İSTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

PHYSICAL PROPERTIES OF CHITOSAN/GRAPHENE OXIDE COMPOSITE FILMS

M.Sc. THESIS

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Department of Chemistry

Chemistry Programme

JUNE 2016

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Thesis Advisor: Prof. Dr. F. Bedia Erim BERKER

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

KİTOSAN/GRAFEN OKSİT KOMPOZİT FİLMLERİNİN FİZİKSEL ÖZELLİKLERİNİN İNCELENMESİ

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Semira BENER, a M.Sc student of ITU Graduate School of Science Engineering and Technology student ID 509131033, successfully defended the thesis entitled "PHYSICAL PROPERTIES OF CHITOSAN/GRAPHENE OXIDE COMPOSITE FILMS", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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FOREWORD

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May 2016 Semira BENER

TABLE OF CONTENTS

Page

ABBREVIATIONS

CS	**:** Chitosan
GO	**:** Graphene Oxide
DA	**:** Degree of Acetylation
FTIR	**:** Fourier Transform Infrared
TGA	**:** Thermogravimetric Analysis
DTG	**:** Derivative Thermogravimetric Analysis
IPDT	**:** Integral Procedural Degradation Temperature

SYMBOLS

T_{max}	: Temperature of the Fastest Degradation Date
$T_{-5\%}$	: Temperature Corresponding to 5% Weight Loss
$T_{-10\%}$	: Temperature Corresponding to 10% Weight Loss
$T_{-50\%}$	: Temperature Corresponding to 50% Weight Loss
T_0	: Polymer Degradation Temperature
T_i	: Initial Experimental Temperature
T_f	: Final Experimental Temperature
A*, K*	: Ratios Related to the Total TGA Thermogram
σ	: Engineering stress
ε	: Engineering strain

LIST OF TABLES

Page

LIST OF FIGURES

Page

PHYSICAL PROPERTIES OF CHITOSAN/GRAPHENE OXIDE COMPOSITE FILMS

SUMMARY

Chitosan is a natural, biodegradable, non-toxic and commercial polymer with excellent properties such as low toxicity, biocompatibility, antibacterial and antifungal properties and film forming ability. It has been utilized in various applications in industry such as food packaging to extend shelf life of food products. Despite these favorable properties, relatively poor mechanical properties restrict its applications. In order to develop the physical properties of chitosan, various fillers or polymeric materials might be used to prepare many chitosan blends that confer improved structural and physical properties.

Graphene oxide, a functionalized form of graphene, is considered as an ideal reinforcing agent in composite films due to its excellent properties such as thermal stability and high dispersibility in water. In this study, chitosan and chitosan/graphene oxide composite films were prepared by casting from solutions in the form of transparent films and the prepared films were treated with 1% and 20% Na_2SO_4 crosslinking solution. The formation of the films were verified by Fourier transform infrared (FT-IR) spectroscopy.

Thermogravimetric measurements were carried out in the temperature range of 30-800 °C at a constant heating rate of 10°C/min. From thermogravimetry (TG) and DTG curves, characteristic parameters of degradation of the tested composite films such as temperature corresponding to 5 wt. %, 10 wt.% and 50 wt.% weight loss, temperature of the fastest degradation rate, polymer degradation temperature and char residuals were determined. The results obtained from this study revealed that the chitosan/graphene oxide demonstrated higher thermal stability than that of neat chitosan as it is expected. On the other hand, thermal parameters of the cross-linked composite films were not altered significantly. The temperatures at which the polymer decomposition starts, for the cross-linked films are lower than that of neat chitosan which indicates lower thermal stability.

Mechanical properties of these films were investigated by mechanical testing (Instron 3345) at a speed of 0.5 mm/s. Modulus of elasticity and the resilience of the composite films were determined from the stress-strain curves. Modulus of elasticity of the composite films were higher than that of neat chitosan. Resilience of the composite films were determined calculating the area just under the stress-strain curve of the elastic region. Composite films did not have the same trend in the resilience with the increase in the elastic modulus. Chitosan film blended with graphene oxide and cross-linked with 20% Na_2SO_4 has the highest elastic modulus and the highest resilience which resulted in cross-linked film having the highest strength but being more brittle. Therefore these composite materials with enhanced physical properties may find real-life applications in various fields.

KİTOSAN/GRAFEN OKSİT FİLMLERİNİN FİZİKSEL ÖZELLİKLERİNİN İNCELENMESİ

ÖZET

Kitosan, düşük toksisite, biyouyumluluk, antibakteriyel ve antifungal özellikler ve üstün film oluşturma yeteneği gibi özelliklere sahip doğal, biyobozunur ve piyasada ticari olarak bulunabilen bir polimerdir. Günümüzde, plastik kökenli gıda paketleme malzemelerinden kaynaklanan çevresel kirlilik ve sınırlı doğal kaynaklar sebebiyle bu tip doğal polimerlere olan ilgi hızla artmıştır.

Kitosanın; düşük toksisite, biyouyumluluk, antibakteriyel ve antifungal özellikler ve film oluşturma yeteneği gibi özelliklerinden dolayı gıda endüstrisinden tekstile, kağıt endüstrisinden atık su arıtımına kadar birçok alanda uygulamaları mevcuttur. Aynı zamanda ilaç salım sistemleri, doku mühendisliği, yapay deri gibi biyomedikal uygulamaları da bulunmaktadır. Özellikle gıda endüstrisinde yiyeceklerin raf ömrünü uzatmak amaçlı kullanımları mevcuttur.

Kitosan, kitinden deasetilasyon yoluyla elde edilir ve kimyasal formülü β-(1, 4)-2-amino-2-deoksi-D-glukopiranozdur. Kitin ise kabuklu deniz canlılarının kabuklarından elde edilen doğal bir polimerdir. Kitinin kimyasal yapısı kitosanınkiyle aynı olmasına rağmen tek fark; asetilamino (-NH-CO-CH_3) gruplarının deasetilasyon yoluyla amin (-NH_2) gruplarına dönüşmüş olmasıdır. Bu iki yapı arasındaki oran da deasetilasyon derecesini (DA) verir. Bu oran, kitosanın çözünürlüğünü ve birçok fiziksel özelliğini etkilemektedir. Kitosan, kimyasal yapısında bulunan amin gruplarının zayıf asidik çözeltilerde protonlanmasından dolayı pozitif yüklü bir polielektrolite dönüşür ve bu da polimerin suda çözünmesini sağlar.

Grafen; grafitin, hekzagonal olarak düzenlenmiş karbon atomlarından oluşan katmanlarına verilen isimdir. Olağanüstü optik, mekanik ve elektronik özelliklerinden dolayı 21. yüzyılın en önemli malzemelerinden biri haline gelmiştir. Grafenin fonksiyonelleştirilmiş hali olan grafen oksit, grafen gibi sahip olduğu elektronik ve mekanik özelliklerden dolayı nanoelektronik, iletken ince film yapımı, superkapasitör, nanosensor ve biyomedikal uygulamalar gibi bir çok alanda uygulamaları mevcuttur. Elde edilişi grafitin sülfürik asit ve potasyum permanganat karışımı gibi kuvvetli oksitleyici ajanlarla oksidasyonu yoluyla olur. Sp^2 hibrit yapısındaki grafen tabakaları oksidasyonla birlikte kırılarak tabakalar arası uzaklık artar. Azalan etkileşimlerle birlikte grafenoksit tabakaları birbirinden ayrılmış olur. Bu yolla sulu çözeltide grafenoksit dispersiyonları hazırlanmış olur.

Grafen oksit, kimyasal yapısında hidroksi ve epoksi grupları gibi birçok oksijen içerikli fonksiyonel grup barındırır. Yapının kenarı boyunca da düşük oranlarda karboksilik asit grupları bağlı olarak bulunur. Bu fonksiyonel gruplar sayesinde su ile grafen oksit arasında kuvvetli hidrojen bağları oluşur ve böylelikle grafen oksit suda etkili bir şekilde dağılabilir.

Grafen oksit, yüzeyine bağlı olan bu hidrofilik fonsiyonel gruplar yoluyla hem suda hem organik solventlerde yüksek derecede dağılabilme özelliğine sahip bir malzeme olarak kümeleşmeyi önler; polimerler ve dolgu maddeleri arasında güçlü etkileşimler sağlar. Dolayısıyla suda yüsek dağılabilirliği ve termal kararlılığıyla kompozit malzemeler için ideal bir katkı maddesidir.

Grafen esaslı malzemelerin dolgu veya katkı malzemesi olarak kullanılmasının kompozit filmlerin elastisite, çekme dayanımı, termal kararlılık ve elektriksel iletkenlik gibi birçok fiziksel özelliğinde önemli iyileşmeler meydana getirdiği bilinmektedir. Bu özelliklerden biri olan termal kararlılık, kitosan filmleri gibi gıda ve ilaç endüstrisinde kullanılan doğal polimerler için önemli bir fiziksel özellliktir. Çünkü bu tip malzemeler hazırlanmaları, işlem görmeleri veya tüketilmeleri esnasında ısıl işlemlere maruz kalabilmektedirler. Diğer bir traftan, antifungal, antibakteriyel, biyouyumluluk, biyobozunurluk ve düşük toksisite gibi önemli özelliklerinin dışında zayıf mekanik ve fiziksel özellikleri kitosanın uygulama alanlarını sınırlandırmaktadır. Dolayısıyla farklı katkı ve dolgu malzemesi veya polimer katkılarıyla kitosan kompozit filmler meydana getirilerek fiziksel özelliklerin iyileştirilmesine dayalı çalışmalar önem kazanmıştır. Sonuç olarak $–NH_2$ ve –OH gruplarına sahip hidrofilik bir polimer olan kitosan, asidik koşullarda bu grupların protonlanmasıyla grafen oksit ve polimer zincirleri arasındaki etkileşimler sayesinde grafen oksitle iyi bir dispersiyon oluşturabilir.

Bu çalışmada kitosan film ve kitosan/grafenoksit kompozit filmleri çözeltiden dökme yoluyla hazırlanmış ve hazırlanan filmler 1% ve 20% Na_2SO_4 çaprazbağlayıcı çözeltileriyle muamele edilerek 5 farklı kompozit film içeren bir seri kompozit film hazırlanmıştır. Filmlerin karakterizasyonu Fourier transform infrared (FT-IR) spektroskopisiyle gerçekleştirilmiştir.

