a load-free sample, reattachment of de-bonded chains can be considered in two ways: reattachment from longer chain to the shorter chains (see Fig. 7.5-a), and random reattachment (see Fig. 7.5-b). We are involved with the random attachment of broken chains due to the fact that it is physically more

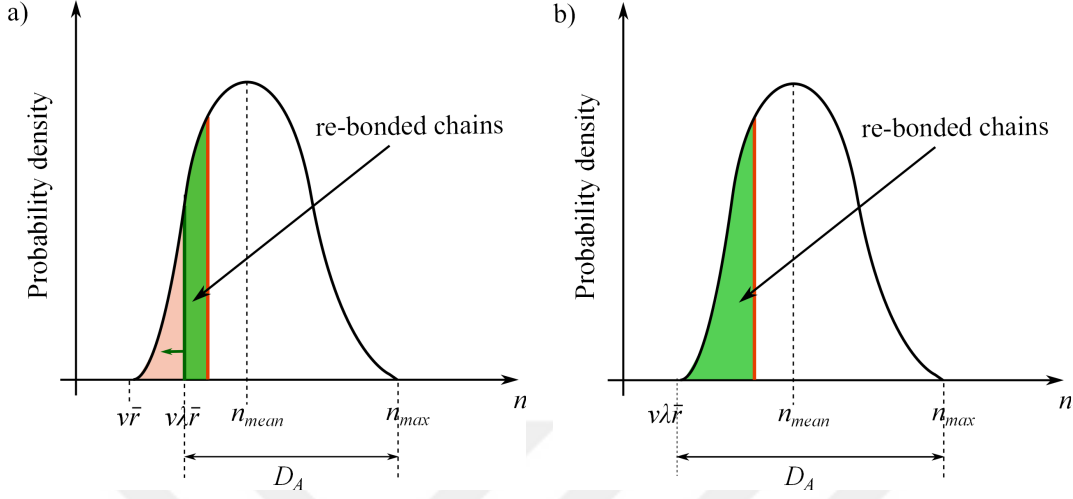


Figure 7.5: Schematic view of re-bonded chains in probability density after healing process. a) Reattachment from longer chains to shorter ones. b) Random reattachment.

feasible in a interpenetrating polymer network. In a random reattachment, the probability distribution remains unchanged. However, the number of active chains and the number of cross-linking are changed due to the healing ratio. The number of broken chains $\check{N}$ during the primary loading is written as

$$\check{N} = \tilde{N} \binom{d}{\lambda_m} \int_{\binom{d}{\lambda_m}} P(n, \bar{r}, \kappa) dn. \quad (7.17)$$

Accordingly, the number of reattached chains in the healing network is represented as

$$N_{r,heal} = \mathcal{K}_M \check{N}_r. \quad (7.18)$$

Also, the density of cross-linking site κ for the reversible network in the model is represented as

$$\kappa_{r,heal} = \mathcal{K}_M \kappa_r, \quad (7.19)$$

where κ_{heal} is the material parameter κ after healing.

7.2.4 Reloading

In addition to the healed network, alginate-PAAm hydrogel matrix contains two irreversibly cross-linked damaged network during re-loading. Also, the

reversibly cross-linked network may still contain damaged chains due to the healing ratio. Therefore, strain energy of the hydrogel matrix after healing $\hat{\Psi}$ is written as,

$$\hat{\Psi}_M = \underbrace{\mathcal{K}_M \Psi_r}_{\hat{\Psi}_r} + (1 - \mathcal{K}_M) \check{\Psi}_r + \check{\Psi}_{ir,n} + \check{\Psi}_{ir,int}, \quad (7.20)$$

where $\hat{\Psi}$ is the strain energy of healed network, $\check{\Psi}_r$, $\check{\Psi}_{ir,n}$ and $\check{\Psi}_{ir,int}$ denote the strain energies of damaged networks during re-loading, respectively. Considering $\lambda_m = 0$ during re-loading up to the maximum stretch applied in the previous loading cycle and the numerical scheme by Bažant and Oh [11] integration over the unit sphere for three-dimensional strain energy, one can rewrite $\hat{\Psi}_M$ as

$$\begin{aligned} \hat{\Psi}_M = \sum_{i=1}^{21} \omega_i \left[\mathcal{K}_M N_r \left(\frac{d}{\lambda_m} \right) \int_{D_A^r \left(\frac{d}{\lambda_m} \right)} P(n, \bar{r}_r, \mathcal{K}_M \kappa_r) \psi(n, \lambda_m \bar{r}_r) dn \right. \\ + (1 - \mathcal{K}_M) N_r \left(\frac{d}{\lambda_m} \right) \int_{D_A^r \left(\frac{d}{\lambda_m} \right)} P(n, \bar{r}_r, \kappa_r) \psi(n, \lambda_m^{max} \bar{r}_r) dn \\ + N_{ir,n} \left(\frac{d}{\lambda_m} \right) \int_{D_A^{ir,n} \left(\frac{d}{\lambda_m} \right)} P(n, \bar{r}_{ir,n}, \kappa_{ir,n}) \psi(n, \lambda_m^{max} \bar{r}_{ir,n}) dn \\ \left. + N_{ir,int} \left(\frac{d}{\lambda_m} \right) \int_{D_A^{ir,int} \left(\frac{d}{\lambda_m} \right)} P(n, \bar{r}_{ir,int}, \kappa_{ir,int}) \psi(n, \lambda_m^{max} \bar{r}_{ir,int}) dn \right], \quad (7.21) \end{aligned}$$

where λ_m^{max} is the maximum stretch applied in the primary loading cycle.

Evolution equation during self-healing

The first Piola-Kirchhoff stress tensor with respect to the incompressibility condition is written as

$$\begin{aligned}
 \mathbf{P} &= \frac{\partial \Psi_M}{\partial \mathbf{F}} = \mathcal{K}_M \frac{\partial \Psi_r}{\partial \mathbf{F}} + (1 - \mathcal{K}_M) \frac{\partial \check{\Psi}_r}{\partial \mathbf{F}} + \frac{\partial \check{\Psi}_{ir,n}}{\partial \mathbf{F}} + \frac{\partial \check{\Psi}_{ir,int}}{\partial \mathbf{F}} - p \mathbf{F}^{-T} \\
 &= \sum_{i=1}^{21} \omega_i \left[\mathcal{K}_M N_r \left(\frac{\mathbf{d}}{\lambda_m} \right) \int_{D_A^r \left(\frac{\mathbf{d}}{\lambda_m} \right)} P(n, \bar{r}_r, \kappa_r) \frac{\partial \psi(n, \bar{r}_r \lambda)}{\partial \lambda} dn \right. \\
 &\quad + (1 - \mathcal{K}_M) N_r \left(\frac{\mathbf{d}}{\lambda_m} \right) \int_{D_A^r \left(\frac{\mathbf{d}}{\lambda_m} \right)} P(n, \bar{r}_r, \kappa_r) \frac{\partial \psi(n, \bar{r}_r \lambda^{max})}{\partial \lambda} dn \\
 &\quad + N_{ir,n} \left(\frac{\mathbf{d}}{\lambda_m} \right) \int_{D_A^{ir,n} \left(\frac{\mathbf{d}}{\lambda_m} \right)} P(n, \bar{r}_{ir,n}, \kappa_{ir,n}) \frac{\partial \psi(n, \bar{r}_{ir,n} \lambda^{max})}{\partial \lambda} dn \\
 &\quad \left. + N_{ir,int} \left(\frac{\mathbf{d}}{\lambda_m} \right) \int_{D_A^{ir,int} \left(\frac{\mathbf{d}}{\lambda_m} \right)} P(n, \bar{r}_{ir,int}, \kappa_{ir,int}) \frac{\partial \psi(n, \bar{r}_{ir,int} \lambda^{max})}{\partial \lambda} dn \right] \\
 &\quad + \frac{1}{\lambda} \mathbf{F} (\mathbf{d}_i \otimes \mathbf{d}_i) - p \mathbf{F}^{-T}. \tag{7.22}
 \end{aligned}$$

7.2.5 Thermodynamic consistency

The first law thermodynamics affirms that the change of the total energy in the system is equal to the mechanical and thermal power. In the system, energy that leads to reattachment of cross-links firstly increase the potential energy of the system. Then, this energy is entirely used to re-bond de-bonded chains. Thus, the energy added to the system is written as

$$\begin{aligned}
 \hat{\Psi}_r &= U_{st} + U_{int} \\
 &= U_{st} + U_{int,1} + U_{int,2}. \tag{7.23}
 \end{aligned}$$

