



**MARMARA UNIVERSITY
INSTITUTE FOR GRADUATE STUDIES
IN PURE AND APPLIED SCIENCES**



PREPARATION AND CHARACTERIZATION OF CHITOSAN-EVA BLEND SYSTEMS

PINAR SARIOĞLU

MASTER THESIS

Department of Chemical Engineering

ADVISOR

Prof. Dr. Mehmet S. EROĞLU

ISTANBUL, 2013



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ÖZET

Bu çalışmada gıdaların ambalajında kullanılmak üzere biyobozunur özellikli kitosan(Ch)-etilenvinil asetat (EVA) polimer karışımları ile ambalaj filmleri hazırlanarak karakterizasyonları yapılmıştır. Ch ve EVA birbiri ile uyumlu olmayan polimerlerdir ve bu nedenle homojen bir karışım oluşturmazlar. Bununla birlikte kitosanda yapılabilecek bazı yapısal modifikasyonlar ile karışabilirliği sağlamak mümkündür. Bu nedenle hidrofilik yapıdaki kitosan'a glikoz halkasındaki fonksiyonel -OH ve -NH₂ grupları üzerinden hidrofobik yapıdaki stearik asit aşılansak hidrofobik yapıdaki EVA ile polimer karışımları hazırlanmıştır. Bu karışımların değişik teknikler ile özellikleri incelenmiştir. EVA birçok ambalaj malzemesinden çok daha iyi fiziksel özelliklere sahip olmasına rağmen kitosan gibi biyobozunur olmaması nedeniyle çevre kirliliği açısından dezavantajları olan bir endüstriyel polimerdir. EVA'nın fiziksel özelliklerini değiştirmeden %3 veya %5 gibi oldukça düşük oranlarda stearik asit aşlanmış kitosan (Ch-Sa) katılmasının EVA'nın biyobozunurluğunda dikkate değer bir artış sağlayacağı düşünülmüştür. Bu amaçla değişik oranlarda Ch-Sa içeren karışım filmleri hazırlanarak spektroskopik ve termo-mekanik karakterizasyon çalışmaları ile birlikte yüzey özellikleri de incelenmiştir. %5 oranında Ch-Sa içeren karışım filmlerinin DSC analizi sonucunda EVA'da morfolojik açıdan dikkate değer bir yapısal değişim gözlenmemiştir. Bununla birlikte doğal ortamda toprağa gömülerek muhafaza edilen örneklerin SEM analizi sonucunda %5 Ch-Sa içeren karışım filmlerinin yüzeyinde 3 ay sonunda önemli ölçüde deformasyon olduğu gözlenmiştir. Bu çalışmalar %5 oranında Ch-Sa içeren EVA filmlerinin biyobozunurluk ve çevre açısından önemli bir avantaj oluşturacağını göstermektedir.

Anahtar Kelimeler: Etilen-vinil asetat, kitosan, blend, film, biyobozunurluk

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ABSTRACT

In this thesis, biodegradable blend films of chitosan (Ch) and ethylene vinyl acetate (EVA) were prepared as food packaging materials, and their characterizations were performed. Ch and EVA are incompatible polymers as they do not form blends. However, increasing miscibility of the polymers could be possible with some chemical modifications of Ch. Hydrophobic stearic acid (Sa) was grafted to Ch via functional –OH and –NH₂ groups, which resulted in a more hydrophobic and miscible structure. Then their blend films were prepared. Although EVA has many desirable physical and chemical properties compared to other industrial packaging materials, due to the lack of its biodegradable feature, it has disadvantage from the point of environmental pollution. Without scarifying the physical properties, addition of Ch-Sa to EVA in 3-5% was expected to increase biodegradability feature. The blend films of EVA and Ch-Sa at various proportions were prepared and their spectroscopic, thermo-mechanical and surface characterization studies were performed. Differential scanning calorimetry (DSC) measurements indicated that the morphological structure of the blend film containing 5% of Ch-Sa was not different than that of pure EVA. Additionally, scanning electron microscopy (SEM) analysis of the blend film containing 5% Ch-Sa, which was weathered by burying for 3 months, showed important structural defects on surface caused by bacteria. As a result, the use of Ch-Sa as biodegradable additive in blend formulation results in important advantage for environmental pollution.

Keywords: Ethylene vinyl acetate, chitosan, blend, film, biodegradation

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SYMBOLS

ΔH_{ex}	: Experimental heat of fusion (J/g)
ΔH_{fusion}	: Heat of fusion (J/g)
ΔH_{th}	: Theoretical heat of fusion (J/g)
ΔH_0	: The heat of fusion of the component of the blend (J/g)
M_w	: Molecular weight
δ_L	: The total surface free energy of the liquid (mJ/m ²)
δ_L^-	: The electron donor surface free energy of the liquid (mJ/m ²)
δ_L^+	: The electron acceptor surface free energy of the liquid (mJ/m ²)
δ_L^{LW}	: The apolar Lifshitz–Van der Waals of the liquid (mJ/m ²)
δ_S^{AB}	: Acid-base components of the solid (mJ/m ²)
δ_S^{TOT}	: The total surface energy of solid (mJ/m ²)
δ_S^-	: The electron donor surface free energy of the solid (mJ/m ²)
δ_S^+	: The electron acceptor surface free energy of the solid (mJ/m ²)
δ_S^{LW}	: The apolar Lifshitz–Van der Waals of the solid (mJ/m ²)
ΔH	: The heat of fusion of the blend (J/g)
E'	: Storage modulus
E''	: Loss modulus
f_w	: The weight fraction of the components
T_g	: Glass transition temperature (°C)
T_m	: Melting temperature (°C)
X_c	: Crystallinity
θ	: The contact angle(°)

ABBREVIATIONS

AES	: Auger Electron Spectroscopy
Ch	: Chitosan
Ch-Sa	: Synthesis of Ch Stearic Acid Grafted Polymer
DCP	: Dicumyl Peroxide
DMA	: Dynamic Mechanical Analyzer
DSC	: Differential Scanning Calorimetry
EC	: Ethyl Cellulose
ESCA	: Electron Spectroscopy For Chemical Analysis
EVA	: Ethylene Vinyl Acetate Copolymer
EVOH	: Ethylene Vinyl Alcohol
FT-IR	: Fourier Transform Infrared Spectroscopy
HDPE	: High Density Polyethylene
IPA	: Isopropyl Alcohol
IR	: Infrared
LDPE	: Low Density Polyethylene
MAH	: Maleic Anhydride
PBT	: Poly (Butylene Terephthalate)
PCL	: Polycaprolactone
PVA	: Poly (Vinyl Acetate)
PVDC	: Poly (Vinylidene Chloride)
Sa	: Stearic Acid
SEM	: Scanning Electron Microscope
SIMS	: Secondary Ion Mass Spectroscopy
TEA	: Triethylamine
TGA	: Thermal Gravimetric Analyzer
USFDA	: The United States Food and Drug Administration
UV	: Ultra Violet
VA	: Vinyl Acetate
wt	: Weight

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1. INTRODUCTION

1.1. Purpose of the Thesis

The use of biodegradable polymers as packaging material has generated considerable interest in the recent years in order to reduce the environmental pollution caused by plastic wastes. EVA has a broad range of industrial applications like scratch films, hoses, coatings and adhesives. Random incorporation of the vinyl acetate unit into polyethylene progressively suppress the crystallinity resulted in more transparent and amorphous material. EVA copolymer having 50% (w/w) vinyl acetate (VA) is amorphous [1]. EVA behaves either a plastic or an elastomer depending on its VA content [2].