Termogravimetrik analizler 30-800 °C sıcaklık aralığında ve 10 °C/dk sabit ısıtma hızında gerçekleştirilmiştir. Termogravimetri eğrileri ve türev eğrilerinden 5%, 10% ve 50% kütle kaybının olduğu sıcaklık değerleri, bozunma basamaklarında bozunmanın en hızlı gerçekleştiği sıcaklık değerleri, bozunmanın başladığı sıcaklık değerleri ve analiz sonucu kalan kütle gibi termal parametreler elde edilmiştir.

Elde edilen sonuçlara göre sadece grafen oksit katkılı kompozit film beklendiği üzere kitosana göre biraz daha yüksek bir termal kararlılık göstermiştir. 80 ppm gibi düşük miktarda bir katkıya göre iyi bir gelişme olarak yorumlanmıştır. Diğer taraftan çapraz bağlayıcı kullanılan filmlerde kitosan ve kitosan/grafenoksit filmlerine göre fazladan bir bozunma basamağı daha görülmüş fakat bu basamaklarda bozunmanın en hızlı gerçekleştikleri sıcaklık değerlerinin kitosana göre daha düşük olduğu görülmüştür. Aynı zamanda polimer bozunmasının başladığı sıcaklıkların çapraz bağlı filmlerde daha düşük olduğu belirlenmiştir. Çapraz bağlı filmlerde 5%, 10% kütle kaybının olduğu sıcaklıklarda ve kalan kütlelerde artış görülürken diğer termal parametrelerde düşüş görülmüştür. Artış görülen termal parametreler, çapraz bağlanmanın kitosandaki polimerik zincirlerin hareketini sınırlandırdığının; polimer ve katkı arasındaki etkileşimin bir kanıtı olarak yorumlanmış ve bu sonuçlar FT-IR analiz, sonuçlarıyla da tutarlılık göstermiştir. Fakat bunlara rağmen polimerin bozunmaya başladığı ilk sıcaklıkların çapraz bağlı filmlerde kitosana göre daha düşük olması çapraz bağlı filmlerin daha düşük termal kararlılığa sahip olması şeklinde yorumlanmıştır. Filmlerin ayrıca integral yöntemsel bozunma sıcaklıkları (IPDT) da termogramların altında kalan alanların hesaplanması yardımıyla belirlenmiş ve karşılaştırılmıştır.

Bu karşılaştırmaya göre komposit filmlerin tamamı kitosana göre daha yüksek bir IPDT değeri göstermiş fakat hesaplanan bu değerler tam anlamıyla deneysel verilerle örtüşmemiştir.

Kitosan çözeltisine 80 ppm grafen oksit katılarak hazırlanan grafen oksit/kitosan kompozit filmlerde ve çapraz bağlayıcı ile muamele edilen kompozit filmlerde, grafen oksitin filmlerin mekanik özelliklerinde meydana getireceği değişimler çekme deneyleri ile belirlenmiştir. Kompozit filmlerin elastiklik modülü ve rezilyans değerleri gerilme-birim şekil değimi eğrileri yardımıyla hesaplanmıştır.

1% kitosan filmlerde esneklik özelliği, filmde çapraz bağlayıcı miktarı ile azalmıştır. Buna gösterge; esneklik modulü değerinin filmde çapraz bağlayıcı sodyum sülfat miktarının artışı ile artmasıdır. Modülü yüksek olan filmin kuvvete dayanımı daha fazladır, esneklik kabiliyeti en düşüktür. 1% sodyum sülfat miktarı kitosan filmin esnekliğini bir miktar azaltırken; 20% sodyum sülfat ise daha belirgin bir fark ile azaltmıştır. Filmde çapraz bağlayıcı sodyum sülfat miktarı arttıkça; elastisite modülü de değişmiştir. 1% sodyum sülfat çapraz bağlı filmde, çapraz bağ sonrası görünüşü değiştirme ve bükülme meydana getirmektedir; 20% sodyum sülfat çapraz bağlı film ise daha engebesiz yüzeye sahiptir. Sodyum sülfat ile kitosan filmleri çapraz bağlama; hem filmlerin suda dekompoze olmalarının önüne geçmiş, hem de filmlerin kuvvete dirençlerini arttırmıştır. En esnek ve elastiklik modülü en düşük olan malzemenin (kuvvete en dayanımsız olan) çapraz bağ yapmamış sadece kitosan filmdir.

Grafen oksitin katkısı ile 0%, 1% ve 20% sodyum sülfat çapraz bağlı film serisinde esnekliğin azaldığı görülmektedir. Çapraz bağsız kitosan ve kitosan/grafenoksit; %1 çapraz bağlı kitosan ve kitosan/grafenoksit ve %20 çapraz bağlı kitosan ve kitosan/grafenoksit filmlerinin esneklik modülleri birbiri ile karşılaştırıldığında; grafen oksit katkılı filmlerin esneklik modülünün artmış olduğu görülmüştür. Elastiklik modülünün artması filmde esneklik özelliğinin azaldığını göstermektedir. Bu esneklik farkı en çok 1% çapraz bağlı kitosan/grafenoksit numunesinde görülmüştür.Film serisi içerisinde en fazla mekanik dayanım kazanan film, %1 sodyum sülfat çapraz bağlı 80 ppm grafen oksit içeren filmdir. Seri içerisinde bu numune; esneklik özelliği en az olan ve maruz kalacağı kuvvetin etkisinde en kırılgan olan malzemedir.

Filmlerin esneklik gösterdikleri zaman içerisinde absorpladığı enerji değeri olan rezilyans hesaplamaları da yapılmıştır. Filmlerin esneklik gösterdiği bölgede, uygulanan kuvvetin etkisiyle filmde şekil değişikliği meydana gelmemektedir. Filmde esneklik modülünün artmasıyla; uygulanan kuvvet ortadan kalktığında filmin eski haline dönebilmesi için depolayacağı enerjinin de yani rezilyansın da artması beklenmektedir. Tüm kitosan film serisi içinde bağıl bir karşılaştırma yapıldığında; kitosan/grafenoksit ve 20% çapraz bağlı kitosan/grafenoksit filmlerinde esneklik modülü arttıkça rezilyans değerlerinde de aynı gidişatta bir artış görülmüştür. Kitosan ve 20% çapraz bağlı kitosan filmlerinin esneklik modülü ile rezilyans değerlerindeki değişim aynı şekilde gerçekleşmemiştir. Sodyum sülfat ile çapraz yapmamış olan katkısız kitosan filmin rezilyans değeri yüksek çıkmıştır. Bunun nedeninin; filmde kuvvet dayanımı kazandıracak sodyum sülfat çapraz bağlanma veya grafen oksit katkısı gibi bir geçiş malzemesinin olmaması düşünülmüştür. Filmdeki bağlar sadece kitosanın kendi zincirleri arasındaki bağlanmadır; bu bağlar katkılı malzemeye göre daha zayıftır. Film bu sayede esnektir ve esneklik gösterdiği zaman içerisinde sahip olduğu rezilyansı, 1% ve 20% çapraz bağlı filmlerine oranla daha yüksek bir değerdedir.Kitosan filmlerde çapraz bağlayıcı sodyum sülfatın ve filmlerde bulunan

grafen oksitin esnekliğe olan etkisi birlikte düşünüldüğünde; kuvvete dayanımı en fazla olan fakat en gevrek olan malzemenin %1 sodyum sülfat çapraz bağlı 80 ppm grafen oksit katkılı film olduğu görülmüştür.

1. INTRODUCTION

Recently more attention has been paid to development and application of natural biopolymers derived from a range of food waste products [1]. This attention has increased because of the limited natural sources and the environmental pollution caused by plastic food packaging materials which are not biodegradable [2]. Over the last few decades several biopolymers have been increasingly paid attention due to their chemical, biomedical and food applications in industry [3].

Chitosan (CS), a derivative of chitin, is a natural polymer with a formula of [β-(1, 4)-2-amino-2-deoxy-ɒ-glucopyranose], which is the second most found polysaccharide on earth after cellulose. It is a natural, biodegradable and commercial polymer with low toxicity, which has been utilized in various applications in food packaging industry to extend shelf life of food products. It may find a field of application in food packaging industry by forming transparent films [4].

With its some of excellent properties such as low toxicity, biocompatibility, antibacterial and antifungal properties and film forming ability, chitosan has numerous industrial applications, e.g., in cosmetics, paper industry, textile industry, food processing ,sorbent material in chromatographic separations and adsorbent for wastewater treatment [5-10]. Chitosan also have been studied for use in several biomedical applications including drug delivery systems, tissue engineering, artificial skin and wound healing [11-14].

Chitosan was first discovered by C. Rouget in 1859, after his experiment with chitin in hot and concentrated potassium hydroxide and he proposed “modified chitin” for the name of this new product. Although the name “chitosan” is now strongly used in the scientific terminology, it poses a problem due to the fact that it has one chemical structure differing in terms of amine groups only but two names, which depends on the degree of deacetylation (DA) [15]. The contemporary development of the research on chitosan has specifically begun when serious concerns has raised about the remarkable amount of food waste generated from processing of crabs and shrimps in the food industry. In the early 1970s, it was suggested converting this waste material

into a more useful product. After 1970s, the number of publications on chitosan has increased continuously [16].

Chitosan is prepared from chitin which is the waste product of the canning industry of seafood such as crab and shrimp [17], by partial deacetylation using concentrated sodium hydroxide or enzymatic hydrolysis in the existence of chitin deacetylase[18].

The chemical structure of chitosan involve three types of functional groups which are amino groups, primary and secondary hydroxyl groups at the C-2, C-3 and C-6 positions in the repeating units, respectively [19] (**Fig. 1.1**). Presence of these amino groups are also related with the degree of N–acetylation of chitosan (DA) [20]. This is an important parameter which is the ratio of structural units of chitin and chitosan and it has a significant effect on the solubility and physical properties of chitosan[5].