The Clasius-Duhem inequality is satisfied in first loading cycle as shown in Chapter 5. In the reloading of alginate-PAAm hydrogel, the Clasius-Duhem

inequality is written as

$$-\frac{\partial \hat{\Psi}_M}{\partial \lambda_m} \cdot \left(\frac{d}{\lambda_m} \right) \geq 0 \quad \forall \mathbf{d} \quad (7.24)$$

$$\begin{aligned} & - \left(\mathcal{K}_M \frac{\partial \hat{\Psi}_r}{\partial \lambda_m} \cdot \left(\frac{d}{\lambda_m} \right) + (1 - \mathcal{K}_M) \frac{\partial \hat{\Psi}_r}{\partial \lambda_m} \cdot \left(\frac{d}{\lambda_m} \right) \right. \\ & \left. + \frac{\partial \hat{\Psi}_{ir,n}}{\partial \lambda_m} \cdot \left(\frac{d}{\lambda_m} \right) + \frac{\partial \hat{\Psi}_{ir,int}}{\partial \lambda_m} \cdot \left(\frac{d}{\lambda_m} \right) \right) \geq 0 \quad \forall \mathbf{d}. \end{aligned} \quad (7.25)$$

Considering the energy dissipation during unloading and reloading of the networks that does not exhibit self-healing is 0 and consequently $\frac{d}{\lambda_m} = 0$, Eq. 7.25 is rewritten as

$$-\frac{\partial \hat{\Psi}_r}{\partial \lambda_m} \cdot \left(\frac{d}{\lambda_m} \right) \geq 0 \quad \forall \mathbf{d}. \quad (7.26)$$

If the energy dissipation during re-loading is assumed to be the result of self-healing, one can state that $\frac{d}{\lambda_m} > 0$ for healed network. Thus,

$$-\frac{\partial \hat{\Psi}_r}{\partial \lambda_m} \geq 0 \quad \forall \mathbf{d}. \quad (7.27)$$

As the same probability distribution is assumed for this network, the conditions shown in Chapter 5 is satisfied for the healing network during reloading. To this end, one can state that thermodynamic consistency is testified.

7.3 Validation

The model is validated against the experimental data of alginate-PAAm hydrogel [126]. The alginate-to-acrylamide ratio is 1:6 ($M_r = 1, M_{ir,n} = 6$). Energy dissipation is approximately 70% for each cyclic loading, which is very close to the conventional DN gels. Therefore, active chain ratio a is approximated to 0.01. Furthermore, in order to simplify fitting procedure, material parameters for the network of interactions between alginate and PAAm is taken to be the mean value of material parameters for alginate and

Table 7.1: Material parameters for DN gel exhibiting self-healing

$\bar{r}_r$	$\bar{r}_{ir,n}$	κ_r	$\kappa_{ir,n}$	n_{max}	ν
6.5	12	100.5	25	300	1.035

PAAm ($\bar{r}_{ir,int} = (\bar{r}_r + \bar{r}_{ir,n})/2$ and $\kappa_{ir,int} = (\kappa_r + \kappa_{ir,n})/2$). The material parameters shown in Table 7.1 are used to validate the model under cyclic loading.

Two independent first-loading cycles are validated, and the model exhibits high level of agreement with experimental data (see Fig. 7.6-a). The behavior of individual networks in the model is presented in Fig. 7.6-b. The reversible network contributes to the stress significantly, and the energy dissipation in this network is significantly higher than other parts.

To investigate self healing behavior, let us consider the values shown in Table 7.2 as material parameters. The values of h , c and ϵ are associated with the properties of water. For the reaction of $CaSO_4$ with guluronic acid, A is taken in the range mentioned in Sub-section 7.2.2.

Table 7.2: Material parameters for self-healing behavior of DN gel

h	c	ϵ	A
20000	4.1813	0.83	$4.3 \cdot 10^{20}$

Fig. 7.7 shows the comparison of the self-healing model against experimental data obtained at different time durations. Good agreement is obtained between the model and experimental data.

It should be noted here that it may be rather difficult to cut double shape samples, and to clamp them due to sticky structure of hydrogels. Therefore, international tensile test standards for rubber-like materials has not been followed in the experimental procedure of alginate-PAAm hydrogels shown in [127, 126]. This necessitates more detailed experimental study for such hydrogels in future.

7.4 Concluding remarks

In the present chapter, self-healing behavior is explained in reference to the reattachment of de-bonded cross-linkers. The reattachment is assumed to be the result of internal kinetic energy and the external energy supplied by the heating process.

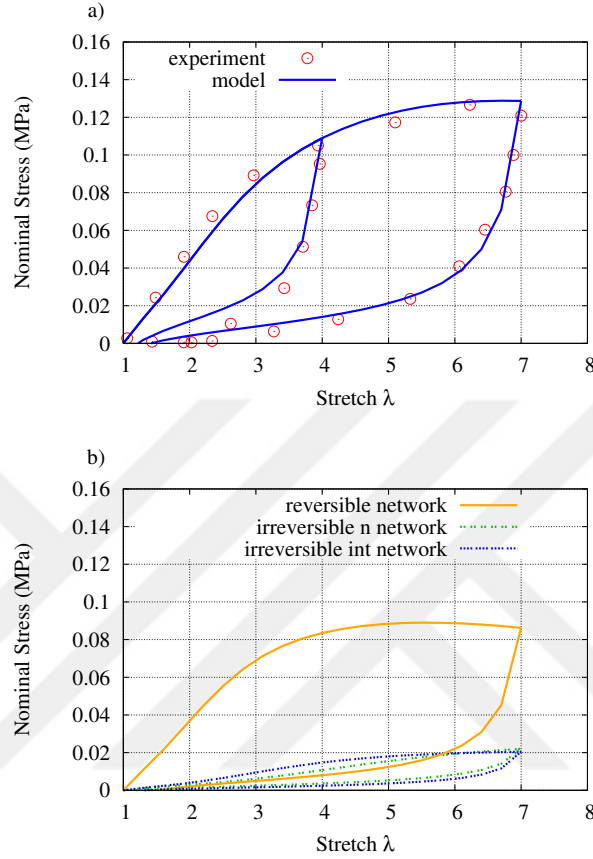


Figure 7.6: a) Comparison of the stress softening model for two independent first loading cycles against experimental data of DN gel showing self healing behavior. b) Behavior of the individual networks in the model

A chemical reaction requires activation energy to prompt the reaction. Activation energy can be supplied by a heating process. Therefore, the amount and rate of energy transferred to the sample is estimated by measuring convection and radiation heat transfer in a sample stored in an oven. This energy may be assumed to be the source of the activation energy for the reattachment process.

Internal kinetic energy depends upon the intermolecular forces, but in some circumstances it can lead to the activation of a chemical process. Even if no heat flows into the system, a chemical process may still be able to start by utilizing the internal kinetic energy. The internal kinetic energy of a chemical process is explained with the reaction rate defined by Arrhenius' equation. Using Arrhenius equation with experimental data, the range of the activation

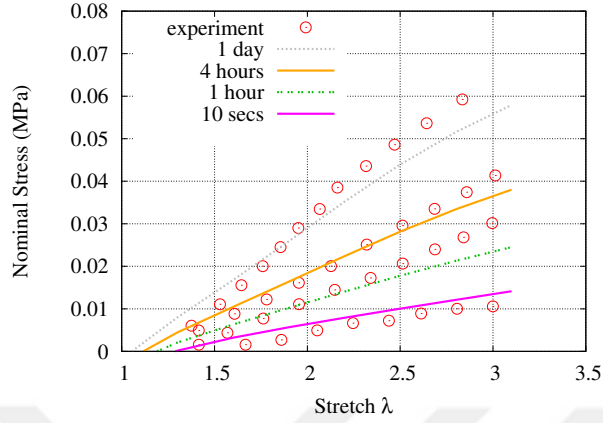


Figure 7.7: Self-healing behavior at different time durations of samples in a thermal chamber between tests

energy for a chemical reaction is determined. Then, the number of reactions that appear to reattach polymer chains at particular time is calculated and summed over the healing duration.

Finally, the total number of reattachment of polymer chains is found by summing up the total number of chains can be re-bonded due to heating process and internal kinetic energy.



Part IV

General conclusion and appendices

8 General conclusion

This thesis considers the characterization of double network hydrogels under large deformation through constitutive modeling. The model integrates the “continuum damage” approach with the concept of interpenetrating polymer networks. Investigation of the model incorporates various non-linear inelastic features of double network hydrogels such as stress softening, yielding, and necking. Additionally, self-healing behavior after deformation is described.