On the other hand, Ch is a high molecular weight polysaccharide derived from naturally occurred chitin by fully or partly N-deacetylation. Nowadays, because of its excellent biodegradability, biocompatibility and bioactivity and property of having enormous structural potential for chemical and mechanical modifications to create unusual features, Ch becomes significantly attractive in many applications including biomedical, agriculture, food, food packaging, cosmetics [3, 4]. Ch possesses free reactive amino and hydroxymethyl groups along the polysaccharide main chain. Amino groups can be easily protonated in aqueous medium and thus formed the positively charged Ch has high solubility in acidic pHs. This property renders Ch pH sensitive polymer which is highly soluble in aqueous acid solutions and insoluble in water at alkaline and neutral pHs as well as common organic solvents. In addition to this, the protonation of free amino groups causes to binding of Ch to some drugs and bio-macromolecules such as protein, DNA, enzymes and antibody which makes Ch suitable to use for transport of biomolecules and some drugs [5, 6]. In many cases, the relatively poor mechanical properties and film forming capability of Ch make some limitation in its use in industrial applications such as food packaging and biomedical applications. These drawbacks have been partly overcome by some modification using its reactive groups and thus incorporated novel properties such as water solubility and compatibility with other polymers resulted in diversify of utilization [6-10].

Ethylene vinyl acetate (EVA) has better physical properties than most of the packaging materials but has less biodegradability. One of the easy ways increasing biodegradability property of a plastic is to insert a biodegradable component into the polymer matrix to form a blend. Therefore, aiming to prepare EVA based biodegradable food packaging materials, Sa grafted Ch was synthesized and a series of blend films with EVA were prepared. Increasing the hydrophobic property of Ch was expected to increase the compatibility with EVA to some extent and to result in more biodegradable blend film.

1.2. General Background

1.2.1. Chitosan (Ch)

A large amount of work has been reported on Ch and its potential applications since the year 1859, when Rouget [11] revealed the deacetylated forms of the family chitin natural polymer firstly. Chitin, source material of Ch, is a long chain polymer that is found in many places throughout the natural world. It is the main component of the cell walls of fungi, the exoskeletons of arthropods such as crustaceans and insects, the radulas of mollusks, and the beaks and internal shells of cephalopods, including squid and octopuses [12]. Ch polymers are semi-synthetically formed aminopolysaccharides that have unique structures, multidimensional properties, highly complicated functionality and an enormous range of applications in biomedical and other industrial areas [13, 14]. They have become the center of attention because they are made from generous renewable resource and they are very compatible and effective biomaterials that are used in many various applications [15, 16].

Ch is a linear copolymer of β -(1-4) linked 2-acetamido-2-deoxy- β -D-glucopyranose and 2-amino-2-deoxy- β -D-glycopyranose (Figure 1.1). It can be easily derived from partial deacetylation of the natural polymer chitin (Figure 1.2.). The deacetylation degree of Ch is known as an indication of the number of amino groups along the chains and it is calculated as the ratio of D-glucosamine to the sum of D-glucosamine and N-acetyl D-glucosamine. If the deacetylated chitin contains at least 60% of D-glucosamine residues, it is named “Ch” [17, 18]. Because of chitin’s poor solubility in aqueous solution and organic solvents, it does not find practical applications as much as Ch [19]. The properties of perfect biocompatibility and praise worthy biodegradability with

ecological safety and low toxicity with versatile biological activities such as antimicrobial activity and low immunogenicity have provided abundant opportunities for further development [20, 21]

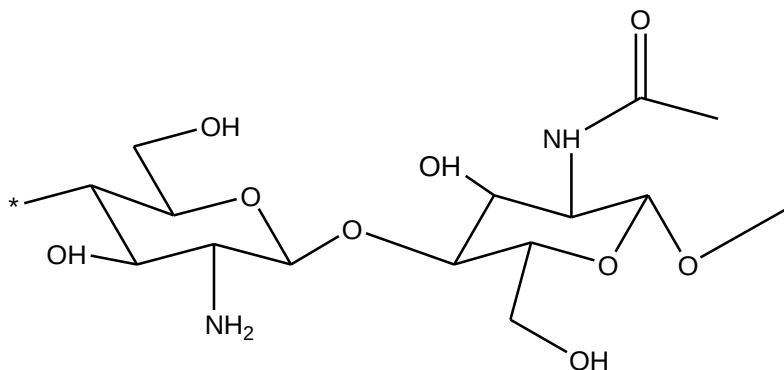


Figure 1.1. Chemical structure of Ch

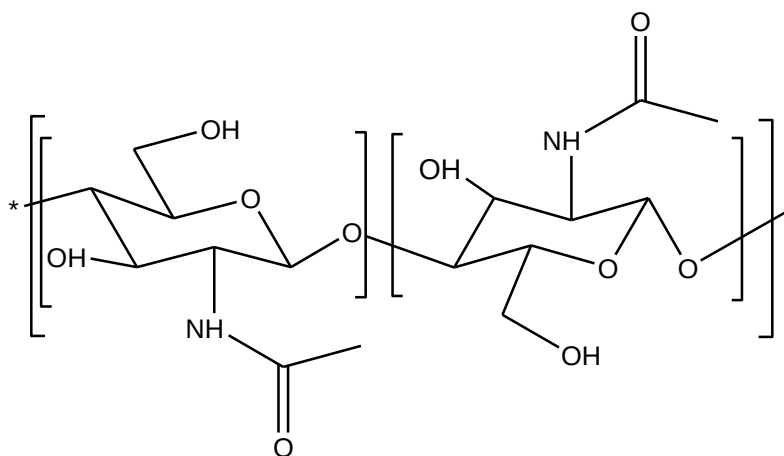


Figure 1.2. Chemical structure of chitin

Ch has reactive amino and hydroxyl groups in its linear polyglucosamine chains of high molecular weight, suitable for chemical modifications. The possible reaction areas for chitin and Ch are shown in Figure 1.3. Chitin and Ch can take place in many of the reactions such as etherification, esterification, cross-linking, graft copolymerization, etc. The amino functionality gives rise to chemical reactions such as acetylation, quaternization, reactions with aldehydes and ketones, alkylation, grafting, chelation of metals, etc. to provide a variety of products with properties such as antibacterial, anti-fungal, anti-viral, anti-acid, antiulcer, non-toxic, non-allergenic, total biocompatibility and biodegradability, etc. The hydroxyl functional groups also give various reactions such as o-acetylation, H-bonding with polar atoms, grafting, etc. [22, 23].