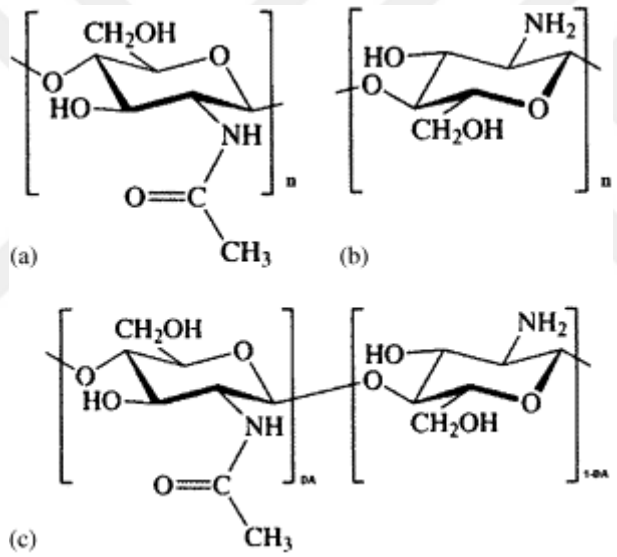

Figure 1.1 : Chemical structure of chitin (a) and chitosan (b) repeating units and structure of partially deacetylated chitosan (c) (From ref. [18]).

Chitosan is easily dissolved in dilute acidic solutions at pH below 6.0 while it is insoluble at neutral pH. The reason for this is that chitosan might be regarded as a mild-strong base since the polymer contains primary amino groups which has a pK_a value of 6.3, in its repeating units. With these amino groups, pH can considerably change the properties and the charged state of chitosan [21]. These amine groups of chitosan take H^+ and become positively charged in acidic media. Thus, chitosan is considered as a water-soluble cationic polyelectrolyte due to these charged groups in its repeating units. However amine units of chitosan are deprotonated and chitosan

loses its positive charge which results in becoming insoluble of the polymer in water when the pH increases above 6. The transition between solubility and insolubility states takes place at pK_a value of the polymer which correspond to pH between around 6.3.Since the pK_a value heavily depends on the degree of acetylation (DA), solubility of chitosan also depends on the deacetylation degree [22]. Considering the solubility properties of chitosan, 1% acetic acid solution at pH about 4.0, is the most commonly used solution to dissolve CS [23].

Besides all of these unique properties, chitosan is a biopolymer that has an excellent film forming capability [16].

1.1 Graphene Oxide

Graphene, a single atomic plane of graphite, consists of pure carbon atoms arranged in a regular hexagonal pattern [24, 25], has been an exciting material of the 21st century and received great attention due to its extraordinary optical, mechanical and electronic properties [26, 27]. A method was first used to isolate graphene in 2004 by A. Geim and K. Novoselov. After this invention, some intensive interest and a number of research on graphene increased dramatically [26].

Due to its excellent mechanical and electronic properties, functionalized form of graphene, graphene oxide (GO), is considered as a promising material in applications such as nano electronics, conductive thin films, super capacitors, nano sensors, and bio medicals [24, 28].

Chemical structure of graphene oxide has been debated over the years due to the complexity of the material arising from its amorphous character, and present analytical methods are insufficient to characterize such materials [29]. The most well-known model for graphene oxide was proposed by Lerf and Klinowski (**Fig. 1.2**) [30, 31]. It consists many oxygen containing hydrophilic functional groups such as hydroxyl and epoxy [32]. There also exists carbonyl groups with low proportions, quite possibly carboxylic acids along the side of the sheet[29]. When graphene oxide is dispersed in water, the surface becomes negatively charged due to these functional groups such as phenolic hydroxyl and carboxylic acid groups [33]. **Fig. 1.3** displays the interactions

between water and the epoxides and hydroxyl groups of GO by means of hydrogen bonds resulting the water is strongly bound to GO [34, 35].

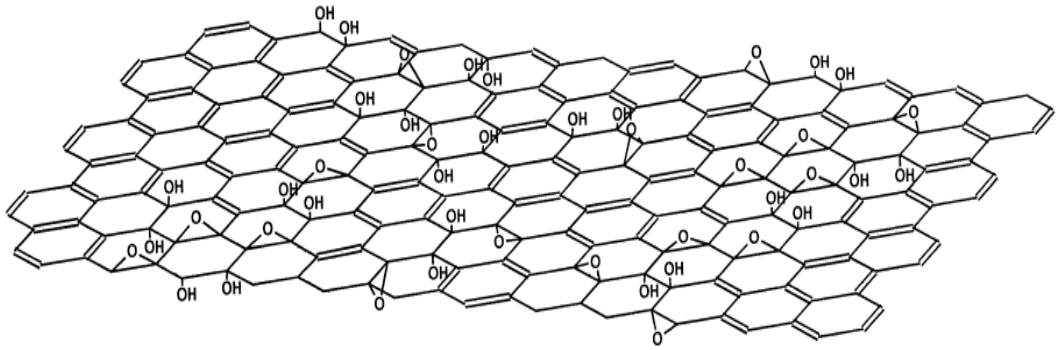

Figure 1.2 : Structure of graphene oxide proposed by Lerf. A and Klinowski J. (From ref. [30]).

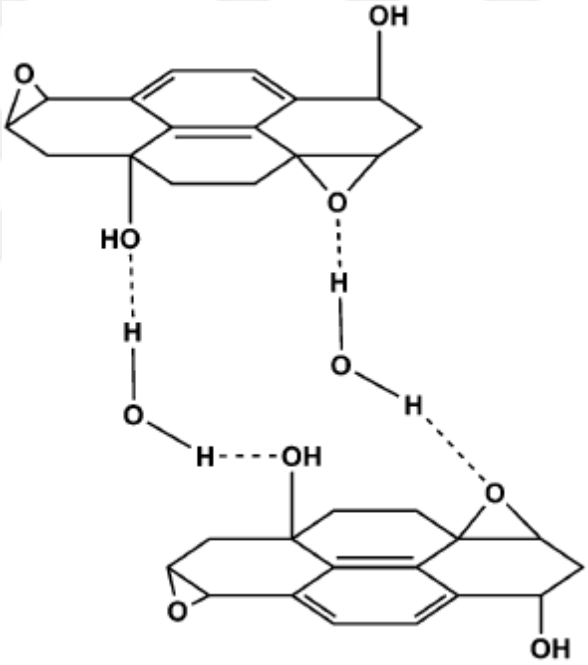

Figure 1.3 : Hydrogen network between functional groups on GO and water (From ref. [29]).

The most widely used approach for synthesis of GO was proposed by Hummers et al. [36]. In this method, oxidation of graphite is performed using a combination of oxidizing acids which are potassium permanganate ($KMnO_4$) and sulfuric acid (H_2SO_4). The sp^2-hybridized structure of the stacked graphene layers is broken up by the oxidation of graphite to GO and thus the distance between these layers are increased. This reduces the interaction between the sheets and encourages GO to separate into single graphene oxide layers under sonication process in water. Under weakly alkaline conditions, dispersions of these layers in aqueous media can be

stabilized by surface-bound, negatively charged, hydrophilic and oxygen functional groups of GO [37]. Graphene oxide and many graphene-based materials are prepared by such dispersions.

1.2 Chitosan/Graphene Oxide Composite Films

Chitosan is widely considered as a very good film-forming material like all the other polysaccharides linked with β (1-4) [16]. Due to its physicochemical, biological and film-forming property [38], it has been successfully used in various applications such as food packaging, pharmaceuticals, wound covering and tissue engineering.

It has been reported that cross-linking agents such as glutaraldehyde, some metal ions, polyanions or anionic polysaccharides can be used to form rigid chitosan films [39-41]. However chitosan films are generally non-rigid, durable, tough and hard to tear materials. Although majority of these mechanical properties can compare to many medium-strength commercial materials, they restrict applications of chitosan in various fields [42]. On the other hand, due to its variety of hydrophilic functional groups bound to the surface and high dispersibility in water and organic solvents as well, graphene oxide prevents aggregation by means of encouraging strong interactions between polymers and fillers [32]. Graphene-based materials have the potential for a wide range of applications and have been used in polymer nanocomposites as a filler [43]. Blending with graphene-based materials as a filler have dramatically improved the properties such as modulus of elasticity, tensile modulus, thermal stability and electrical conductivity of the composite films [27]. Such properties like thermal stability of the films is a crucial property in terms of their applications in food and pharmaceutical industry because they might be exposed to heat process while they are being prepared, processed or consumed [44].

In conclusion, chitosan as a hydrophilic biopolymer with $–NH_2$ and –OH groups can be protonated under acidic conditions leading an interaction between polymer chains and graphene oxide and a good dispersion is obtained [45].

In the present study, chitosan/graphene oxide composite films cross-linking with different level of Na_2SO_4 were prepared. Physical properties of Chitosan/graphene oxide composite films with various proportions of crosslinking agent were investigated. Thermal and mechanical properties of the composite films were

evaluated with this study on the basis of measurements of thermogravimetric analysis and tensile tests.

2. EXPERIMENTAL

2.1 Materials and Methods

2.1.1 Materials

Chitosan (low molecular weight) was purchased from Sigma Aldrich. Asetic acid (%100, Merck) was used to dissolve chitosan in distilled water. Graphene oxide suspension (4 mg/mL) was purchased from Graphenea. Na_2SO_4 (Merck) was used as a crosslinking agent with various weight percent.

2.1.2 Preparation of composite films

2.1.2.1 Chitosan film

1% (w/v) chitosan solution was prepared by dissolving chitosan (CS) in a 1% (v/v) aqueous acetic acid solution under mechanical stirring for 6 hours at room temperature. Then 30 mL of mixture was poured into a plastic petri dish to form the film and stored in the refrigerator until film forming.

2.1.2.2 Blending with graphene oxide

As for the films blending with graphene oxide, 1% (v/v) acetic acid solution was added to 80 ppm of graphene oxide (GO) dispersion. After dispersion of graphene oxide into acetic acid, 1% (w/v) chitosan solution was added to the mixture. Chitosan mixtures with 80 ppm graphene oxide dispersion were mixed under mechanical stirring for 6 hours at room temperature and 30 ml of mixture was poured into plastic petri dishes. They were stored in the refrigerator until film forming.