The first part of the thesis describes the fundamentals of polymer physics – particularly the mechanics of polymer chains – and a hyperelasticity model for double network hydrogels. To this end, the energy and force of a single chain are described by Gaussian and non-Gaussian statistics. Gaussian and non-Gaussian energies of polymer chains are then utilized to calculate the energy of a double network hydrogel matrix in a particular directions. By using the well-established method of integration over the unit sphere, the one-dimensional energy of double network hydrogel is conveyed into three-dimensions. Several numerical schemes of the integration over the unit sphere are compared and a numerical scheme was chosen by considering the accuracy of schemes and the computation time for entire modeling concepts explained in subsequent chapters.

In the second part, our main contribution – a constitutive model – is described. The model is developed gradually. First, the stress softening is characterized. To achieve this, a network evolution is introduced into the hyperelastic model. The idea is based on the ‘network decomposition’ concept and the “continuum damage” approach. The double network hydrogel matrix is decomposed into parts due to the behaviors of components within the matrix. The decomposition concept serves the purpose of clarifying and describing different deformation responses in a double network hydrogel. In this model, the double network hydrogel matrix splits into polyelectrolyte and neutral polymer networks. The damage is assumed to be de-bonding of polymer chains at cross-linking. The evolution of the damage is rendered with respect to the chain length starting from the shortest chain and continuing onto longer chains. The Gaussian probability distribution with a set of available chains is used to illustrate active and de-bonded chains.

In a DN gel showing yielding and necking, the double network hydrogel

matrix consists of three main parts. The double network hydrogel matrix decomposed into: clusters, chains between clusters, and the neutral polymer networks. Tensile behavior of a material showing yielding and necking is split into: pre-necking, necking and hardening. At the end of the pre-necking stage, a sharp stress reduction is observed due to complete failure of chains between clusters. During necking nearly constant nominal stress occurs. Then, the material hardens up to the sample's point of rupture. To describe these phenomena, the failure criterion of a network is introduced into the stress softening model. This failure criterion is based on the critical force of a single chain. The force developed by chains of a network in a direction is calculated with respect to the set of available chain within the network. The failure criterion is considered as the de-bonding of the all available chains when the maximum applicable force to a network is reached. This point is where the stiffness of a network in a direction is zero. The complete failure of a network in a direction rapidly leads to failure in other directions rapidly. Thus, the sharp stress reduction is described as the de-bonding of all chains between clusters. To explain plateau during the necking, the cluster network is split into sub-networks with different mean end-to-end distances. The failure criterion is then applied to sub-networks. Sequential failure of sub-networks leads to the decrease of the response of the cluster network to the stress. Due to high stretch values, the neutral network reacts to the deformation and increasingly contributes to the stress. Thus, the plateau in the necking is demonstrated. The hardening is defined as a result of the dramatic increase of the contribution of the neutral network to the stress.

In the last part of the constitutive modeling, the self-healing behavior of double network hydrogels is investigated. Double network hydrogels exhibiting self-healing behavior consist of reversible ionic and irreversible covalent bonds. The self-healing is related to the reattachment of de-bonded reversible polymer chains. In light of this, the double network hydrogel matrix is decomposed into reversible, irreversible, and neutral polymer networks. Re-bonding of polymer chains occurs using internal kinetic energy and external energy inserted to the system such as heating samples. Internal energy and heat transfer from external sources are time- and temperature-dependent processes. The reaction rate induced by internal kinetic energy is calculated by the Arrhenius equation to determine the number of polymer chains re-bonded by internal kinetic. Utilizing heat transfer equations, the energy transfer to the sample is estimated. Considering the activation energy of the chemical reaction to re-bonding of polymer chains, the number of polymer chain by external energy is counted. If the re-bonding process is assumed to appear randomly, the probability distribution may remains the same. After

self-healing, the sample is reloaded with re-bonded polymer chains.

The modeling stages contain a number of material parameters, that are in general micro-mechanically motivated. The predictions of the model against experimental data regarding the materials shown in Table 1.1 demonstrates good agreement. This means that the model describes plausible behavior of double network hydrogels under large deformation.



A Tensor analysis

Tensor and tensor analysis are briefly presented in present chapter following the textbook by Prof. Itskov [75]. The tensor and vector notations correspond with one presented in reference book.

A.1 Vector operations

Let us consider a three-dimensional Euclidian space $\mathbb{E}$ and a three-dimensional vector space $\mathbb{V}$ within $\mathbb{E}$. $\mathbf{x}$, $\mathbf{y}$ and $\mathbf{z}$ of vectors in $\mathbb{V}$ satisfies the following axioms.

- The sum of mentioned vectors is written as

$$\mathbf{x} + \mathbf{y} = \mathbf{y} + \mathbf{x}, \quad (\text{A.1})$$

$$\mathbf{x} + (\mathbf{y} + \mathbf{z}) = (\mathbf{x} + \mathbf{y}) + \mathbf{z}, \quad (\text{A.2})$$

$$\mathbf{x} + (-\mathbf{x}) = 0. \quad (\text{A.3})$$

- The product of these vectors with a scalar real numbers α and β in $\mathbb{V}$ is

$$\alpha(\beta\mathbf{x}) = (\alpha\beta)\mathbf{x}, \quad (\text{A.4})$$

$$1\mathbf{x} = \mathbf{x}, \quad (\text{A.5})$$

$$\alpha(\mathbf{x} + \mathbf{y}) = \alpha\mathbf{x} + \alpha\mathbf{y}, \quad (\text{A.6})$$

$$(\alpha + \beta)\mathbf{x} = \alpha\mathbf{x} + \beta\mathbf{x}, \quad (\text{A.7})$$

If there exists any non-zero term within a set of scalar real numbers α_i ($i = 1, 2, \dots, n$), the set of vectors $\mathbf{x}_i$ within

$$\sum_{i=1}^n \alpha_i \mathbf{x}_i = 0 \quad (\text{A.8})$$

is called linearly dependent. Otherwise, values of $\mathbf{x}_i$ ($i = 1, 2, \dots, n$) is always non-zero, the set of vectors is called linearly independent. Any arbitrary set of linearly independent vectors can be considered as basis for $\mathbb{V}$. Thus, using

the basis given as $\mathcal{G} = \mathbf{g}_1, \mathbf{g}_2, \mathbf{g}_3, \dots, \mathbf{g}_n$, arbitrary vector $\mathbf{x}$ is defined within $\mathbb{V}$ as

$$\mathbf{x} = \sum_{i=1}^n x^i \mathbf{g}_i, \quad \forall \mathbf{x} \in \mathbb{V}. \quad (\text{A.9})$$

By using the Einstein summation convention, Eq. A.9 is rewritten as

$$\mathbf{x} = x^i \mathbf{g}_i, \quad \forall \mathbf{x} \in \mathbb{V}. \quad (\text{A.10})$$

Summation is done over the number of indices from 1 to n .

The scalar product of vectors within $\mathbb{V}$ is important for vector and tensor algebra. The scalar product of vectors satisfies the following conditions as

$$\mathbf{x} \cdot \mathbf{y} = \mathbf{y} \cdot \mathbf{x}, \quad (\text{A.11})$$

$$\mathbf{x}(\mathbf{y} \cdot \mathbf{z}) = \mathbf{x} \cdot \mathbf{y} + \mathbf{x} \cdot \mathbf{z}, \quad (\text{A.12})$$

$$\alpha(\mathbf{x} \cdot \mathbf{y}) = (\alpha \mathbf{x}) \cdot \mathbf{y} = \mathbf{x} \cdot (\alpha \mathbf{y}), \quad (\text{A.13})$$

$$\mathbf{x} \cdot \mathbf{x} \geq 0. \quad (\text{A.14})$$

The Euclidian length of a vector is defined in $\mathbb{V}$

$$\|\mathbf{x}\| = \sqrt{\mathbf{x} \cdot \mathbf{x}}. \quad (\text{A.15})$$

Two vectors $\mathbf{x}$ and $\mathbf{y}$ are perpendicular to each other, if

$$\mathbf{x} \cdot \mathbf{y} = 0. \quad (\text{A.16})$$

Thus, a basis called orthonormal, if

$$\mathbf{e}_i \cdot \mathbf{e}_j = \delta_{ij} \quad (i, j = 1, 2, \dots, n), \quad (\text{A.17})$$

where δ represents Kronecker delta and is

$$\delta_{ij} = \delta^{ij} = \delta_i^j = \begin{cases} 1 & i = j \\ 0 & i \neq j. \end{cases} \quad (\text{A.18})$$