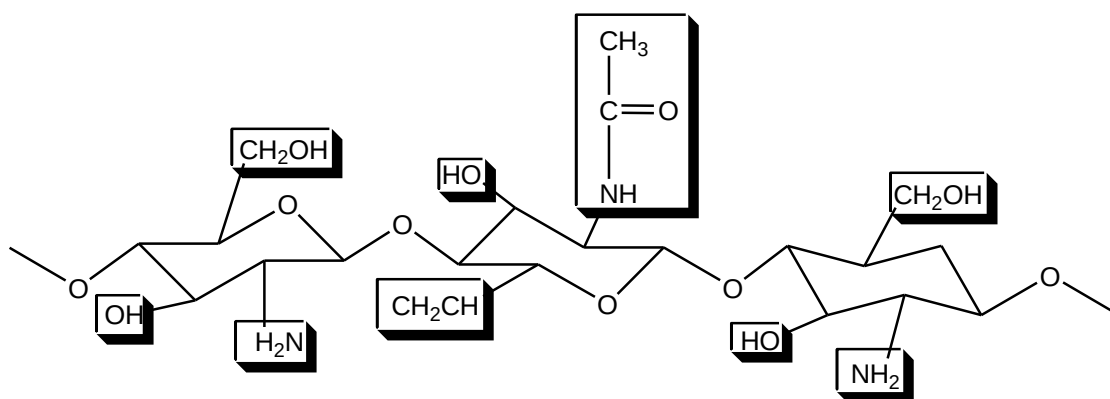


Figure 1.3. The possible reaction sites for chitin and Ch

The solubilization of Ch occurs by protonation of the -NH_2 function on the C_2 position of the D-glucosamine repeat unit, whereby the polysaccharide is converted to a polyelectrolyte in dilute acidic solutions below pH 6.0. Ch can be considered a strong base as it possesses primary amino groups with $\text{pH} < 6$. This amino group shows that pH significantly changes the charged state and properties of Ch [21]. At low pH, these amines get protonated and become positively charged [23]. Ch is the only pseudonatural cationic polymer and thus, it finds many applications that follow from its unique character [24]. The solubility is related to the ionic concentration, the degree of acetylation, the pH, the nature of the acid used for protonation, and the distribution of acetyl groups along the chain, additionally the conditions of isolation and drying of the polysaccharide. As well as, to consider the intra-chain H bonds involving the hydroxyl is important [25].

1.2.1.1. Biodegradation and biodegradation of chitosan

Plastic materials have found wide applications in every aspect of life and industries with the advanced technology and the increased global population. However, most conventional plastics such as polyethylene, polypropylene, polystyrene, polyvinyl chloride, polyethylene terephthalate, polyethylene vinyl acetate, are non-biodegradable, and their increasing aggregation in the environment has been a risk for the earth. The most important strategy is involved production of plastics with high degree of degradability to overcome these problems. Biodegradation is the most important typical of synthetic polymers. Biodegradable polymers provide a lot of advantages such as increased soil productivity, decreased accumulation of bulky plastic materials in the

environment, and reduction in the cost of waste management. In addition to this, biodegradable polymers can be recycled to useful metabolites by microorganisms and enzymes [26, 27].

When all these properties are regarded, biodegradation is a useful feature to obtain plastics for main applications where biodegradation increases the value of an application (e.g., mulching films, food-packaging materials or polymers used in oil-field and gas-field chemicals), in polymer researches. So biodegradation is an important criteria at certain applications to success lesser or no environmental risk. In recent years, the literature has described 'biodegradable polymers' [28, 29].

There are two different types of polymer can be degraded in general. The first one of them is essentially turned to carbon dioxide and water in an appropriate environment [e.g., cellulose, starch and aliphatic polyesters] and the second one of them contains the class of oxo-biodegradable polymers (natural rubber and lignocelluloses and some oxo-polyolefins) that is disintegrated but not mineralized in the main [30,32].

While the importance of the biodegradation is increasing, Ch is become more popular in scientific researches because of its biodegradability [32]. Although Ch does not come from mammals, it can be degraded in vivo by various proteases (e.g., lysozyme, papain). Its biodegradation results in the release of non-toxic oligosaccharides of various length which can be subsequently incorporated to glycosaminoglycans and glycoproteins, to metabolic pathways or be excreted [33]. Non-specific proteases present seem to cause degradation for Ch. The degradation kinetic brings to mind to be inversely depended on the degree of crystallinity which is related essentially to the degree of deacetylation. In addition to this, biodegradability of Ch depends on acetyl groups which Ch have on its long chains. This is established because of researches that show when acetyl groups and their homogeneous distribution are nonexistence, enzymatic degradation occurs at very low rates [12, 34].

Moreover, the recent studies show that the degradation rate is affected from the length of the chains (Mw) [35]. The degradation rate affects the biocompatibility because very fast rates of degradation mean that it will produce an accumulation of the amino sugars and produce an enthusing response. Ch samples with low degree of deacetylation create an extreme enthusing response whereas Ch samples with high degree of deacetylation create a minimal response. So biodegradation has been established to increase while

degree of deacetylation decreases [36]. In a study, the enzymatic behaviors of several Ch species by observing changes in the viscosity of Ch solution in the presence of lysozyme were investigated. It was said that it was impossible to estimate biodegradation rate from the degree of deacetylation only and they determined the Ch functions were affected by several characteristics of the Ch, such as molecular weight, degree of deacetylation, viscosity of the solution, and distribution of acetamide groups [37]. Consequently, when its all characteristic features is regarded, Ch is an important biodegradable polymer which has substantially application areas.

1.2.1.2. Applications of chitosan

Ch is biopolymer having enormous structural potential for chemical and mechanical modifications to create unusual properties, functions and applications. The fact that Ch is as an effective material for sutures essentially because of its biocompatibility, biodegradability and non-toxicity together with its antimicrobial activity and lowimmunogenicity, points to immense potential for future development. By reason of its physical and chemical properties, Ch is being used in a vast array of widely different products and applications, ranging from pharmaceutical and cosmetic products to water treatment and plant protection. Different properties of Ch are preferred for every kind of applications [10].

Biomedical Applications

Because of its biocompatibility, biodegradability, renewability and its other properties like being film forming, nontoxic, a hydrating agent, hydrolyzed by lysozyme, efficient against bacteria, viruses, fungi, and having biological tolerance, wound healing possibilities, Ch is used in a great deal of biomedical applications like surgical sutures, dental implants, artificial skin, rebuilding of bone, corneal contact lenses, time release drugs for animals and humans encapsulating material [10].

Food and Beverage Applications

Ch is used in food and beverage applications, because it is not digestible by humans like dietary fibers, behaves like lipids and reduces cholesterol, and it is preservative, thickener and stabilizer for sauces, protective, fungistatic, antibacterial, coating for

fruits. Ch in food applications depends on its property of behaving as dietary fibre and as functional ingredients. The United States Food and Drug Administration (USFDA) approved Ch as a food additive in 1983. Ch is also used in the food applications as a food quality improved in certain countries. Due to its hypocholester olemic feature, Japan produces dietary cookies, potato chips and noodles enriched with Ch. And also Japan manufactures and solds its vinegar products containing Ch so that it reduces cholesterol [38].

Food Packaging Applications

It is getting more and more important to develop and test films with antimicrobial properties in order to improve food safety and shelf life in the recent days. With all positive properties, Ch and its derivatives have an important role in food application areas considering that recent outbreaks of contaminations associated with food products as well as increasing concerns regarding the negative environmental effects of packaging materials in use. Ch based films shows to be very effective in food preservation. Ch based polymeric materials can be turned into fibers, films, gels, sponges, beads or even nanoparticles. Ch films have great potential to be used as a packaging material for the quality preservation of a variety of food. Because of its antimicrobial properties Ch has widely been used in antimicrobial films to provide edible protective coating, in dipping and spraying for the food products.