2.1.2.3 Crosslinking with Na_2SO_4

1% (w/v) and 20% (w/v) aqueous solutions of Na_2SO_4 were prepared as crosslinking agent. Chitosan and the composite films were treated with 50 mL of Na_2SO_4 crosslinking solution for 1 hour. After this process, all the films were washed with distilled water.

A series of composite films were prepared by following method by changing the weight ratio of crosslinking agent such as neat CS, CS film cross linked with 1% Na_2SO_4, CS film cross linked with 20% Na_2SO_4, CS-GO film without crosslinking, CS-GO film cross linked with 1% Na_2SO_4 and CS-GO film cross linked with 20% Na_2SO_4 and they were coded as CS, CS-1, CS-20, CS/GO, CS/GO-1 and CS/GO-20 respectively.

2.2 Characterization

Fourier transform infrared (FTIR) analysis were performed using a Perkin Elmer FT-IR 100 Spectrometer in the range of 600-4000 cm^{-1} to obtain the information about interactions in the composite films.

Thermogravimetric analysis (TGA) was carried out using a SEIKO EXTAR 6200 TG/DTA instrument under nitrogen flow of 150 mL/min. The samples about 5-10 mg were heated from 30 °C to 800 °C at a heating rate of 10 °C/min.

Tensile tests of the composite films were performed using INSTRON 3345 tensile test machine to determine the mechanical parameters of the composite films. The tensile testing machine, set at crosshead speed of 0.05 mm/s, and load cell of 500 N sensibility were used to perform uniaxial tensile.

3. RESULTS AND DISCUSSION

3.1 FT-IR Analysis

Chitosan and its composite films were characterized by FT-IR, as shown in **Fig. 3.1** and **Fig. 3.2**. In the spectrum of neat chitosan, broad peak centered at 3189 is corresponding to the stretching vibrations of hydroxyl groups. Absorption peaks appeared 2800-3000 cm^{-1} are due to the symmetric or asymmetric -CH_2 stretching vibrations attributed to pyranose ring and –CH_2OH and –CH_3 groups. The absorption peak at 1500-1640 cm^{-1} of N-H bending vibrations in –NH_2 groups in chitosan. The absorption bands at 1019 cm^{-1} and 1152 cm^{-1} are ascribed to primary alcohol group linked to C_6 and the secondary alcohol group linked to C_3. The peak at 1152 cm^{-1} is assigned to -C-O-C- bonding in glycosidic linkage.

As for the Na_2SO_4 cross-linked film and broad stretching band of –OH around 3200-3600 cm^{-1} can be observed. Compared to pure chitosan, characteristic peaks related to the –NH bending vibrations in –NH_2 groups and the C=O stretching vibration in -NHCO group shifted to a lower wavenumber and are downshifted due to the electrostatic interactions between the crosslinking agent and the amine groups of polycationic chitosan. Moreover, there is a decrease in the intensity of the bands.

For the chitosan film blended with graphene oxide appeared to have approximately similar characteristic absorption peaks with neat chitosan.

3.2 Thermogravimetric Analysis of Chitosan and Composite Films

Thermal degradation behavior of the samples is displayed in **Fig. 3.3** and **3.4**. All of the composite films which is cross-linked with Na_2SO_4 shows three step degradation while the non-cross-linked films appeared to have two-step degradation. The first decomposition step for all type of the films occurred from approximately 30-136°C which is resulted from the moist content and the evaporation of water molecules or volatilization of small molecules [46].

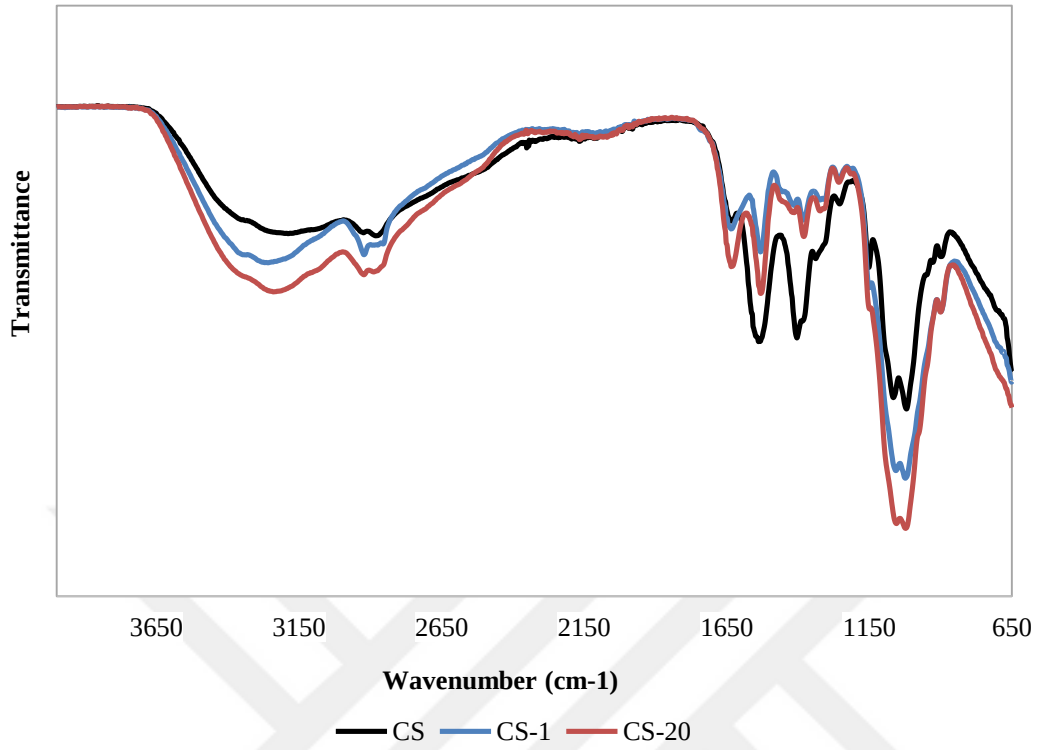

Figure 3.1 : FT-IR spectra of CS, CS-1 and CS-20 composite films.

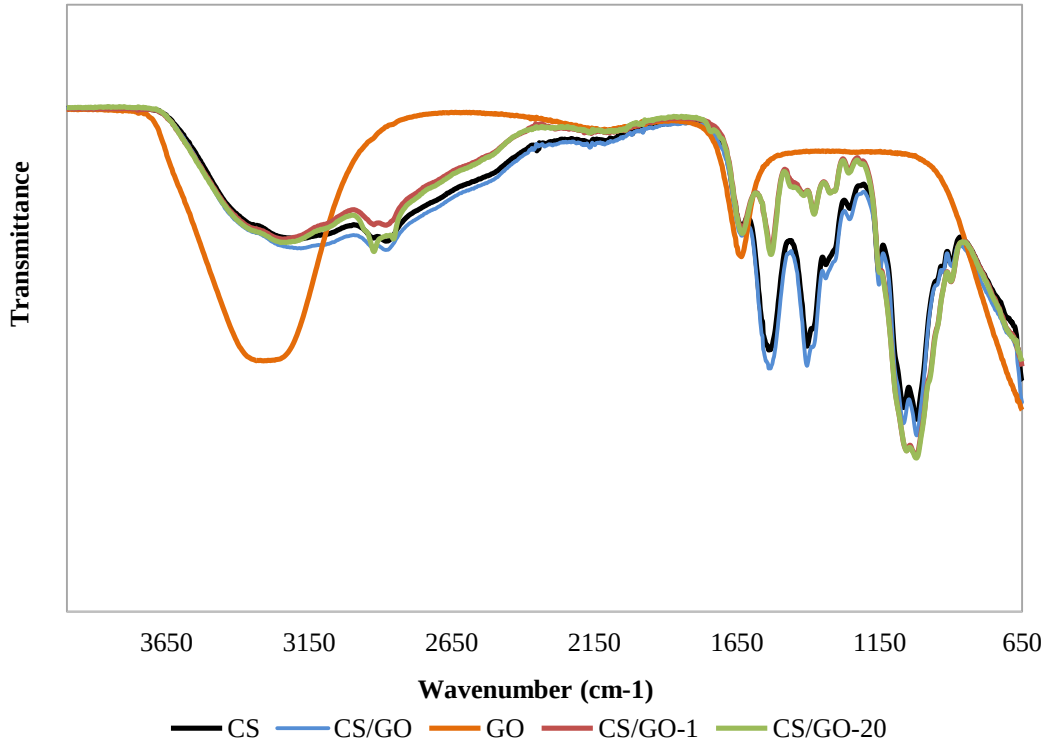

Figure 3.2 : FT-IR spectra of CS, CS/GO, GO, CS/GO-1 and CS/GO-20 composite films.