A.2 Tensor operations

Let us consider $\mathbf{Lin}$ as the linear mapping of a vector into another one in $\mathbb{V}$. The elements of $\mathbf{Lin}$ are called the second order tensors and form a vector space. Thus, the linear mapping of a vector $\mathbf{x}$ into vector $\mathbf{y}$ is written as

$$\mathbf{y} = \mathbf{A}\mathbf{x}, \quad \mathbf{A} \in \mathbf{Lin}, \mathbf{y} \in \mathbb{V} \quad \text{and} \quad \forall \mathbf{x} \in \mathbb{V}. \quad (\text{A.19})$$

The left mapping is defined based on the right mapping by

$$(\mathbf{y}\mathbf{A}) \cdot \mathbf{x} = \mathbf{y} \cdot (\mathbf{a}\mathbf{x}) = \mathbf{y}\mathbf{A}\mathbf{x}, \quad \mathbf{A} \in \mathbf{Lin}, \quad \forall \mathbf{y} \text{ and } \mathbf{x} \in \mathbb{V} \quad (\text{A.20})$$

The tensor product of two vectors $\mathbf{a}$, $\mathbf{b}$ defines a second-order tensor, and the right and left mapping of an arbitrary vector $\mathbf{x}$ into second-order tensor are represented by

$$(\mathbf{a} \otimes \mathbf{b})\mathbf{x} = \mathbf{a}(\mathbf{b} \cdot \mathbf{x}) \quad \mathbf{a}, \mathbf{b} \in \mathbb{V}, \quad \forall \mathbf{x} \in \mathbb{V}, \quad (\text{A.21})$$

$$\mathbf{y}(\mathbf{a} \otimes \mathbf{b}) = (\mathbf{y} \cdot \mathbf{a})\mathbf{b} \quad \mathbf{a}, \mathbf{b} \in \mathbb{V}, \quad \forall \mathbf{y} \in \mathbb{V}, \quad (\text{A.22})$$

respectively. The second-order tensor is also represented using the basis $\mathcal{G}$ as

$$\mathbf{A} = A^{ij} \mathbf{g}_i \otimes \mathbf{g}_j = A_{ij} \mathbf{g}^i \otimes \mathbf{g}^j = A^i_j \mathbf{g}_i \otimes \mathbf{g}^j = A^j_i \mathbf{g}^i \otimes \mathbf{g}_j, \quad (\text{A.23})$$

where

$$A^{ij} = \mathbf{g}^i \mathbf{A} \mathbf{g}^j, \quad A_{ij} = \mathbf{g}_i \mathbf{A} \mathbf{g}_j, \quad (\text{A.24})$$

$$A^i_j = \mathbf{g}^i \mathbf{A} \mathbf{g}_j, \quad A^j_i = \mathbf{g}_i \mathbf{A} \mathbf{g}^j \quad (i = 1, 2, \dots, n). \quad (\text{A.25})$$

The zero tensor and the identity tensor is defined as

$$\mathbf{0}\mathbf{x} = \mathbf{0}, \quad \mathbf{I}\mathbf{x} = \mathbf{x} \quad \forall \mathbf{x} \in \mathbb{V}. \quad (\text{A.26})$$

The identity tensor is also rewritten as

$$\mathbf{I} = \sum_{i=1}^n \mathbf{e}_i \otimes \mathbf{e}_i. \quad (\text{A.27})$$

Let us consider two second-order tensor $\mathbf{A}, \mathbf{B} \in \mathbf{Lin}$. The composition of $\mathbf{A}$ and $\mathbf{B}$ is $\mathbf{C}$, if

$$\mathbf{C}\mathbf{x} = (\mathbf{A}\mathbf{B})\mathbf{x}, \quad \forall \mathbf{x} \in \mathbb{V}. \quad (\text{A.28})$$

Generally, the composition tensors is not commutative ($\mathbf{A}\mathbf{B} \neq \mathbf{B}\mathbf{A}$). Furthermore, one can write that

$$\mathbf{A}\mathbf{0} = \mathbf{0}\mathbf{A} = \mathbf{0}, \quad (\text{A.29})$$

$$\mathbf{A}\mathbf{I} = \mathbf{I}\mathbf{A} = \mathbf{A}, \quad (\text{A.30})$$

$$\mathbf{A}(\mathbf{B} + \mathbf{C}) = \mathbf{A}\mathbf{B} + \mathbf{A}\mathbf{C}, \quad (\text{A.31})$$

$$\mathbf{A}(\mathbf{B}\mathbf{C}) = (\mathbf{A}\mathbf{B})\mathbf{C}. \quad (\text{A.32})$$

Also, using tensor product, Eq. A.28 is written as

$$(\mathbf{a} \otimes \mathbf{b})(\mathbf{c} \otimes \mathbf{d})\mathbf{x} = (\mathbf{d} \cdot \mathbf{x})(\mathbf{a} \otimes \mathbf{b})\mathbf{c} \quad (\text{A.33})$$

$$= (\mathbf{d} \cdot \mathbf{x})(\mathbf{b} \cdot \mathbf{c})\mathbf{a} = (\mathbf{b} \cdot \mathbf{c})(\mathbf{a} \otimes \mathbf{d})\mathbf{x} \quad (\text{A.34})$$

Thus, one can represent

$$\begin{aligned} \mathbf{AB} &= A^{ik} B_{k.}^j \mathbf{g}_i \otimes \mathbf{g}_j = A_{ik} B^{kj} \mathbf{g}^i \otimes \mathbf{g}_j \\ &= A_{.k}^i B_{.j}^k \mathbf{g}_i \otimes \mathbf{g}^j = A_{i.}^k B_{kj} \mathbf{g}^i \otimes \mathbf{g}^j. \end{aligned} \quad (\text{A.35})$$

The transpose of a tensor $\mathbf{A}^T$ is defined by

$$\mathbf{A}^T \mathbf{x} = \mathbf{x} \mathbf{A} \quad \forall \mathbf{x} \in \mathbb{V}. \quad (\text{A.36})$$

The inverse of a tensor $\mathbf{A}^{-1}$ is written that

$$\mathbf{Ax} = \mathbf{y} \quad (\text{A.37})$$

$$\mathbf{x} = \mathbf{A}^{-1} \mathbf{y}. \quad (\text{A.38})$$

Using the inverse and the transpose of a tensor, one can define symmetric, skew-symmetric and orthogonal tensors as

$$\text{Sym} = \{\mathbf{M} \in \text{Lin} : \mathbf{M} = \mathbf{M}^T\}, \quad (\text{A.39})$$

$$\text{Skew} = \{\mathbf{W} \in \text{Lin} : \mathbf{W}^T = -\mathbf{W}\}, \quad (\text{A.40})$$

$$\text{Orth} = \{\mathbf{Q} \in \text{Lin} : \mathbf{Q} = \mathbf{Q}^{-T}\}. \quad (\text{A.41})$$

Every second order tensor can be decomposed into symmetric and skew-symmetric parts as

$$\mathbf{A} = \text{Sym}(\mathbf{A}) + \text{Skew}(\mathbf{A}), \quad (\text{A.42})$$

where

$$\text{Sym}(\mathbf{A}) = \frac{1}{2}(\mathbf{A} + \mathbf{A}^T), \quad \text{Skew}(\mathbf{A}) = \frac{1}{2}(\mathbf{A} - \mathbf{A}^T). \quad (\text{A.43})$$

The scalar product of two tensors $\mathbf{A}$ and $\mathbf{B}$ is given

$$\mathbf{A} : \mathbf{B} = A_{ij} B^{ij} = A_{.j}^i B_i^j \quad (\text{A.44})$$

$$= (\mathbf{a} \otimes \mathbf{b})(\mathbf{c} \otimes \mathbf{d}) = (\mathbf{a} \cdot \mathbf{c})(\mathbf{b} \cdot \mathbf{d}) \quad (\text{A.45})$$

Using the scalar product of a tensor, the trace of a tensor is represented as

$$\begin{aligned}\text{tr} \mathbf{A} &= \mathbf{A} : \mathbf{I}, \\ \text{tr}(\mathbf{a} \otimes \mathbf{b}) &= \mathbf{a} \cdot \mathbf{b}.\end{aligned}\tag{A.46}$$

For every second-order tensor can be divided into spherical and deviatoric parts as

$$\mathbf{A} = \text{Sph}(\mathbf{A}) + \text{Dev}(\mathbf{A}),\tag{A.47}$$

where

$$\text{Sph}(\mathbf{A}) = \frac{1}{3} \text{tr}(\mathbf{A}) \mathbf{I}, \quad \text{Dev}(\mathbf{A}) = \mathbf{A} - \frac{1}{3}(\mathbf{A} - \mathbf{A}^T)\tag{A.48}$$

in $\mathbb{V}$.