Ch films also potentially have an important role to incorporate and improve the food value along with other additives such as flavoring, coloring, antioxidant and antimicrobial agents. As Ch has great antimicrobial activity against a wide variety of pathogenic and spoilage microorganisms, including fungi, and bacteria, it also improves shelf life of food products and the storability of perishable foods. Because of its functional properties Ch can be combined with other film forming materials. This creates new various opportunities to make films with different properties for wide food packaging applications [39, 41].

Agricultural Applications

Recently, Ch is also getting an important polymer in agricultural applications. Ch is used as a defensive mechanism in plants and it creates opportunity for stimulation of

plants growth. Due to its physical and chemical properties Ch can be used as a seed coating, a frost protection, time release of fertilizers and nutrients into the soil in this application area. It is also used for protecting plants against the microorganisms. Furthermore, Ch is known to reduce postharvest decay of fruit and vegetables. Application of Ch to control pre and postharvest diseases enables an improvement of fruit and vegetables quality and it is getting the center of interest attracted much because of its low toxicity to mammals and as an environmentally safe mean of plant disease control [42, 43].

Water and waste treatment applications

Because of its property of flocculant to clarify water, drinking water, pools, ability of removing metal ions, features of ecological polymer and reducing odors, Ch can be used in water and waste treatment applications. Ch, owing to the presence of amino groups within its main chain effectively connects various metal ions. Ch and its water insoluble derivatives have exhibits great connecting potential against toxic and hazardous heavy metal ions such as Sn^{2+} and Sn^{4+} , Hg^{2+} , Pb^{2+} , U^{6+} ; and transition metal ions e.g. Cd^{2+} , Cu^{2+} , Cr^{3+} , Zn^{2+} , Ni^{2+} , V^{4+} etc. It is seemed that the metal adsorption capacity depends on the particle size and amount of Ch being in the adsorbing material, and on the concentration of metal ions in solution from which they are adsorbed. Antimicrobial activity of Ch has been shown useful in removing waterborne pathogens [44, 45].

Cosmetic applications

Ch is used for maintain skin moisture, treating acne, improving suppleness of hair reduce static electricity in hair, toning skin, oral care as toothpaste and chewing gum. It is the only naturally occurring cationic gum which turns viscous upon dissolution in mildly acidic medium. This property has been used in various cosmetic applications, particularly in hair products and setting agents, hair conditioners and shampoo. It forms a clear, elastic film on hair, increasing its softness and mechanical strength and can be used in shampoos, permanent wave agents, hair colorants, styling lotions, hair sprays and hair tonics. Ch can behave as a moisturizer and works as an antiagent for skin applications. At the same, it has great potential to be as an alternative to collagen in treating wrinkles, acne, scars and other injuries for other soft skin applications. Ch is already found in creams, pack materials, lotions, nail enamels, foundations, eye

shadows, lipsticks, cleansing materials and bath agents. Furthermore, Ch can be used in toothpastes, mouth washes and chewing gums [10-44].

1.2.2. Ethylene vinyl acetate copolymer (EVA)

EVA is a class of random copolymers that shows intermediate properties between the two homopolymers polyethylene and poly(vinyl acetate) (PVA) depending on the proportion of both comonomers. These intermediate properties come from the complex morphological structure of these copolymers. It is combined of a crystalline phase (contained polymethylenic units), an interfacial phase (with both ethylene and vinyl acetate (VA) segments) and a mixed amorphous phase (with non-crystallized methylenic segments and VA units). EVA copolymer is a widely used thermoplastic resin which is produced by random copolymerization of ethylene and VA monomers, which are mainly recognized for their flexibility, toughness, especially at low temperatures, and adhesion characteristics [46]. Chemical structure of EVA is as seen Figure 1.4.

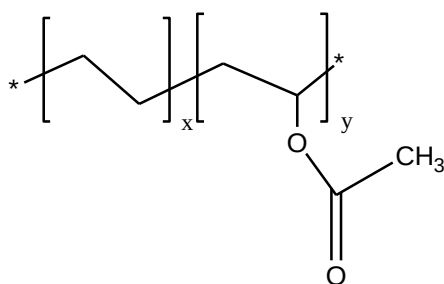


Figure 1.4. Chemical structure of EVA

The percentage weight of VA, molecular weight and distribution, and molecular branching certainly determine the properties of EVA copolymer. VA content has two important effects that influence the properties of EVA copolymers. Disrupting the crystalline regions formed by the polyethylene segments of the copolymer is the first effect. Degrees of crystallinity in the range of 40-65% are seen at low and medium density polyethylenes which are produced by the high pressure bulk process in usual. Until weight percentage of VA becomes between 40 and 50, degree of crystallinity gradually reduced by increasing VA content and at that point the material becomes completely amorphous. The degree of crystallinity which shows variety has created an

ability to control properties for particular end uses for EVA and causes coming up the important versatility of these products.

It can be said that some physical properties like stiffness modulus, surface hardness, crystalline melting point and softening point, tensile yield strength, and chemical resistance decrease as a function of decreased crystallinity due to increasing VA content. Beside this impact strength, optical clarity, gas permeability, environmental stress crack resistance, coefficient of friction, retention of mechanical strength at high fibre loadings increase as a function of decreased crystallinity due to increasing VA content [47, 48].

The polar nature of the acetoxy side chain causes the second effect of VA content. While the VA content increases, the polarity of the copolymer increase. Although it is not as influential as crystallinity changes, increased polarity changes some important properties and thus, it creates new diversity at applications of EVA. It can be said that some physical properties like dielectric loss factor, compatibility with polar resins, plasticizers, specific adhesion in adhesive formulations, and printability increase with increased polarity due to increasing VA content [47-49].

Average molecular weight also has an important influence on properties, as with all polymers. Some physical properties like viscosity, softening point, and environmental stress crack resistance, impact strength, tensile strength at break, stiffness modulus, resistance to the chemicals and processability increase and solubility decreases with a function of increasing molecular weight. As VA content is increasing, chain transfer increases and this causes broader molecular weight distribution. Broadening molecular weight distribution on EVA affects its melt flow characteristics. The long chains in broad molecular weight distribution polymers tend to be entangled more than shorter chains. Consequently, these long chains accept a disproportionately large amount of any deformational stress and show above average elastic response. This elastic response is also delayed by viscous resistance of the smaller molecules at the same VA content. And also broad molecular weight distribution EVA copolymers will have relatively high viscosity at very low shear stress, while at high shear stress, the flow will be easier than for narrow molecular weight distribution EVA copolymers. This viscosity/shear stress relationship results from molecular weight distribution differences also may create an

important criteria for choosing an EVA copolymer for a certain process or application [50].

Molecular branching is also another important criteria which effects properties of EVA. Short chain branches with less than six carbon atoms are differentiated from “long chain” branches with six carbon atoms that become part of the crystalline network. Separate from the pendant acetoxy groups from the vinyl acetate, the primary effect of short chain branches, mostly pendant methyl groups from the use of propylene as a chain transfer agent and butyl groups produced by intramolecular chain transfer, is to disrupt the crystallinity of the polyethylene segments. Thus the effect of short chain branches on EVA copolymer properties is similar to percentage weight of VA but to a much lesser extent is due to the relatively low number of short branches. The primary influence of long chain branches, formed by chain transfer by a growing polymer radical, is to increase the melt elasticity of the EVA copolymer [47].