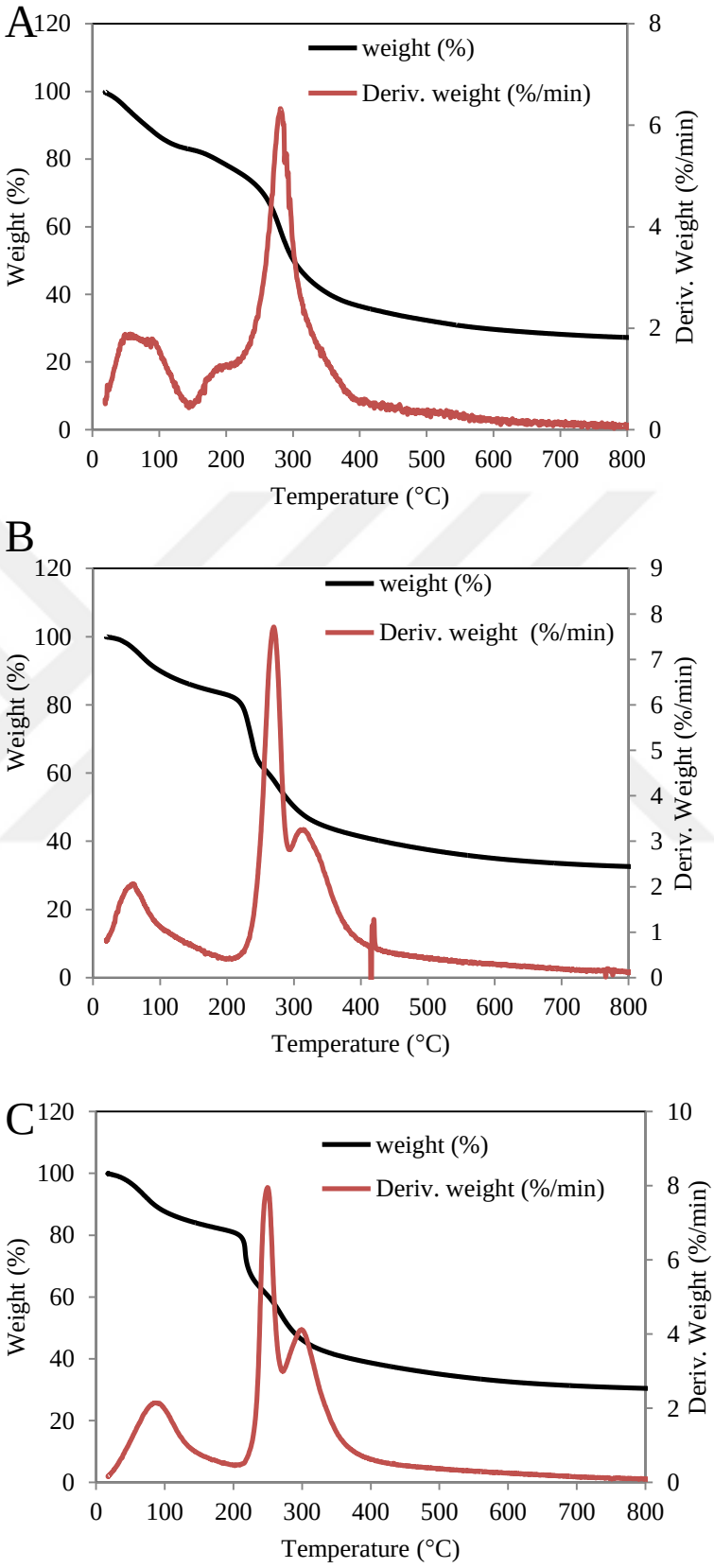

Figure 3.3 : TGA and DTG curves of (A) CS, (B) CS-1 and (C) CS-20 composite films.

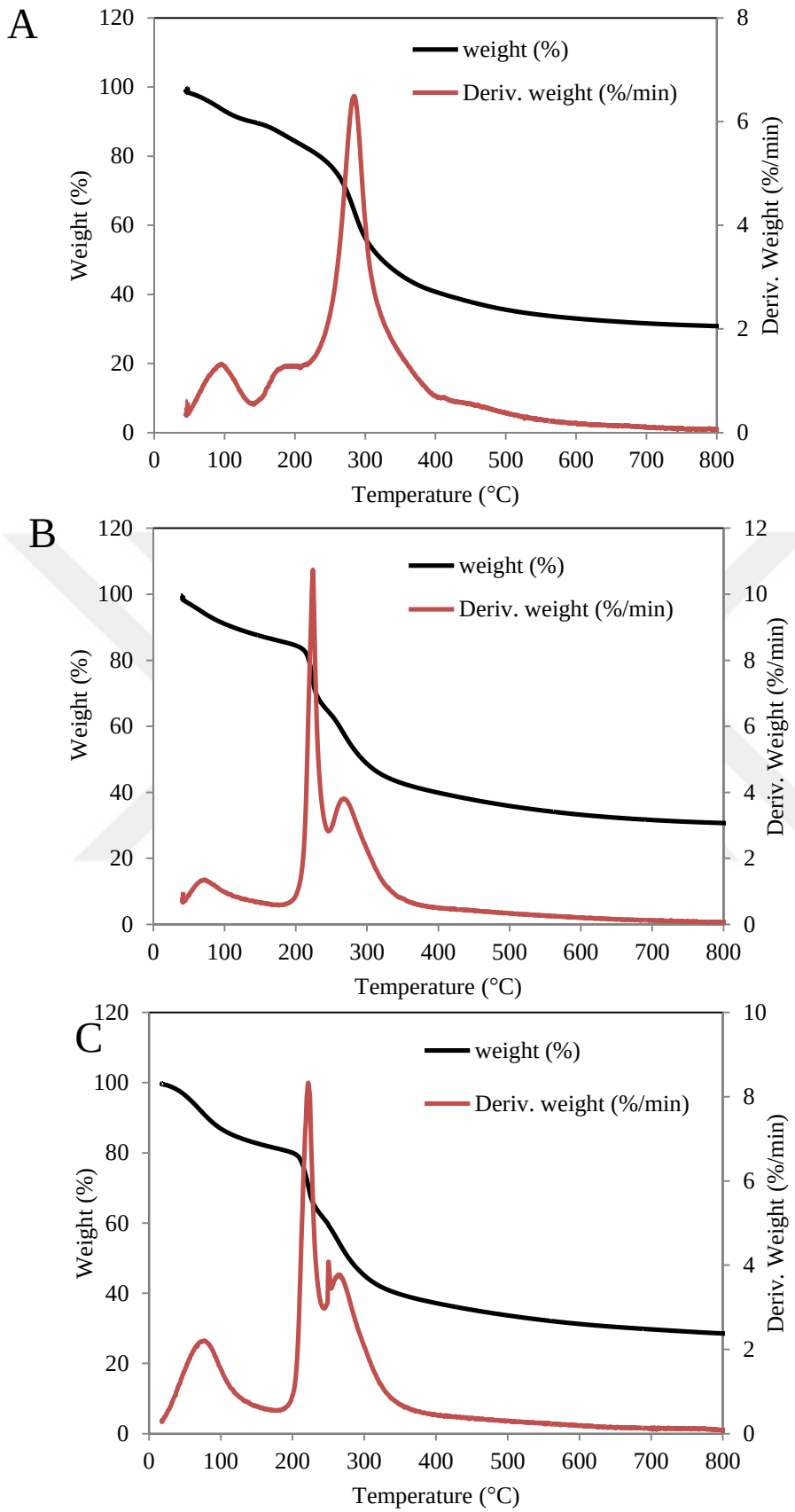

Figure 3.4 : TGA and DTG curves of (A) CS/GO, (B) CS/GO-1, (C) CS/GO-20 composite films.

The temperature of the fastest degradation rate (T_{max}) for each stages which is read from the DTG curve and the temperature corresponding to 5 wt.%, 10 wt.% and 50 wt.% weight loss and char residuals at 800˚C are listed in **Table 3.1**.

Table 3.1 : Values of thermal parameters of chitosan and its composites.

Samples	$T_{-5\%}$	$T_{-10\%}$	$T_{-50\%}$	Char residual (%) at 800°C	T_{max}	
					Stage I	Stage II
CS	51,3	79,5	300,9	27,3	282,3	-
CS-1	68,6	99,8	301,1	32,6	238,9	276,4
CS-20	63,3	88,2	282,6	30,4	224,9	270,2
CS/GO	84,7	138,3	324,1	30,8	283,8	-
CS/GO-1	66,3	112,2	293,5	30,7	223,8	266,7
CS/GO-20	58	81,5	278,5	28,6	221,8	264,6

For the chitosan film the second degradation step starts at 225.8 °C (T_0) with a weight loss of 37.3% and this process reaches a maximum at 281.3 °C. This process might be the degradation of amine units of chitosan [47].

The second stage degradation of CS/GO film starts at 223.8 °C with a weight loss of 40.2% and reaches a maximum at 283.8 °C. For the cross-linked films the second degradation step occurs in the range of 193- 199 ˚C, that reaches a maximum in the range of 221.8-283.9 °C and correspond to a weight loss of 19% - 21.1%.

It is expected that CS/GO composite films exhibit improved thermal stability compared to neat chitosan indicating the interaction between chitosan and graphene oxide [48]. In comparing of these results (**Fig. 3.5**) it can be seen that TG and DTG curves are almost identical and the thermal parameters are slightly higher for CS/GO composite film compared to chitosan film. This might be attributed to very low loading level of graphene oxide into chitosan. Cross-linked chitosan films have slightly higher $T_{-5\%}$, $T_{-10\%}$ and char residual values while there is a decrease in the first stage T_{max} and $T_{-50\%}$ values compared to neat chitosan (**Table 3.1**). From these results it might be suggested that crosslinking with sodium sulfate had no significant influence on the

thermal stability of the films due to their lower T_0 temperatures compared to the neat chitosan although $T_{-5\%}$, $T_{-10\%}$ and char residual values of cross-linked films increased.