The determinant of a tensor $\mathbf{A}$ in the mixed basis can be calculated

$$\det(\mathbf{A}) = |A_{\cdot j}^i| = |A_{\cdot i}^j|,\tag{A.49}$$

where $|\bullet|$ is the norm of a tensor and given by

$$|\mathbf{A}| = \sqrt{\mathbf{A} : \mathbf{A}}.\tag{A.50}$$

Based on the Cayley-Hamilton theorem, determinant of a second-order tensor regardless of its basis is written by

$$\det \mathbf{A} = \frac{1}{3} \left(\text{tr} \mathbf{A}^3 - \frac{3}{2} \text{tr} \mathbf{A}^2 \text{tr} \mathbf{A} + \frac{1}{2} \text{tr}^3 \mathbf{A} \right).\tag{A.51}$$

A.2.1 Derivation with respect to a tensor

Let us represent a scalar-valued tensor function $f(\mathbf{A}) : \mathbf{Lin} \rightarrow \mathbb{R}$. The derivative of a scalar-valued tensor function is shown as $f(\mathbf{A})_{,\mathbf{A}}$ and defined by

$$\frac{d}{dt} f(\mathbf{A} + t\mathbf{X})|_{t=0} = f(\mathbf{A})_{,\mathbf{A}} : \mathbf{X}, \quad \forall \mathbf{X} \in \mathbf{Lin}.\tag{A.52}$$

Due to Eq. A.52, the Gateaux derivative exists and continuous at $\mathbf{A}$. By using arbitrary basis $\mathbf{g}_i \otimes \mathbf{g}_j$, Eq. A.52 can be represented as

$$\begin{aligned}f(\mathbf{A})_{,\mathbf{A}} &= \frac{\partial f}{\partial A_i^j} \mathbf{g}_i \otimes \mathbf{g}^j = \frac{\partial f}{\partial A_{ij}} \mathbf{g}_i \otimes \mathbf{g}_j \\ &= \frac{\partial f}{\partial A^{ij}} \mathbf{g}^i \otimes \mathbf{g}^j = \frac{\partial f}{\partial A_j^i} \mathbf{g}^i \otimes \mathbf{g}_j.\end{aligned}\tag{A.53}$$

B Foundations of the continuum mechanics

This chapter represents briefly kinematics, stress measures and balance laws for a continuous solid that is subjected to the finite large deformation. The notations and the matters studied in this chapter is based on the lecture notes of Prof. Itskov [76].

B.1 Kinematics of deformation

B.1.1 Material configurations

If we consider a body in three-dimensional space, the mapping of every point on the body B into a bounded region $\mathcal{B}$ is assumed to be one to one. This one to one relationship is referred to as configuration. If a body B is assumed to be at a configuration B at time t_0 , and at this point all characteristics of the body are known, then the configuration B is called the reference configuration, and any other configuration $\mathcal{B}$ at time t is called the current configuration (see Fig. B.1).

Then any point P_0 within body B in the reference configuration can be identified with an arbitrary vector $\mathbf{X} \in \mathbb{E}^3$ and the same point in the current configuration $\mathcal{B}$ can be represented by another arbitrary vector $\mathbf{x} \in \mathbb{E}^3$.

If a coordinate system $\theta^i (i = 1, 2, 3)$ is introduced, then the vectors $\mathbf{X}$ and $\mathbf{x}$ can be further represented as follows:

$$\mathbf{x} = \mathbf{x}(\theta^1, \theta^2, \theta^3, t); \quad \theta^i = \theta^i(\mathbf{x}, t) \quad (\text{B.1})$$

$$\mathbf{X} = \mathbf{x}(\theta^1, \theta^2, \theta^3, t_0) = \mathbf{X}(\theta^1, \theta^2, \theta^3); \quad \theta^i = \theta^i(\mathbf{X}, t_0) \quad (\text{B.2})$$

The coordinates $\theta^i (i = 1, 2, 3)$ are referred to as convective coordinates since these lines are embedded into the material and deformed with the body.

We can now define displacement of a body as the difference between the position vectors of the points in the current and reference configuration. It is represented mathematically as follows:

$$\mathbf{u} = \mathbf{x}(\theta^1, \theta^2, \theta^3, t) - \mathbf{X} \quad (\text{B.3})$$

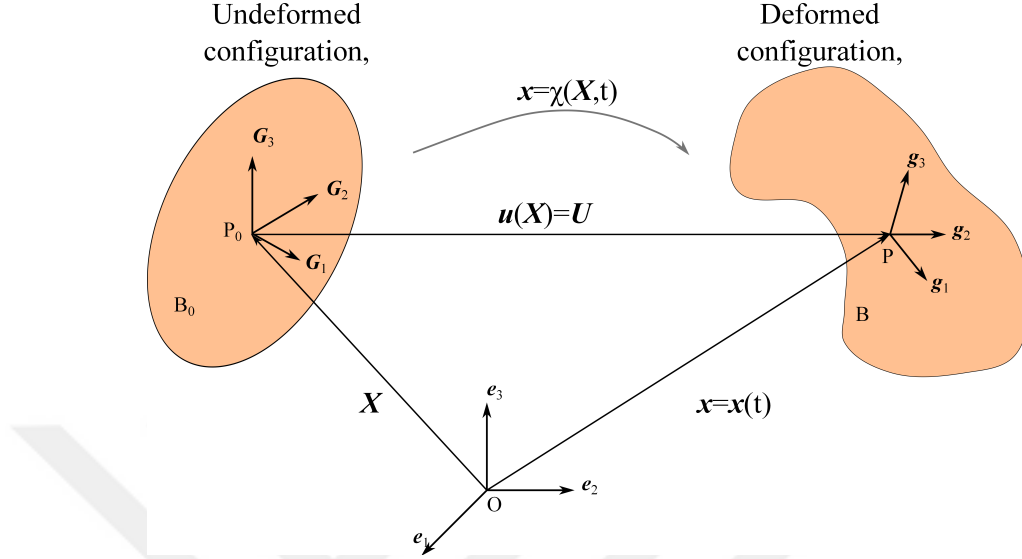


Figure B.1: Illustration for motion of a continuum body

where $\mathbf{u}$ is displacement vector.

If we consider the Euclidean space $\mathbb{E}^3$, which is characterized by the presence of an orthonormal basis vectors $\mathbf{e}_i$, with the property $\mathbf{e}_i \cdot \mathbf{e}_j = \delta_{ij}$, where δ_{ij} denotes the Kronecker delta, then the vectors $\mathbf{X}$, $\mathbf{x}$ and $\mathbf{u}$ with respect to orthonormal basis is written as

$$\mathbf{X} = X^i \mathbf{e}_i, \quad X^j = \mathbf{X} \cdot \mathbf{e}_j \quad (\text{B.4})$$

$$\mathbf{x} = x^i \mathbf{e}_i, \quad x^j = \mathbf{x} \cdot \mathbf{e}_j \quad (\text{B.5})$$

$$\mathbf{u} = u^i \mathbf{e}_i, \quad u^j = \mathbf{u} \cdot \mathbf{e}_j, \quad (\text{B.6})$$

where and henceforth, the Einstein's summation convention over repeated indices is applied ($i, j = 1, 2, 3$). X^j and x^j are called reference (Lagrangian) and current (Eulerian) coordinates, respectively.

B.1.2 Tangent vectors and dual bases

The vectors tangent to the coordinate lines in the reference and current configurations are preferred for the description of large deformations and they also form a basis. These tangent vector bases can be obtained as

$$\begin{aligned} \mathbf{G}_i &= \frac{\partial \mathbf{X}}{\partial \theta^i} = \mathbf{X}_{,i} = X^j_{,i} \mathbf{e}_j \\ \mathbf{g}_i &= \frac{\partial \mathbf{x}}{\partial \theta^i} = \mathbf{x}_{,i} = x^j_{,i} \mathbf{e}_j \quad (i, j = 1, 2, 3). \end{aligned} \quad (\text{B.7})$$

It is feasible to assume that the functions $\mathbf{X} = \mathbf{X}(\theta^1, \theta^2, \theta^3)$ and $\mathbf{x} = \mathbf{x}(\theta^1, \theta^2, \theta^3, t)$ are sufficiently differentiable.