The appearance of EVA can be varied in thick sections from an opaque plastic to a crystal clear, tacky, rubbery material at higher VA contents. At low VA contents the copolymer surface is relatively soft. Although at the low VA content materials are opaque in thick sections it is transparent, in thin sections. This is due to their lower degree of crystallinity. The degree of crystallinity is not used to predict density. The density of EVA is more closely related with VA content. The surface hardness of EVA is related to molecular weight and the degree of crystallinity. The hardness reduces with increasing VA content and also increasing lower crystallinity. EVA copolymers, being semi-crystalline, soften gradually as the temperature is increased until, at a certain point that varies with VA content and chain branching, the crystalline regions start to melt. At this point the copolymer viscosity begins to decrease rapidly with further increase in temperature until all the crystallites have completely melted [47].

The increasing VA content in EVA allows better incorporation of inorganic fillers or fillers such as carbon black with active surfaces and gives greater tackiness and adhesion to most substrates and reduces resistance to chemicals. EVA copolymer is influenced by most of organic solvents and high concentrations of oxidizing acids. This effect increases with increasing VA content. Halogens attack EVA and causes embrittlement, although dilute solutions of chlorine and bleach have little effect. Aqueous salt solutions do not influence EVA copolymers. Due to their polar nature,

EVA copolymers are permeable for gases and moisture vapor and are thermally stable [47].

Degradation occurs primarily by two mechanisms: oxidation and elimination of acetic acid. Oxidation can be minimized by use of antioxidants, but the elimination of acetic acid cannot be prevented. This problem is minimal at processing temperatures up to 210 °C, which is higher than most processors require. Above 230 °C, acetic acid elimination increases rapidly. UV light causes photo-oxidation of EVA copolymers. This can be minimized by incorporating 2-3% carbon black or other UV stabilizers. Like polyethylene and PVA, EVA copolymers crosslink when irradiated by γ -rays or an electron beam. As well, EVA crosslinks easily when peroxides are used as free radical sources. Thermal degradation of ethylene–VA copolymer nanocomposites [51, 52].

1.2.2.1. Applications of EVA

The fundamental applications for EVA copolymers are packaging film-coextrusion layers, adhesives-paper coatings, wire and cable insulation, carpet backing, molding and extrusion, foam, and sound damping-sound barrier sheet.

Wire and cable insulation applications

The ability of accepting high filler loadings without embrittlement or loss of mechanical integrity, and the easy of crosslinking makes EVA can be used in the wire and cable industry. Typical applications include heat shrinkable insulation, semi-conductive insulation shielding, and flame retardant insulation compounds. EVA is characterized by a high flammability which limits its applications in remarkable manner in numerous fields. It is usually blended with flame retardant additives to improve its flame retardancy properties. Inorganic hydroxides, such as aluminum trihydrate and magnesium hydroxide, have been traditionally used for this aim so that they are capable to increase the resistance of EVA to ignition and, to slow down the combustion kinetics of this copolymer [53].

Packaging film-coextrusion layers applications

Because of its clarity, toughness, stretch properties, good low temperature properties, low heat seal temperatures, the ability to radio-frequency seal and low toxicity and odor due to the absence of plasticizers and other volatile species, EVA is required for packaging film-coextrusion layer applications. Batch incorporation bags, intravenous pouches, stretch-cling film, and bag-in box packages are given as example to single layer films are used in usual. EVA is extrusion coated onto polyvinylidene chloride (PVDC), metallized film, and polyester to form the heat seal layer for cheese wrap, cereal packaging, and meat packaging. Its good sealing properties through contaminated areas, low temperature flexibility which allows it use in frozen food packaging, and ease of coating heat-sensitive substrates containing oriented polypropylene or metallized film, and broad low heat sealing makes EVA films or coatings more useful than low density polyethylene (LDPE) is [47,55].

Adhesives/paper coatings applications

Because of its strength, flexibility, adhesion to substrate, low melting temperature, and compatibility with both crystalline waxes EVA is used in adhesive industry especially in hot melt adhesive industry. It is the most popular thermoplastic polymer used in the hot melt adhesive industry. EVA which has 18–40 wt % of VA content is required for hot melt adhesive industry. For their formulation, tackifiers are used to improve their properties of adhesion, viscosity, and rheology. EVA is also compatible with these tackifiers.

For the purpose of producing "wax" paper with improved properties due to the increased toughness and elongation of the paraffin coating EVA copolymers are blended with waxes.

By the mean of this that the "flexible" coating is occurred to retain good moisture vapor barrier properties after creasing and its heat seal strength is improved. EVA copolymers which have 28 wt % of VA content can be compatible with the waxes to make blends. Thus, its the best properties can be improved [47, 54].

Carpet backing applications

Carpet backing is an important application due to providing shape, structural stability, and protection to the carpet backs. There are a number of different styles of carpet backing, and it can be made from an enormous variety of materials, ranging from natural fibers to polyurethane. EVA can be preserving its adhesion and flexibility properties over a large range of temperatures. This makes EVA useful in carpet backing applications such as natural fibers and polyurethane. EVA with 18-28 wt% VA can be used in carpet backing applications [47].

Molding and extrusion applications

Extrusion molding of polymers is used to make a long shape which has a constant cross section. Pipes, gutters, window sections and decorative trims can all be made using the process. Thermoplastics such as polyvinylchloride), low-density polyethylene, high density polyethylene and polypropylene can all be extruded. The most common polymer extruded is polyvinylchloride. But EVA can enable faster molding cycles due to the absence of the curing step according to other polymers. When it is compared with polyvinylchloride, EVA has a complete absence of plasticizers. Mainly products include disposable medical respirator hoses, wires and cables, rope, bristles and synthetic textile fibres, flat plastic sheets, refrigerator interiors, baby nursing nipples, beverage dispensing tubing, and corrugated vacuum cleaner, swimming pool hoses [47, 56].

Foam applications

Due to its foaming capabilities, EVA is used for typical applications including shoe soles and shoe mid-soles, cushion padding, beach sandals, sports equipment like athletic shoe inner soles, golf cart tires sports and insulation. Its properties like good weather and chemical resistance, low water absorption, good acoustic properties, oil resistance, high energy absorption make EVA preferable in foam industry. EVA creates a decreasing in the weight of the polymer in a mouth guard, which could bring savings in manufacturing costs by decreasing the amount of raw material used. In these applications usually seen problems such as mouldability, durability, finishing requirements, and the consequent problems are also reduced with EVA [57, 58].

Sound damping/sound barrier sheet

Heavily filled flexible compositions are very useful in vibration and absorption. As a noise barrier between the engine and passenger compartments of cars, it is also extending to other parts of cars and to the lining of ducts and other components of noisy factory equipment. EVA copolymers containing up to 80% filler are useful for manufacturing flexible automotive sound damping or a sound barrier sheet that is cut to shape and placed inside the chassis. EVA copolymer that includes 18-28 wt percent of VA, takes a role as a binder for the sound-reducing fillers. Due to its ability to absorb filler, its flexibility, and thermoformability, EVA is preferred for this kind of applications. [47, 59]

1.2.3. Polymer blend systems

It can be said that new polymers always cannot be necessary for the new products required during improving technology. Due to its advantages like rapidness in implements, cheapness in manufacturing, blending of existing commodity or engineering polymers, it is more preferable than comprehension of new polymer chemistry including development of monomer synthesis and polymerization technology. At the same time, it has been known as one of the most applicable methods for modification of polymers, due to the possibility of attaining a wide range of properties through blending of two or more polymers. Blending of commodity and high-tech polymers which has properties of electroconducting, photoactive, biodegradable is a typically developing area. Moreover, blending of virgin and used polymers is a hopeful approach to ecological and economical recycling of waste plastics. Polymer blending has a developed scientific base and the effectual increase in commercialization of blends is one of the most prominent and speedily growing properties of the advanced polymer industry.