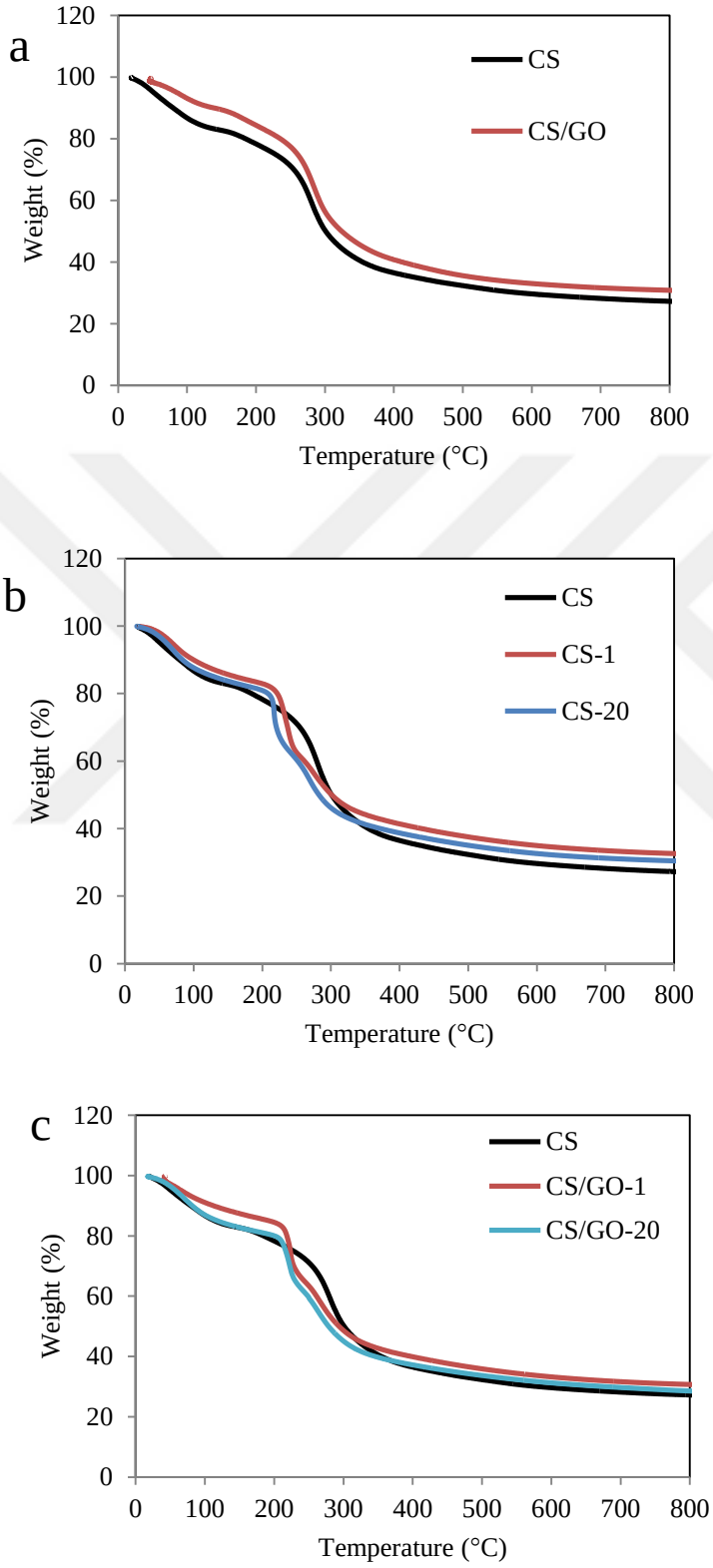

Figure 3.5 : Comparison of TG curves of (a) CS and CS/GO; (b) CS and cross-linked films; (c) CS and CS/GO cross-linked with sodium sulfate.

3.3 Integral Procedural Degradation Temperature

The integral procedural degradation temperature (IPDT) is a value which is related to volatile parts of the polymeric materials. It was first proposed by Doyle in 1961 [49] which could help to estimate the thermal stability of the polymeric materials [50]. It sums up the whole shape of the thermogram in a single number [51]. IPDT values of the composite films were calculated from the equations (3.1), (3.2) and (3.3).

$$IPDT\ (°C) = A^*K^*\ (T_f - T_i) + T_i \quad 3.1$$

$$A^* = \frac{S_1 + S_2}{S_1 + S_2 + S_3} \quad 3.2$$

$$K^* = \frac{S_1 + S_2}{S_3} \quad 3.3$$

A* and K* are the area ratios related to the total TGA thermogram (**Fig. 3.6**) , T_i is the initial temperature and T_f is the final temperature of the experiment [52].

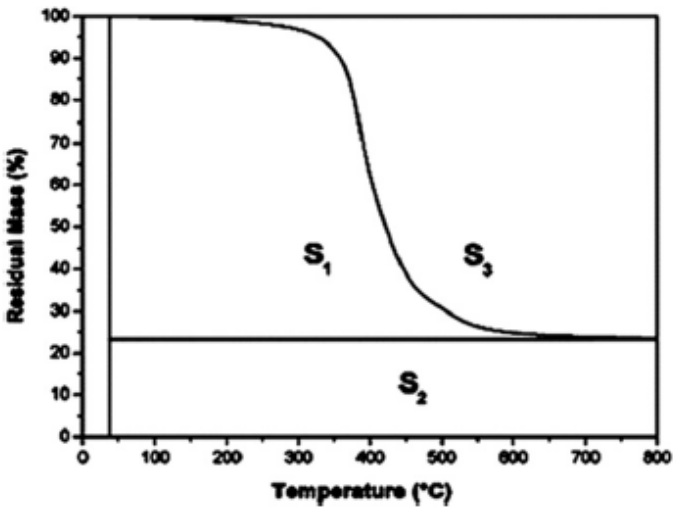

Figure 3.6 : Schematic representation of S_1, S_2 and S_3 (From ref. [51]).

The obtained IPDT values of the CS, CS-1, CS-20, CS/GO, CSGO-1 and CS/GO-20 composite films are 857.7, 971.1, 969.3, 938.7, 974.9 and 912.8 °C, respectively (**Fig. 3.7**).

It can bee seen that all type of the composite films have higher IPDT values than that of neat chitosan. But the results did not agree with the experimental data and the observations.

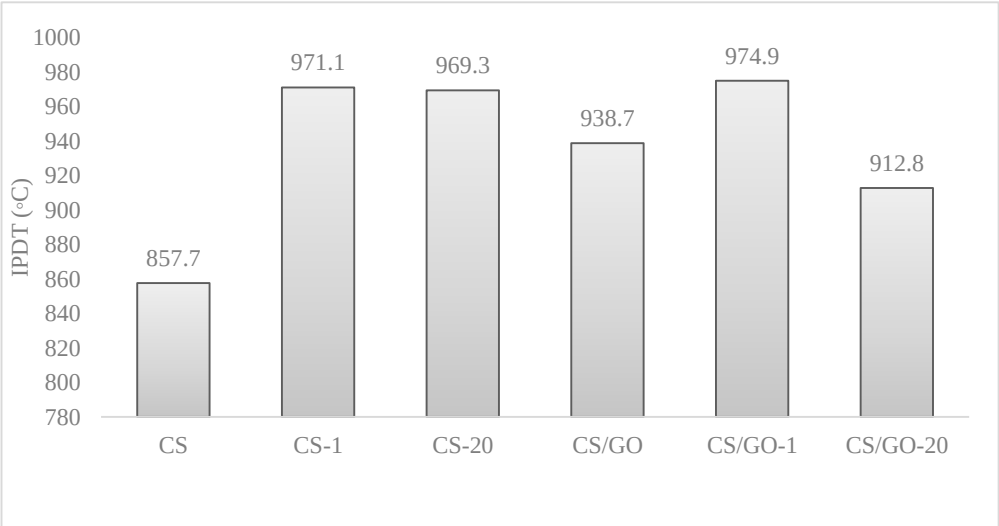

Figure 3.7 : IPDT values of the composites films.

3.4 Mechanical Analysis

3.4.1 Effect of different loading levels of cross-linker on the elasticity of the composite films

The typical stress-strain (σ vs.ε) curve of the prepared films are shown in **Fig 3.8**. Compared with 1% (w/v) pure chitosan film, elasticity of the composite films decreased with the addition of cross-linking agent, sodium sulfate. This is because that the modulus of elasticity values increased with the increase in the level of crosslinking agent (**Fig. 3.9).** Films with higher modulus of elasticity, exhibits more resistance to the stress while it has the lowest elasticity. Elasticity of the composite film decreased slightly with 1% sodium sulfate crosslinking while there is a significant decrease in the elasticity of the one with 20% sodium sulfate crosslinking. Modulus of elasticity has changed with the increase in the amount of sodium sulfate. After crosslinking with 1% sodium sulfate, deformation and distortion occurred on the film while 20% sodium sulfate cross-linked film has smoother surface (**Fig. 3.10**). It may also suggested that crosslinking with sodium sulfate prevents the decomposition of the films in water and increases their strength to the stress.

3.4.2 Effect of graphene oxide on the elasticity of cross-linked chitosan films

Chitosan/graphene oxide composite films were prepared by adding 80 ppm of graphene oxide solution into a clear solution of 1.0 wt. % chitosan and the mechanical behavior of the samples were investigated by tensile tests.

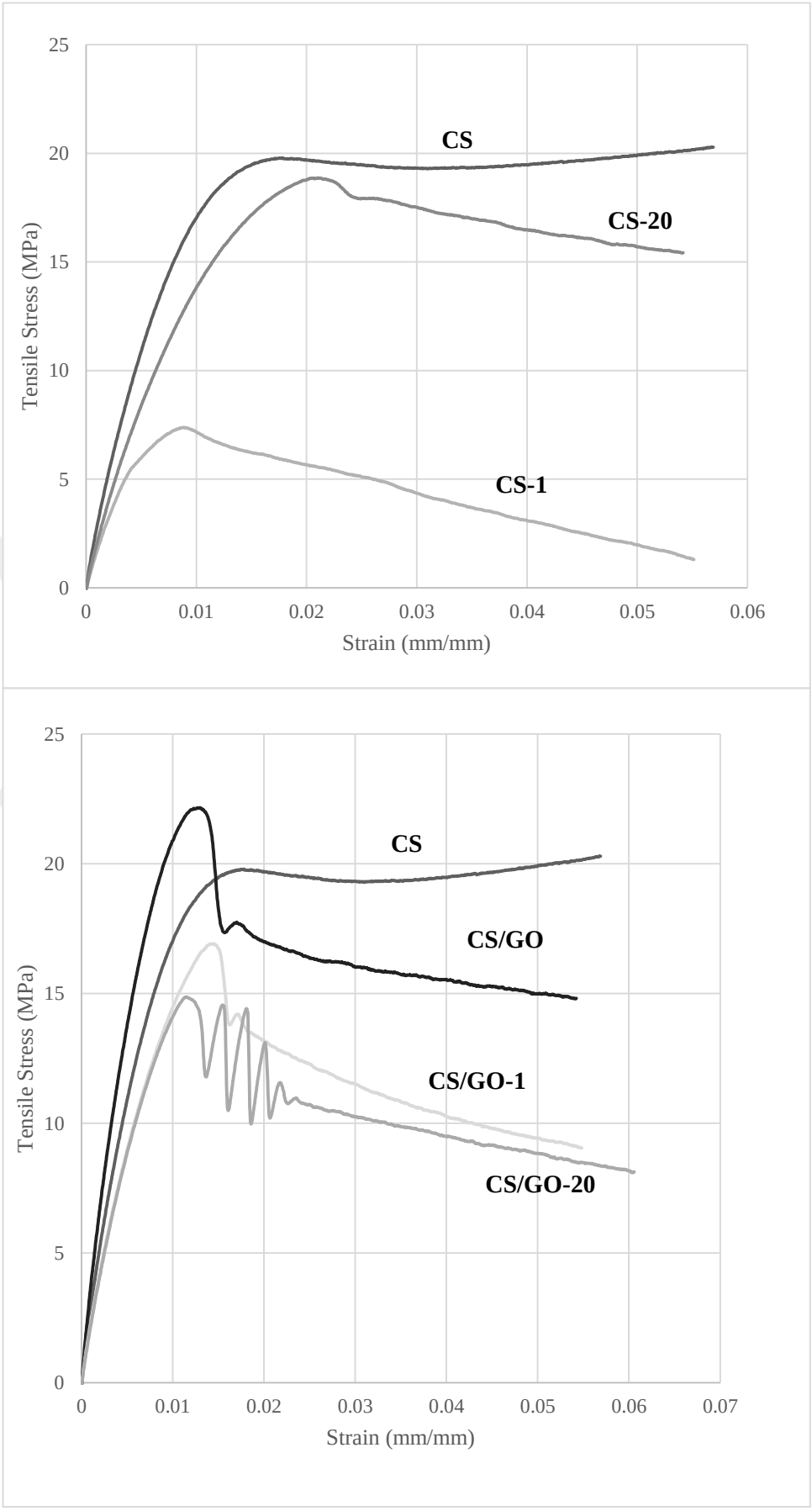

Figure 3.8 : Stress-strain curves of the composite films.