It is always important to define the dual of any basis in order to completely understand the coordinate space. Therefore, the bases dual to $\mathbf{G}_i$ and $\mathbf{g}_i$ is represented as

$$\mathbf{G}_i \cdot \mathbf{G}^j = \delta_i^j, \quad (\text{B.8})$$

$$\mathbf{g}_i \cdot \mathbf{g}^j = \delta_i^j \quad (i, j = 1, 2, 3). \quad (\text{B.9})$$

B.1.3 Deformation gradient

If all points within a body undergo the same amount of displacement from the reference configuration to the current configuration, then deformation of the body does not occur. Therefore, it is important to know how fast the vectors representing a point change with respect to its neighboring points. In other words, it is necessary to know the "velocity" of the displacement changes. This velocity depends on the direction fixed by some vector $\mathbf{a}$. Using the directional derivative, deformation of a body is written as

$$\begin{aligned} \frac{d}{ds} \mathbf{x}(\mathbf{X} + s\mathbf{a}) \Big|_{s=0} &= \lim_{\Delta s \rightarrow 0} \frac{\mathbf{x}(\mathbf{X} + s\mathbf{a}) - \mathbf{x}(\mathbf{X})}{\Delta s} \\ &= \text{Grad}(\mathbf{x})\mathbf{a}. \end{aligned} \quad (\text{B.10})$$

It can be shown clearly that the mapping of the vector $\mathbf{a}$ into the vector B.10 is linear, and can therefore be described using a second order tensor, referred to as the gradient of the vector function $\mathbf{x}(\mathbf{X})$, such that

$$\mathbf{F} = \text{Grad}(\mathbf{x}) \quad (\text{B.11})$$

A direct expression for the deformation gradient $\mathbf{F}$ is represented with the help of dual bases formulated in B.8 and B.9 as

$$\mathbf{F} = \mathbf{g}_k \otimes \mathbf{G}^k. \quad (\text{B.12})$$

$\mathbf{F}$ is not a measure of gradient of deformation, but a measure of gradient of position. Thus, another representation of the deformation gradient can be done with the help of infinitesimal line elements $d\mathbf{X}$ in the reference configuration and $d\mathbf{x}$ in the current configuration, and this is given by:

$$d\mathbf{x} = \mathbf{F}d\mathbf{X}, \quad (\text{B.13})$$

$$d\mathbf{X} = \mathbf{F}^{-1}d\mathbf{x}. \quad (\text{B.14})$$

where $\mathbf{F}^{-1}$ is known as the spatial gradient.

B.1.4 Deformation of surface and volume elements: Nanson's Formula

The deformation of surface and volume elements can be described with the help of the deformation gradient in a simple manner. Firstly, three non-coplanar positively oriented vectors in the reference configuration are considered as

$$d\mathbf{A} = dA^i \mathbf{e}_i, \quad d\mathbf{B} = dB^j \mathbf{e}_j, \quad d\mathbf{C} = dC^k \mathbf{e}_k. \quad (\text{B.15})$$

Then, the volume of this infinitesimal parallelepiped is obtained as

$$dV_0 = [d\mathbf{A}d\mathbf{B}d\mathbf{C}], \quad (\text{B.16})$$

where $[d\mathbf{A}d\mathbf{B}d\mathbf{C}]$ denotes the triple scalar product or the mixed product.

If the parallelepiped undergoes deformation, then the deformed edges can be represented with the help of the deformation gradient as

$$d\mathbf{a} = \mathbf{F}d\mathbf{A}, \quad d\mathbf{b} = \mathbf{F}d\mathbf{B}, \quad d\mathbf{c} = \mathbf{F}d\mathbf{C} \quad (\text{B.17})$$

The volume of this infinitesimal parallelepiped in the deformed configuration is obtained as

$$dV = [d\mathbf{a}d\mathbf{b}d\mathbf{c}] = \left| F_{\cdot j}^i \right| dV_0 \quad (\text{B.18})$$

Thus, one can calculate the volume change J as

$$J = \frac{dV}{dV_0} = \left| F_{\cdot j}^i \right| = \det \mathbf{F} \quad (\text{B.19})$$

The consequence of Eq. B.19 is that

$$J = \det \mathbf{F} > 0. \quad (\text{B.20})$$

The above equation can also be written as

$$[d\mathbf{a}d\mathbf{b}d\mathbf{c}] = J [d\mathbf{A}d\mathbf{B}d\mathbf{C}] \quad (\text{B.21})$$

Using the mixed product rule for vectors, we can calculate the volumes in reference and current configurations using B.16, B.18 and B.21 as

$$(d\mathbf{a} \times d\mathbf{b}) \cdot d\mathbf{c} = J (d\mathbf{A} \times d\mathbf{B}) \cdot d\mathbf{C}. \quad (\text{B.22})$$

Then, the surface in the current and reference configurations can be represented as

$$d\mathbf{s} = d\mathbf{a} \times d\mathbf{b} = \mathbf{n}ds, \quad (\text{B.23})$$

$$d\mathbf{S} = d\mathbf{A} \times d\mathbf{B} = \mathbf{N}dS, \quad (\text{B.24})$$

where ds and dS denote the surface areas while $\mathbf{n}$ and $\mathbf{N}$ are the positive unit normals to these surfaces in the current and reference configuration, respectively. With the help of B.17, B.22, B.23 and B.24, we can write

$$ds = J\mathbf{F}^{-T}d\mathbf{S}, \quad (\text{B.25})$$

$$\mathbf{n}ds = J\mathbf{F}^{-T}\mathbf{N}dS. \quad (\text{B.26})$$

Eq.B.26 is referred to as Nanson's Formula, which relates the surface elements in deformed and reference configuration.

B.1.5 Strain and Stretch measures

If the material length changes after deformation, the material is said to be under strain. Therefore, we can write the square lengths of the infinitesimal material elements in the deformed and current configurations as

$$\|d\mathbf{x}\|^2 = d\mathbf{x} \cdot d\mathbf{x} = d\mathbf{X} (\mathbf{F}^T \mathbf{F}) d\mathbf{X} = d\mathbf{X} \mathbf{C} d\mathbf{X}, \quad (\text{B.27})$$

$$\|d\mathbf{X}\|^2 = d\mathbf{X} \cdot d\mathbf{X} = d\mathbf{x} (\mathbf{F}^{-T} \mathbf{F}^{-1}) d\mathbf{x} = d\mathbf{x} \mathbf{b}^{-1} d\mathbf{x}, \quad (\text{B.28})$$

where

$$\mathbf{C} = \mathbf{F}^T \mathbf{F}, \quad (\text{B.29})$$

$$\mathbf{b} = \mathbf{F} \mathbf{F}^T \quad (\text{B.30})$$

and denote the right and left Cauchy-Green tensors, respectively.

Using Eq. B.29 and B.30, the stretch along a given direction $\mathbf{N}$ in the reference configuration and $\mathbf{n}$ in the current configuration is written as

$$\lambda(\mathbf{N}) = (\mathbf{N} \mathbf{C} \mathbf{N})^{\frac{1}{2}}, \quad (\text{B.31})$$

$$\lambda(\mathbf{n}) = (\mathbf{n} \mathbf{b}^{-1} \mathbf{n})^{-\frac{1}{2}}. \quad (\text{B.32})$$

Thus, the right and the left stretch tensors is obtained as

$$\mathbf{U} = \mathbf{C}^{1/2} = \sum_{i=1}^3 \lambda_i \mathbf{N}_i \otimes \mathbf{N}_i, \quad (\text{B.33})$$

$$\mathbf{v} = \mathbf{b}^{1/2} = \sum_{i=1}^3 \lambda_i \mathbf{n}_i \otimes \mathbf{n}_i. \quad (\text{B.34})$$

Accordingly, a proper orthogonal tensor $\mathbf{R}$ is represented by

$$\mathbf{R} = \mathbf{F}\mathbf{U}^{1/2}. \quad (\text{B.35})$$

By representing deformation gradient by

$$\mathbf{F} = \mathbf{R}\mathbf{U}, \quad (\text{B.36})$$

one can obtain

$$\mathbf{F} = \mathbf{v}\mathbf{R}. \quad (\text{B.37})$$

Eq. B.36 and B.37 are referred to as the polar decomposition of the deformation gradient.