There are so many types of polymer blends. These are queued like engineering polymer blends, impact modified polymer blends, emulsion blends, crystalline –crystalline polymer blends, crystalline-amorphous polymer blends, thermosetting polymer blends, molecular composites, biodegradable polymer blends, reactive compatibilized blends, liquid-crystalline polymer blends, polyolefin polymer blends, interpenetrating polymer networks, polyelectrolyte complexes, recycled polymer blends, water soluble polymer

blends, polymer blend composites, block copolymer-homopolymer blends, core-shell polymer blends, elastomer polymer blends [60,61].

Polymer blends do not have covalent bonds between individual components and they are physical mixtures of blend components. Commercial blends are generally prepared from different commercially available polymers. There are different preparation methods of blends systems. These methods are melt-mixing, solution blending, coprecipitation, co-coagulation of systems arising by polymerization of a monomer in a latex medium. Properties of the final materials can be adapted to provide requirements of customers or expectations of specific new applications with pleasurable balance of a wide range of material properties and costs. In most cases, each component polymer contributes in a specific attitude to the overall property profile. The characterization of the final materials can be made by combinations of the useful properties of the every components of the polymer blend, overtop to those of single polymers. The properties of commodity plastics, such as polyolefins, styrenics or polyvinyl chloride are substantially improved by blending. Promising commercial results were acquired with blends containing engineering and speciality plastics, such as polyamides, polycarbonates, polyphenylene oxide or electroconducting polymers, like polyaniline, poly- thiophene, polypyrrole or polyacetylene [62].

The base main of blending is modification of mechanical properties, improvement of impact strength at low temperatures, in particular abrasion resistance and improvement of processability. Furthermore, blending of recycled and virgin plastics is a hopeful technique in plastics waste management. However, mutual influences of polymer components, reflected in changes in long-term resistance of blends against environmental stresses and potential deterioration of beneficial mechanical properties generating from blending, must be expected and cannot be foreseen [60-62].

Miscibility and compatibility of component polymers are important material properties for blend systems. Although polymer blends can be homogeneous or heterogeneous on a microscopic scale, they should not have any obvious inhomogeneity on the macroscopic scale [63]. Being compatible or incompatible means the degree of intimacy in blends. If a blend has heterogeneous look on the macroscopic scale and shows signs of polymer segregation, this blend is considered incompatible. Heterogeneous blends have a variety of morphologies in their appearances. Mixing immiscible polymers can

result various phase morphologies in the liquid state. These depend on the nature and the relative amounts of the polymers used. Immiscible polymers behave as different materials.

The phase morphology is an important property to realize immiscible polymer blends. These morphological properties are the physical properties such as toughness, flowability, transparency and weather resistance. Besides immiscible polymer blends, miscible polymer blends behave similarly like a single phase system. Their properties are a combination of features of every pure component. Their chemical structure and molecular weight, their concentration and intermolecular interactions are the main characteristics of components influencing the properties of miscible blends. If components of blends have a low degree of compatibility, it causes a serious problem in polymer blend systems. But, there is a way to improve the compability and this way is compatibilization process [62]. Compatibilization is the process of modification of interfacial properties in immiscible polymer blends. This results in the reduction of the interfacial tension, stabilization of the desired morphology and improved interaction between phases of solid state. Compatibilization is succeeded by physical or chemical methods. The desired level of dispersion is generated by physical methods, and then physically stabilized by quenching, retardation, cross-linking or cocrystallization in the former cases. At the same time, the morphology does not only relative with the level of mechanical mixing, it can be controlled by the additives. These additives are compatibilizers which are used like third components and are miscible in both cases. Thus, segmentation of particles is decreased and undesirable processes like such as separation of phases, delamination, agglomeration or skinning and ultimate physical failure are prevented [65, 66].

1.2.3. Literature review

There are many researches that were studied about biodegradable polymer blend systems. One of these researches about Ch based blends is ‘Preparation and properties of rice starch-Ch blend biodegradable film’. In this study, biodegradable blend films that are consisted of starch and Ch were developed by casting film solution on leveled trays. Blends which were prepared at the rate of 2:1, 5:1, 1:1 of starch and Ch, were investigated. While the ratio of starch and Ch blend biodegradable films was changing, the changes of the mechanical properties, water barrier properties, and miscibility

viewed. An increase in tensile strength, water vapor permeability, lighter color and yellowness and a decreasing elongation at the break, and film solubility was seen after blending from Ch and starch. In the FT-IR spectrum, the amino group band of the Ch molecule was seen at 1541.15 cm^{-1} but in the Ch film it was at 1621.96 cm^{-1} . Due to these results, it was established that there was a molecular miscibility between these two components. When the properties of rice starch and Ch biodegradable blend films were compared with another blend films that consist of a selected biopolymer and synthetic polymer films, the results about mechanical properties were found similar. Otherwise, the water vapor permeability of rice starch and Ch biodegradable blend film was characterized by relatively lower water vapor permeability than other Ch films but also higher than polyolefin [67].

Another research about Ch based blends is 'Preparation and characterization of Ch/poly(vinyl alcohol) chemically crosslinked blends for biomedical applications'. The aim of this study is development and characterization of polymer blends that consist of Ch and poly(vinyl alcohol) for biomedical applications. These blends were chemically crosslinked by glutaraldehyde and mechanical properties of hybrids were investigated by stress strain tensile tests. At the same time the microstructure, morphology and crystallinity of the blended hydrogels were characterized through X-ray diffraction, Fourier transform infrared spectroscopy and scanning electron microscopy analysis. Furthermore, biocompatibility, cytotoxicity and cell viability of these blends were performed by swelling test in simulated body fluid with cell culture. When the polymeric network was reticulated by glutaraldehyde, the relative crystallinity of pure Ch film was reduced from approximately 23% to 18%. And also pure PVA films were observed. The swelling index of the blends had decreased from about 200% to 80%, and also mobility of the polymer network and the hydrophilic behavior of the blend were decreased, when Ch content was increasing in pure PVA. At the same time, by changing blend composition and chemical crosslinking, the mechanical properties of the polymers were altered. Ch films had shown values of 50 MPa and 45% for maximum tensile strength and tensile elongation, respectively. By increasing Ch content from 25% to 50%, the average blend toughness had decreased about 40%. Furthermore the results of elastic moduli were 0.1 GPa for PVA and 0.8 GPa for Ch. cell It was established that viability, non-toxicity and suitable mechanical properties which can be tailored to for potential use in skin engineering applications were adequate [68].