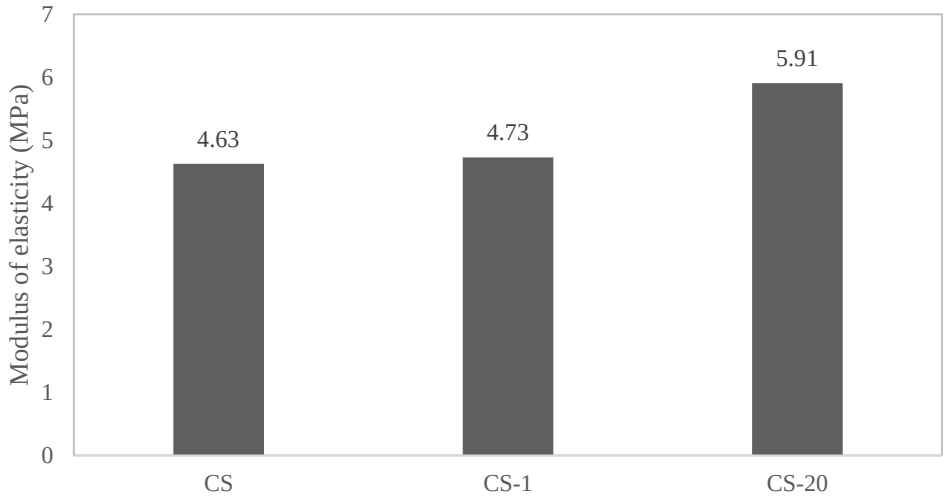

Figure 3.9 : Comparison of the modulus of elasticity of chitosan films with various loadings of crosslinking agent Na_2SO_4.

The obtained modulus of elasticity values of CS/GO, CS/GO-1 and CS/GO-20 composite films were found to be 5.45 ± 0.33, 7.72 ± 0.29 and 6.07 ± 0.56 MPa, respectively (**Table 3.2**). Incorporating of graphene oxide to the chitosan film with sodium sulfate crosslinking ranging from 0% to 20% resulted in a decrease in the flexibility of the films.

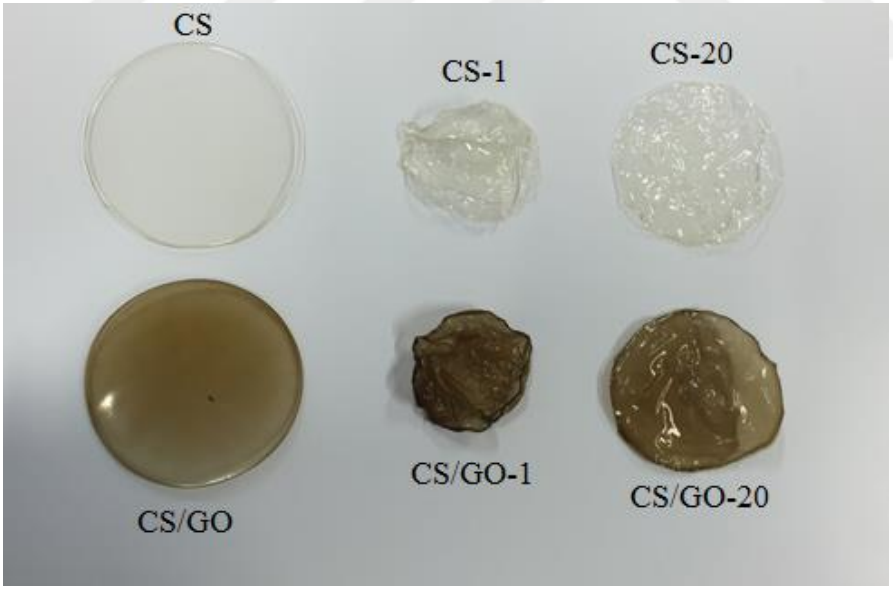

Figure 3.10 : Photo images of (a) CS, (b) CS-1, (c) CS-20, (d) CS/GO, (e) CS/GO-1 and (f) CS/GO-20.

In comparison of non-cross-linked (CS and CS/GO), 1% cross-linked (CS-1 and CS/GO-1) and 20% cross-linked (CS-20 and CS/GO-20) films, it can be noticed that blending with graphene oxide enhanced the elastic modulus of the films (**Fig. 3.11**).

Table 3.2 : Parameters of mechanical properties of the composite films.

Sample	Modulus of Elasticity (MPa)	Resilience (Pa)
CS	4,63 ± 0,11	61,92 ± 14,64
CS-1	4,73 ± 1,08	43,17 ± 21,44
CS-20	5,91 ± 1,25	53,11 ± 14,63
CS/GO	5,45 ± 0,33	48,35 ± 11,46
CS/GO-1	7,72 ± 0,29	103,36 ± 24,78
CS/GO-20	6,07 ± 0,56	66,27 ± 14,82

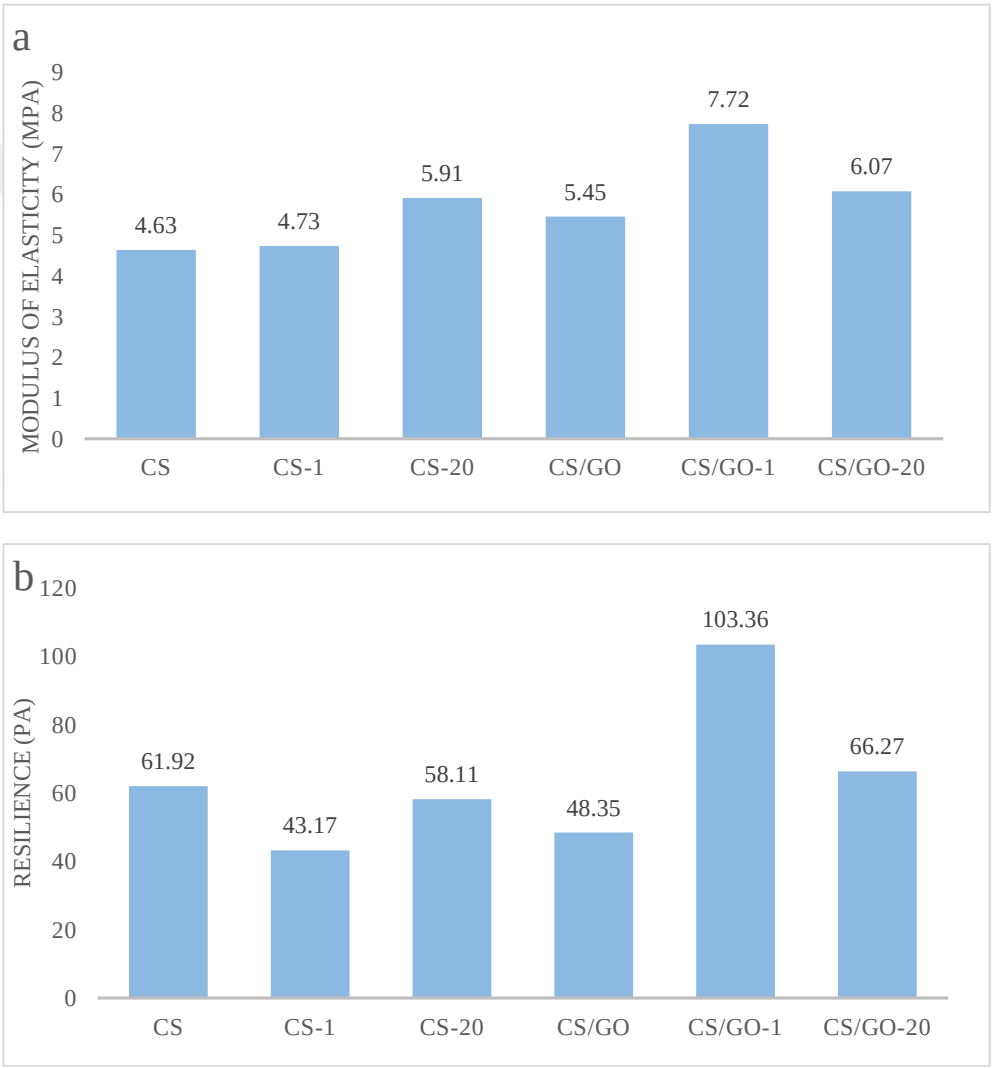

Figure 3.11 : Comparison of the modulus of elasticity (a) and resilience (b) of the samples.

The increase in the elastic modulus indicates that the flexibility of the films are decreased. There is a significant decrease in flexibility of the sample which is prepared

with 80 ppm graphene oxide and 1% crosslinking agent, sodium sulfate. In this series of composite films, CS-1 is the most brittle material with the least flexibility.