B.1.6 Velocity Gradient

The material velocity gradient is defined similar to the deformation gradient B.11 as

$$\mathbf{L} = \text{Grad } \dot{\mathbf{x}} = \dot{\mathbf{F}}. \quad (\text{B.38})$$

We can also define the spatial velocity gradient as

$$\mathbf{l} = \text{Grad } \dot{\mathbf{x}} = \dot{\mathbf{F}}\mathbf{F}^{-1}. \quad (\text{B.39})$$

The spatial velocity gradient is further decomposed into a symmetric and skew symmetric part as

$$\mathbf{l} = \mathbf{d} + \mathbf{w}, \quad (\text{B.40})$$

where

$$\mathbf{d} = \frac{1}{2}(\mathbf{l} + \mathbf{l}^T), \quad (\text{B.41})$$

$$\mathbf{w} = \frac{1}{2}(\mathbf{l} - \mathbf{l}^T). \quad (\text{B.42})$$

B.2 Cauchy theorem and stress measures

Let us consider a body B that is taken to $\mathcal{B}$ by deformation, then cut into two parts to obtain a smooth surface δa that we can define point $\mathcal{P}$. The

force transferred from one part to another part across Δa can be written as Δp and its couple Δm . Tenting δa to zero, one can write

$$\lim_{\delta a \rightarrow 0} \frac{\Delta p}{\Delta a} = \mathbf{t} \quad (\text{B.43})$$

where $\mathbf{t}$ is called the Cauchy stress vector. Same procedure can be applied to the undeformed body and the counterpart of $\mathbf{t}$ in the reference configuration $\mathbf{T}$ is obtained as

$$\Delta p = \mathbf{t} \Delta a = \mathbf{T} \Delta A, \quad (\text{B.44})$$

where ΔA is the surface in the reference configuration. Hence, the Cauchy's stress theorem introduces that the relation between $\mathbf{t}$ and $\mathbf{n}$ and accordingly the relation between $\mathbf{T}$ and $\mathbf{N}$ is linear and represented as

$$\mathbf{t} = \boldsymbol{\sigma} \mathbf{n}, \quad (\text{B.45})$$

$$\mathbf{T} = \mathbf{P} \mathbf{N}, \quad (\text{B.46})$$

where $\boldsymbol{\sigma}$ is called the Cauchy stress tensor and is related to the body in the current configuration. $\mathbf{P}$ refers to the first Piola-Kirchhoff stress tensor which is defined with respect to the body surface in the reference configuration and thus can be considered as a three dimensional generalization of the engineering stress.

With the help of Eq. B.44 and B.26, one can write

$$\Delta p = \mathbf{t} \Delta a = \boldsymbol{\sigma} \mathbf{n} \Delta a = J \boldsymbol{\sigma} \mathbf{F}^{-T} \mathbf{N} \Delta A = \mathbf{P} \mathbf{N} \Delta A, \quad (\text{B.47})$$

which clearly identifies the relation between the Cauchy stress tensor and the first Piola Kirchoff stress tensor as

$$\mathbf{P} = J \boldsymbol{\sigma} \mathbf{F}^{-T} = \mathbf{F} \mathbf{S}. \quad (\text{B.48})$$

Accordingly, the second Piola-Kirchhoff stress tensor is represented as

$$\mathbf{S} = J \mathbf{F}^{-1} \boldsymbol{\sigma} \mathbf{F}^{-T}. \quad (\text{B.49})$$

B.3 Balance principles

B.3.1 Linear momentum balance

Due to the conservation of mass, one can defined the linear momentum as

$$\int_m \mathbf{v} dm = \int_m \dot{\mathbf{x}} dm = \int_V \rho \dot{\mathbf{x}} dV, \quad (\text{B.50})$$

where $\dot{\mathbf{x}} = \frac{\mathbf{v}}{t}$, and m , V , ρ denote mass, volume and mass density of a body. Accordingly, B.50 equals to the force applied to the body as

$$\frac{d}{dt} \int_V \rho \dot{\mathbf{x}} dV = \int_V \mathbf{f} dV + \int_a \mathbf{t} da, \quad (\text{B.51})$$

where $\mathbf{f}$ is the volume force vector per unit volume. The second term of Eq. B.51 in the right hand side represents the surface forces which can also be rewritten as

$$\int_a \mathbf{t} da = \int_a \boldsymbol{\sigma} \mathbf{n} da = \int_V \text{div} \boldsymbol{\sigma} dV. \quad (\text{B.52})$$

Thus, the linear momentum balance of a body can be given with the help of first Euler's law of motion as

$$\text{div} \boldsymbol{\sigma} + \mathbf{f} = \rho \ddot{\mathbf{x}}. \quad (\text{B.53})$$

With the help of the momentum balance equation B.53, we can write

$$\dot{K} + \dot{\mathcal{W}} = \mathcal{P}. \quad (\text{B.54})$$

where

$$K = \int_V \left(\rho \frac{1}{2} \mathbf{v} \cdot \mathbf{v} \right) dV, \quad (\text{B.55})$$

$$\mathcal{P} = \int_A (\mathbf{v} \cdot \mathbf{t}) dA + \int_V (\mathbf{v} \cdot \mathbf{f}) dV, \quad (\text{B.56})$$

$$\mathcal{W} = \int_V (\boldsymbol{\sigma} : \mathbf{d}) dV. \quad (\text{B.57})$$

Finally, the dissipated heat during the deformation $\mathcal{D}$ per unit volume is written as

$$\mathcal{D} = \mathcal{W} - \int_{V_0} \dot{\Psi} dV_0 \quad (\text{B.58})$$

where Ψ is the stored energy during the deformation. It should be noted here that the stress power can also be obtained from other work conjugates such as $(\mathbf{P}, \mathbf{F})$, $(\mathbf{S}, \mathbf{E})$ etc.

B.3.2 Energy balance

The first law of thermodynamics results in the conservation of energy. According to the first law, one can write

$$dU = dW + dQ, \quad (\text{B.59})$$

where dU , dW and dQ are internal energy, work done by the system and heat absorbed by the system, respectively. Using the work conjugates $\boldsymbol{\sigma} : \mathbf{d} = \mathbf{S} : \frac{1}{2}\dot{\mathbf{C}}$, one can write the energy balance as

$$\dot{U} = \mathbf{S} : \frac{1}{2}\dot{\mathbf{C}} - \text{div} \mathbf{Q} + R, \quad (\text{B.60})$$

where $\dot{U}$, $\mathbf{Q}$ and R denote the rate of change of the internal energy, the heat flux vector and an internal heat source, respectively.

B.3.3 Entropy balance and dissipation inequality in constitutive modeling

The second law of thermodynamics states the entropy of the system increases in all natural thermodynamic processes. Therefore, the second law induces a major mathematical restriction in constitutive modeling containing heat conduction or internal energy dissipation. The Clausius-Duhem inequality follows the second law and is given by

$$\mathcal{D} \geq 0, \quad (\text{B.61})$$

where $\mathcal{D}$ is dissipation. $\mathcal{D}$ has to be satisfied at every point in the body B at any times. The Clausius-Duhem inequality is given by

$$\rho \mathcal{D} = \rho T \dot{S} - \rho Q - \text{div} \mathbf{q}, \quad (\text{B.62})$$

where $\mathbf{q}$ is the heat flux vector. Since the heat flow occurs along the direction opposite to the temperature gradient, one can write

$$\mathcal{D} = T \dot{S} - \dot{U} + \frac{1}{pJ} \mathbf{P} : \dot{\mathbf{F}} \geq 0. \quad (\text{B.63})$$

Let us assume the stored energy per unit undeformed volume in functional form as

$$\Psi = \tilde{\Psi}(\mathbf{F}, T, \Omega) \quad (\text{B.64})$$

where Ω is a set of internal variable that can be in scalar, vector or tensor form. Since we deal with solid mechanics, let us consider the Helmholtz free energy for Ψ . Thus, substituting Ψ into Eq. B.63, one can write

$$\mathcal{D} = -\dot{\Psi} - S \dot{T} + \frac{1}{pJ} \mathbf{P} : \dot{\mathbf{F}} \geq 0, \quad (\text{B.65})$$

where

$$\dot{\Psi} = \frac{\partial \Psi}{\partial \mathbf{F}} : \dot{\mathbf{F}} + \frac{\partial \Psi}{\partial T} \dot{T} + \frac{\partial \Psi}{\partial \Omega} \cdot \dot{\Omega}. \quad (\text{B.66})$$

Finally, Eq. B.65 is written as

$$\mathcal{D} = - \left(\frac{\partial \Psi}{\partial T} \dot{T} + \frac{\partial \Psi}{\partial \Omega} \cdot \dot{\Omega} \right) - S \dot{T} + \frac{1}{pJ} \left(\mathbf{P} - \frac{\partial \Psi}{\partial \mathbf{F}} \right) : \dot{\mathbf{F}} \geq 0, \quad (\text{B.67})$$

B.3.4 Incompressible materials

The strain energy function for incompressible hyper-elastic materials is postulated by

$$\Psi = \hat{\Psi}(\mathbf{F}, T, \Omega) - p(J - 1), \quad (\text{B.68})$$

where $J = \det \mathbf{F} = 1$ denotes the incompressibility constraint. The scalar value p is a Lagrange multiplier which is determined from the equilibrium and the boundary conditions.