Another research about Ch based blends is ‘Electrically treated composite films based on Ch and methylcellulose blends’. The target of this study was to reduce environmental problems came from synthetic packaging. For this aim, blend films consist of Ch and methylcellulose were prepared at various rations. These different mixtures of Ch methylcellulose were analyzed for the effect of an electrical field applied during drying on microstructure and macroscopic properties of films. SEM and X-ray diffraction indicated that Ch electrically treated film exhibited a more ordered structure and lower water vapor permeability values than the control films. Longitudinal probes were presented higher elongation values than those of transverse ones, with regard to mechanical properties of electrical treated samples. Ch based films showed higher Young’s modulus values than the control ones in composite control samples. While Ch concentration was increasing, Young’s modulus and tensile strength increased and this was leading to stronger films. It was established that electrical field treatment would have been a good alternative to improve film flexibility and water vapor barrier properties [69].

Another research about Ch based blends is ‘Antibacterial Ch based blends with ethylene vinyl alcohol copolymer’. In this study the formulation, morphology, water barrier and the antimicrobial activity of high and low molecular weight chitosan based solvent cast blends with ethylene vinyl alcohol (EVOH) copolymers were prepared at different rations. Improved phase morphology, transparency, improved water barrier properties and up to 86% water permeability reduction and excellent antimicrobial activity were seen in the blends based on the low molecular weight Ch, compared to pure chitosonium-acetate films. Phase segregation was seen but good interfacial adhesion was still observed, when the fraction of low molecular weight Ch exceeded the phase inversion in the blend. The blends with the high molecular weight Ch grade were translucent, but this component was in the dispersed phase, and separated phase morphology, presented antimicrobial performance was clearly exhibited. In these two cases, the release from the blends of protonated glucosamine groups (so-called active species) correlated well with the antimicrobial phenomenology of the developed materials, being in compliance with previous works in their laboratory. It was established that EVOH copolymers can also have been made antimicrobial by a water sorption-induced release mechanism, if acetic acid was incorporated into the polymer formulation before casting from solution. As a result, it was said that antimicrobial Ch-

based blends with EVOH copolymers, when low molecular weight Ch was used as the dispersed phase in the blend, showed optimum performance from the point of optical properties, water resistance, enhanced water barrier and, therefore, excellent application outlook in antimicrobial applications [70].

Another research about Ch based blends is ‘Characterization of Ch polycaprolactone blends for tissue engineering applications’ The aim of this study was to investigate the effect of blends consisting of Ch and polycaprolactone (PCL) on their biomechanical properties. Ch with a MW >310 kD was selected for use in the blend, because of testing the effect of molecular weight, temperature, and humidity on the tensile properties in dry, wet at 25°C and wet at 37°C conditions. Homogeneous blends were prepared at different ratios like 25%, 50% and 75% PC. For preparing blends, Ch and 80 kD PCL were dissolved in a common solvent of approximately 77% aqueous acetic acid. Due to the low melting point of PCL, blend membranes were processed at 25, 37, 55 °C water bath or 55 °C oven into films. At the same time, membranes were solvent annealed using chloroform vapors. Tensile properties were analyzed in wet conditions at 25 °C. Support for cell viability and distribution of cytoskeletal actin were analyzed by in vitro cell culture of mouse embryonic fibroblasts. Differential scanning calorimetry analyses were showed the miscibility of the two components when approximated using Nishi–Wang equation. The films were dried at 55 °C in an oven formed membranes without separation of two phases. However, the analyzed tensile properties showed no significant alterations relative to Ch. On the contrary, important improvements were observed after solvent annealing. Interestingly, increased viability and redistribution of actin fibers was seen on blends formed with 50% PCL and 75% PCL relative to individual polymers. As a result, 50:50 blends when processed at 55 °C in an oven showed significant improvement in mechanical properties as well as support for cellular activity relative to Ch [71].

As there are so much researches about Ch based blends, also there are great deal of researches about EVA based blends. One of these researches is ‘Foaming of EVA/Starch Blends: Characterization of the Structure, Physical Properties, and Biodegradability’. The aim of this study is to produce foams from blends consisted of EVA with high VA content (28%) and corn starch using an improved compression molding technique. For this aim EVA/starch blends were prepared at different ratios of

100/0%, 70/30%, 50/50%, 30/70% with a constant content of azodicarbonamide (5%). The blends results showed that the corn starch acts as filler for EVA and showed a good compatibility with the polyolefin. The relative density and the amount of starch included in the composition were effected different types of cellular structure (closed, partially interconnected, and fully interconnected) and cell sizes. Furthermore, the addition of starch provided tailoring the physical properties of the composite foams. While the starch contents of blends were increasing, an increase of the density, compressive strength, hardness, and thermal conductivity and a decrease of the elasticity were obtained. Biodegradability tests were made and results showed that the biodegradation was increasing by increasing the amount of starch in the foam, which reaches 60% at 100 days for the foam with 70% of starch. As a result it was said that using an unmodified starch as filler in these materials had several important additional advantages such as the use of natural materials as raw materials and the increase of the biodegradation rate, besides reducing the price of the foams [72].

Another research about EVA based blends is ‘Mechanical and Thermal Properties of EVA Blended with Biodegradable Ethyl Cellulose’. The aim of this study is to prepare biodegradable blends of EVA and Ethyl Cellulose (EC). In this research, EVOH copolymer was used as an interfacial compatibilizer to improve adhesion between EVA and EC. Blends of EVA and EC were prepared by melt mixing at 210 °C and in all blends; the content of EC was varied from 0 to 60%. Furthermore, the compatibilizer EVOH content was varied for 0 to 15% of the filler weight. The melt blended compatibilized biocomposites were examined for mechanical and thermal properties as per the ASTM standards. It was obtained that the EC had a reinforcing effect on EVA leading to enhanced tensile strength and also improving biodegradability. For this reason, it was said that a high loading of 50% EC could have been added without compromising much on the mechanical properties. Analysis of the tensile data using predictive theories showed an enhanced interaction of the dispersed phase EC and the matrix (EVA). The compatibilizing effects of EVOH on these blends were confirmed by the significant improvement in the mechanical properties comparable with neat EVA as also observed by SEM microscopy. The TGA thermograms exhibited that two-stage degradation and as EC content increased, the onset temperature for thermal degradation reduces [73].

Another research about EVA based blends is ‘Dynamic Mechanical Behavior of High-Density Polyethylene/EVA Copolymer Blends: The Effects of the Blend Ratio, Reactive Compatibilization, and Dynamic Vulcanization’. The aim of this study is to analyze high-density polyethylene (HDPE)/EVA blends for showing the effects of the blend ratio, reactive compatibilization, and dynamic vulcanization on the dynamic mechanical properties. As the EVA content was increasing, the storage modulus of the blend was decreasing. The loss factor curve showed two peaks, corresponding to the transitions of HDPE and EVA exhibiting the incompatibility of the blend system. Attempts had been made to correlate the observed viscoelastic properties of the blends with the blend morphology. Because of predicting the dynamic mechanical data, various composite models had been used. The experimental values were close to the Halpin–Tsai model above 50 wt % EVA and close to those of the Coran model up to 50 wt % EVA in the blend. For the Takayanagi model, the theoretical value is in good agreement with the experimental value for a 70/30 HDPE/EVA blend. The area under the loss modulus/ temperature curve (LA) had been analyzed with the integration method from the experimental curve and had been compared with that obtained from group contribution analysis. The LA values calculated with group contribution analysis were found lower than those calculated with the integration method. When a maleic-modified polyethylene compatibilizer added, the storage modulus, loss modulus, and loss factor values of the system were increased and this was said due to the finer dispersion of the EVA domains in the HDPE matrix upon compatibilization. The addition of a maleic-modified polyethylene compatibilizer for 70/30 and 50/50 blends shifted the relaxation temperature of both HDPE and EVA to a lower temperature, and this exhibited increased interdiffusion of the two phases at the interface upon compatibilization. The relaxation temperature for a 30/70 HDPE/EVA blend was not changed by the addition of a compatibilizer change, because of the cocontinuous morphology of the blends. An increase in both the storage and loss moduli of the blends was obtained by the dynamic vulcanization of the EVA phase with dicumyl peroxide. During dynamic vulcanization, an important increase in the relaxation temperature of EVA and a broadening of the relaxation peaks were occurred and this was said to have been showed the increased interaction between the two phases [74].