3.4.3 Resilience

Resilience, capacity of a material to absorb energy during elastic deformation, of the films were determined. Computationally it is just the area under the stress-strain curve taken to yielding. In the elastic region, elastic deformation occurs to an applied load. With increasing elastic modulus; resilience, the energy absorbed for the material to return to its original shape when the applied load is released, is also expected to increase.

Comparing with the composite films, elastic modulus of CS/GO and CS/GO-20 composite films have an increasing trend with the increase in resilience (**Fig. 3.12** and **3.13**). On the other hand, differences in the elastic modulus and the resilience for the CS and CS-20 composite films have not occurred in the same way.

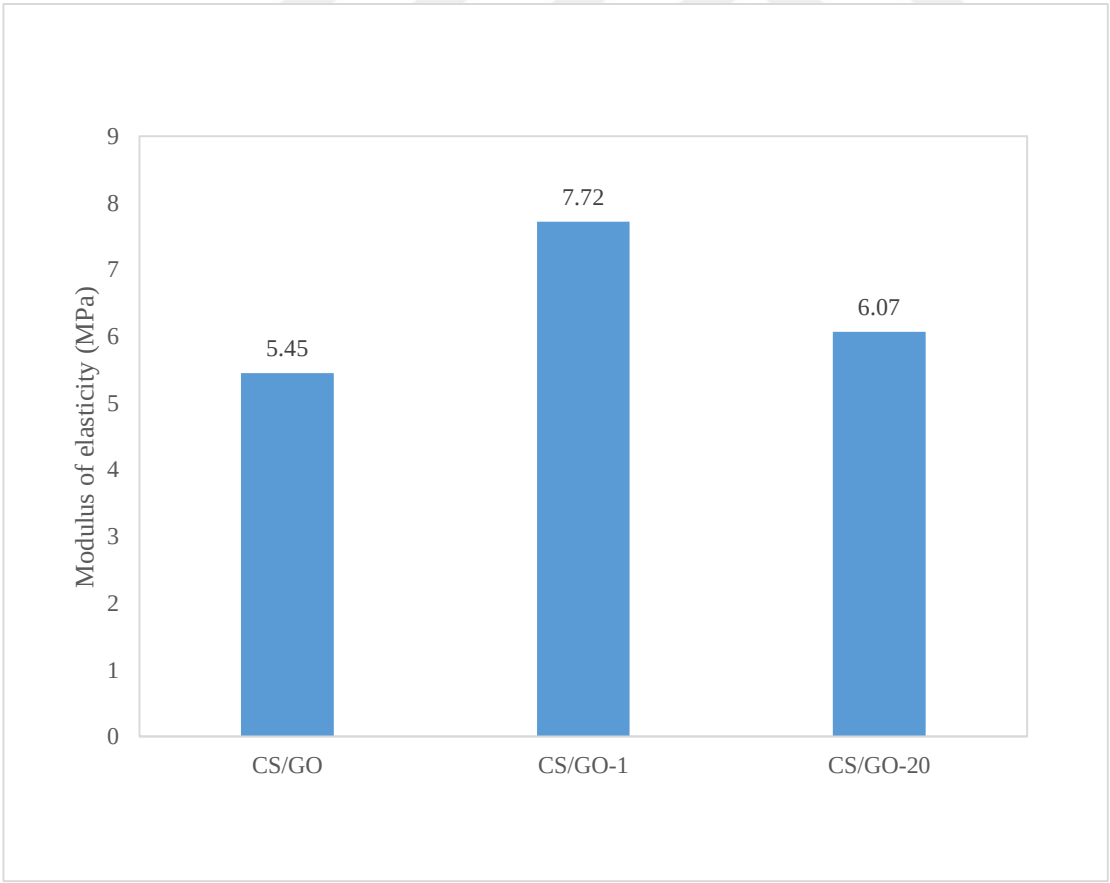

Figure 3.12 : Comparison of the elastic modulus of chitosan composite films incorporated with GO; cross-linked with various concentrations of crosslinking agent Na_2SO_4.

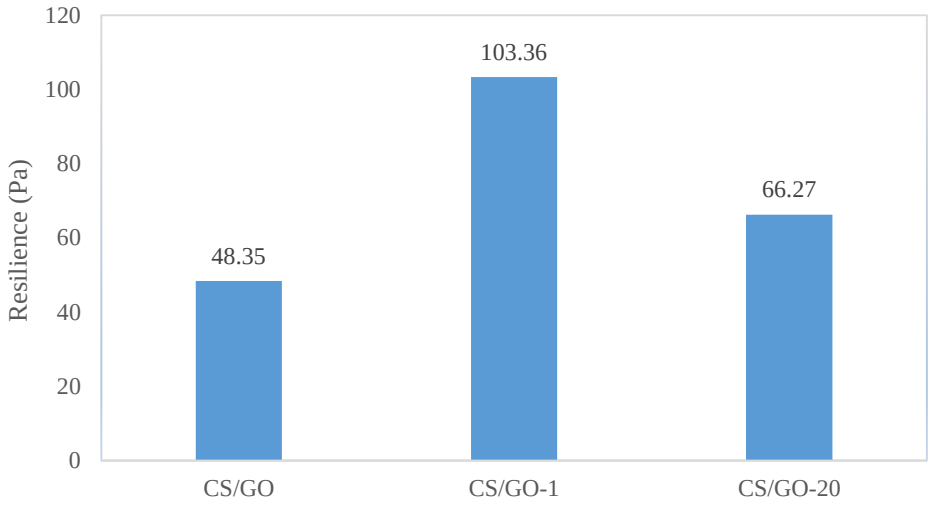

Figure 3.13 : Comparison of the resilience of chitosan composite films incorporated with GO; cross-linked with various concentrations of crosslinking agent Na_2SO_4.

Chitosan film (CS) without crosslinking appeared to have high resilience. This could be attributed to the lack of intermolecular crosslinking and graphene oxide as a filler material. Intermolecular interactions in neat chitosan are relatively low compared to that of the blended films. Thus, neat chitosan film is more flexible and the magnitude of the resilience is higher than that of cross-linked films, CS-1 and CS-20 (**Fig. 3.14**).

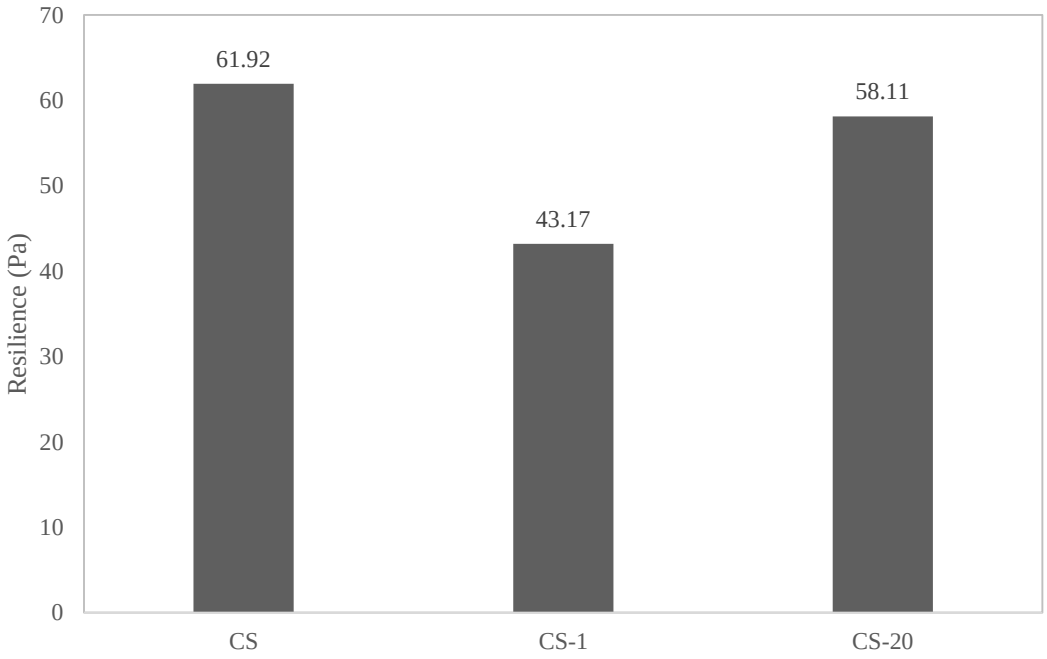

Figure 3.14 : Comparison of the resilience of chitosan films with various loadings of crosslinking agent Na_2SO_4.

When the influence of cross-linking with sodium sulfate and blending with graphene oxide on the mechanical properties are considered together, it can be concluded that, the composite film which has the highest strength to the applied load but the most brittle one is the film with 80 ppm graphene oxide and 1% sodium sulfate. The most flexible film with the lowest elastic modulus is neat chitosan without cross-linking.

4. CONCLUSION

In conclusion, graphene oxide were incorporated successfully into chitosan using acetic acid solution as a solvent and the prepared films were cross-linked with Na_2SO_4 as a crosslinking agent.

Thermogravimetric analysis demonstrated that incorporating graphene oxide into chitosan improved the thermal stability of the chitosan film as it is expected due to the higher thermal parameters of the chitosan/graphene oxide composite film compared to neat chitosan. In spite of very low level of graphene oxide loading which is 80 ppm, this enhancement in the thermal stability can be ascribed to the well dispersion of graphene oxide with its unique structure as a filler material. Higher $T_{-5\%}$, $T_{-10\%}$ and char residual values for all type of the films revealed that crosslinking restricted the mobility of the polymeric chains of the chitosan which results in the increase in some thermal parameters. FT-IR studies also agreed with the char residual values obtained from Thermogravimetric analysis results in terms of the molecular attraction between chitosan and the crosslinking agent. On the other hand, from the DTG curves it was also observed that cross-linked composite films appeared to have one more degradation step compared to non-cross-linked films and lower polymer degradation temperatures which indicates lower thermal stability of the films

All type of the films own higher elastic modulus than that of neat chitosan film. However, the resilience values for the composite films did not have the same trend as the increase in the elastic modulus. Blending with graphene oxide of chitosan crosslinking with Na_2SO_4 up to 1% improved the strength of the material but decreased the elasticity of the material.

Therefore these composite materials with enhanced physical properties may find real-life applications in various fields

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