For an incompressible material with the strain energy function as given in eqn. B.68, the first Piola-Kirchhoff stress tensor is given as

$$\mathbf{P} = \frac{\partial \hat{\Psi}(\mathbf{F}, T, \Omega)}{\partial \mathbf{F}} - p \mathbf{F}^{-\text{T}}. \quad (\text{B.69})$$

The Eq. B.69 is valid, as long as the following conditions are satisfied:

- Incompressible hyperelastic material
- Negligible contribution of internal energy in deformation
- Isothermal deformation
- Moderate and large range of deformation
- Absence of crystallization

C Nomenclature

C.1 Glossary symbols

The nomenclature in the thesis follows the conventions and symbols that are commonly used in modern tensor algebra and tensor analysis [75].

Conventions

Index and suffix conventions

$\bullet_M$	DN gel matrix
$\bullet_p$	Polyelectrolyte network
$\bullet_n$	Neutral network
$\bullet_c$	Network of chains between clusters
$\bullet_{cc}$	Cluster networks
$\bullet_{cc,sub}$	Sub-cluster networks
$\bullet_r$	Reversible network
$\bullet_{ir,n}$	Irreversible neutral network
$\bullet_{ir,int}$	Interactions between alginate and PAAm networks due to irreversible bonds
$\bullet_{sys}$	System
$\bullet_{ext}$	External sources
$\bullet_{int}$	Internal sources
$\bullet_d$	Value of the parameter in the spatial direction d

Tensor conventions and operations

$a, b, \dots$	Scalars (0^{th} order tensors)
$\mathbf{a}, \mathbf{b}, \dots$	Vectors (First order tensors)
$\mathbf{A}, \mathbf{B}, \dots$	Vectors (Second order tensors)
$\mathbf{a} \otimes \mathbf{b}$	Dyadic product of vectors
$\mathbf{A} : \mathbf{B}$	Scalar product of second order tensors
$\bullet^T$	Transpose of a tensor
$\bullet^{-1}$	Inverse of a function (or a tensor)

Table C.3: Glossary symbols in the thesis

Symbol	Description	Eq.
r	Average end-to-end distance of a polymer chain	3.1
n	Number of segments	3.2
l	Length of a segment	3.2
θ	Angle between the directions of two segments	3.2
C	Characteristic ratio	3.5
r_x, r_y, r_z	Average end-to-end distance in a direction of cartesian coordinates	3.7
$\bar{r}$	Normalized mean end-to-end distance of a polymer chain	3.8
$p(n, \bar{r})$	Probability distribution of the end-to-end vectors of a polymer chain	3.8
S	Entropy of a polymer chain	3.10
k	The Boltzmann constant	3.10
ψ	The Helmholtz free energy	3.11
T	The absolute temperature	3.11
ψ_g	The free energy of a gaussian chain	3.12
f	The force applied to a chain	3.13
$\mathcal{P}$	The pressure applied to the system	3.13
V	The volume of the system	3.13
f_g	Entropic force of a gaussian chain	3.14
$\mathcal{L}$	The Langevin function	3.15
c	The normalization factor	3.20
β	The inverse Langevin function	3.20
ψ_{ng}	The free energy of a non-gaussian chain	3.24
f_{ng}	Entropic force of a non-gaussian chain	3.25
$\mathbf{F}_m$	Deformation gradient in micro-scale	4.1
$\mathbf{F}$	Deformation gradient	4.1
$\mathbf{d}$	Particular direction	4.2
$\overset{d}{\chi}$	Macro-stretch applied in the direction $\mathbf{d}$	4.2
$\mathbf{C}$	The right Cauchy-Green tensor	4.2
$\overset{d}{\lambda}$	Micro-stretch applied in the direction $\mathbf{d}$	4.2
$\bar{r}_0$	Normalized mean end-to-end distance of chains in a undeformed configuration	4.3
$\overset{d}{\Psi}$	Strain energy of a network in direction $\mathbf{d}$	4.5
N	Number of active chains in a network	4.5

Continued on next page ...

Table C.3 – continued from previous page

Symbol	Description	Eq.
$\Psi_g^{\mathbf{d}}$	Strain energy of a polymer network in direction $\mathbf{d}$ based on Gaussian statistics	4.6
$\Psi_{ng}^{\mathbf{d}}$	Energy of a polymer network in direction $\mathbf{d}$ based on non-Gaussian statistics	4.7
Ψ	Energy of a polymer network in 3D	4.8
ω	Weight factors	4.9
$\mathbf{P}$	First Piola-Kirchoff stress tensor	4.10
$\mathbf{P}_g$	First Piola-Kirchoff stress tensor based on Gaussian statistics	4.13
$\mathbf{P}_{ng}$	First Piola-Kirchoff stress tensor based on non-Gaussian statistics	4.14
N	Number of active chains	5.2
D_A	Set of available active chain	5.4
n_{min}	Minimum segment number in D_A	5.4
λ	Minimum stretch applied to a network	5.4
n_{max}	Maximum segment number in D_A	5.4
κ	Density of the cross-linking site of a polymer chain	5.9
$P(n, \bar{r}, \kappa)$	Probability of existence of a polymer chain	5.11
$g\left(\frac{\mathbf{d}}{\lambda}\right)$	Normalization function for the probability distribution of a polymer chain	5.17
N_0	Active chain number in an underformed polymer network	5.25
a	Active chain ration of a polymer chains in a polymer network	5.25
N_A	The Avagadro constant	5.25
M	Molar ratio of a polymer network	5.25
n_{mean}	Mean segment number of polymer chains in a polymer network	5.25
$\Phi\left(\frac{\mathbf{d}}{\lambda_j}\right)$	Function for the network re-orientation	5.27
χ	Macro stretch applied to a DN gel matrix	5.28
Ω	Set of internal variables	5.35
$\mathcal{C}$	The ratio of the cross-linking density of the networks	5.47
ξ	Number of sub-cluster networks	6.12
$\bar{r}_{cc,min}$	Minimum normalized mean end-to-end distance of a polymer chains	6.14
$\bar{r}_{cc,max}$	Maximum normalized mean end-to-end distance of a polymer chains	6.14

Continued on next page ...

Table C.3 – continued from previous page

Symbol	Description	Eq.
$\mathcal{F}^d$	Force developed by polymer chains in a direction $\mathbf{d}$	6.15
F	Force developed by a polymer network	6.16
μ	Stiffening ratio of the cluster network to the network of chains between cluster	6.22
$\mathcal{K}$	Ratio of rebonded cross-linking	7.5
U_{st}	Stored energy in a DN matrix due to heat transfer	7.6
U_{conv}	Energy transfer due to convection	7.6
U_{rad}	Energy transfer due to radiation	7.6
ρ	Mass density of the sample	7.6
V	Volume of the sample	7.6
c	Specific heat capacity	7.6
h	Convictional heat transfer rate	7.6
A	Surface area of the sample	7.6
ϵ	Emissivity coefficient	7.6
σ_b	The Stefan-Boltzman constant	7.6
U_a	Activation energy of rebonding process	7.8
k	Chemical reaction rate	7.9
R	Gas constant	7.9
$\mathcal{A}$	Pre-exponential factor	7.9
$\mathcal{K}_{int,1}$	Ratio of rebonded cross-linking due to the internal kinetic energy	7.12
$\mathcal{K}_{int,2}$	Ratio of rebonded cross-linking due to the stored energy	7.14
$\hat{N}$	Total number of broken chains	7.17
N_{heal}	Number of healed polymer chains	7.19
κ_{heal}	Density of the cross-linking site of a polymer chain in a healed polymer network	7.19
$\mathcal{D}$	Energy dissipation in the Clausius–Duhem inequality	B.63

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