Another research about EVA based blends is ‘Reactive compatibilization of the PBT/EVA blend by maleic anhydride’. The aim of this study is to investigate the

reactive compatibilization of the blend of poly(butylene terephthalate) (PBT) and ethylene/Vac copolymer by maleic anhydride (MAH). For this aim, the graft copolymerization of EVA with MAH was carried out by using dicumyl peroxide (DCP) as an initiator by melt free radical grafting in a plasticorder. The concentrations of MAH and DCP were varied from 0 to 3.0 phr and from 0 to 0.4 phr, respectively. EVA g - MAH formed by the grafting reaction of EVA and MAH in the presence of DCP showed an importantly lower torque value than EVA bearing no MAH. PBT was blended with thus obtained EVA- g-MAH using the same plasticorder. For comparison, PBT/EVA blend was also prepared. The FT-IR spectroscopic studies showed that PBT-G -EVA copolymer was formed by the in situation interfacial reaction of MAH grafted onto EVA with the carboxylic and hydroxyl groups at the chain ends of PBT in the blend systems. Because of enhancing interfacial adhesion by the formation of in situation compatibilizer, PBT- g -EVA copolymer, the impact strength of PBT/EVA-g -MAH (80/20) blend showed about three-fold increase in comparison with PBT/EVA (80/20) blend. At the same time, the morphology of the blends was investigated with scanning electron microscope (SEM) [75].

2. MATERIAL AND METHOD

2.1. Materials

Chitosan (Ch)

Ch was supplied from Nantong Qihai Chemicals International Group. In this study, Ch was used as a main polymer. It was explained in detail in Chapter 1 and its chemical structure was shown in Figure 1.1.

Stearoyl chloride

Stearoyl chloride was purchased from Sigma-Aldrich and used in acylation reaction of Ch. The chemical formula is $C_{18}H_{35}ClO$ and synonym is octadecanoyl chloride. Structure and some properties of stearoyl chloride were shown as below:

Formula weight: 302.92 g/mol

Density : 0.897 g/mL at 25 °C

Melting point : 18-22 °C

Boiling point : 202 °C

Flash point : 165 °C

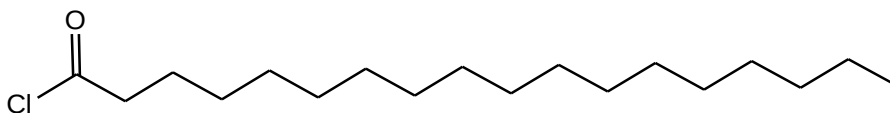


Figure 2.1. Structure of stearoyl chloride

Triethylamine(TEA)

It was purchased from Merck. In this study, TEA was used as a catalyst because of its property of holding HCl from the reaction area during the acylation reaction. Its synonym is N,N-diethylethanamine, N,N,N-triethylamine, (Diethylamino)ethane. Structure and some properties of TEA were shown as below:

Formula weight: 101.19 g/mol

Density : 0.73 g/cm³ (20 °C)

Melting point : -115 °C

Boiling point : 90 °C
Flash point : -11 °C

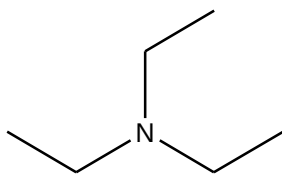


Figure 2.2. Structure of TEA

Chloroform

It was purchased from Tekkim. Due to its volatility and ability to dissolve of organic compounds, it was used as a solvent for this study. Its formula is CHCl_3 and its synonyms are trichloromethane; formyl trichloride; methane trichloride; methyl trichloride; methenyl trichloride. Structure and some properties of chloroform were shown as below:

Formula weight: 119.38 g/mol
Density : 1.48 g/cm³ (20 °C)
Melting point : -63.5 °C
Boiling point : 61.2 °C

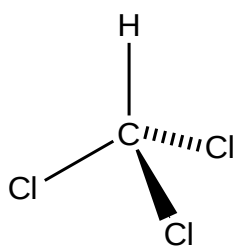


Figure 2.3. Structure of chloroform

Ethylene vinyl acetate (EVA)

EVA was purchased from Polisan Turkey; it was the grade Evatane 28-240. VA content of EVA was determined by using TGA measurements as 29 % by weight. In this study, EVA was used as a main polymer coupled with Ch. EVA was explained in Chapter 1 and chemical structure of EVA was shown in Figure 1.4.

Hydrochloric acid

It was purchased from J.T.Baker. It was a solution of 37% percent of HCl. It was used for washing the product after acylation reaction. Some properties of HCl were shown as below:

Formula weight: 36.46 g/mol

Density : 1.18 g/cm³ (20 °C)

Melting point : -35 °C

Boiling point : 110 °C

Sodium hydroxide

Sodium hydroxide was purchased from Tekkim. Some properties of NaOH were shown as below:

Formula weight: 36.46 g/mol

Density : 2.13 g/cm³ (20 °C)

Melting point : 323 °C

Boiling point : 110 °C

Isopropyl alcohol (IPA)

IPA was purchased from Tekkim. It was used for purification of the product after reaction. Its synonyms are 2-propanol, isopropanol, rubbing alcohol, sec-propyl alcohol or s-propanol. Its formula is C₃H₈O. Structure and some properties of isopropyl alcohol were shown as below:

Formula weight: 60.10 g/mol

Density : 0.786 g/cm³ (20 °C)

Melting point : -89 °C

Boiling point : 82.5 °C

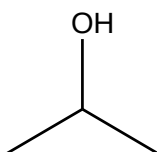


Figure 2.4. Structure of IPA

2.2. Equipments

Magnetic Stirrer (Heidolph MR 3001 K)

Vacuum Pump (Vacucell)

Drying Oven (Ecocell)

Fourier Transform Infrared Spectroscopy (FT-IR) (Thermo Scientific Nicolet 6700)

Thermal Gravimetric Analyzer (TGA) (Perkin Elmer Pyris 6 TGA)

Differential Scanning Calorimetry (DSC) (Perkin Elmer Jade DSC)

Dynamic Mechanical Analyzer (DMA) (Perkin Elmer Pyris Diamond DMA)

Contact Angle Meter (Model G-III Contact Angle Meter (Kernco Instrument Co. Inc., El Paso, TX, USA))

Scanning Electron Microscope (SEM) (JOEL-JSM-5910LV)

2.3. Methodology

This study was carried out with three steps. These steps can be arranged in order like below:

‘Synthesis of Ch- stearic acid grafted polymer (Ch-Sa)’

‘Preparation of Blend Systems EVA and Ch-Stearic Acid Graft Polymer (Ch-Sa)’

‘Characterization of Blends’

2.3.1. Synthesis of chitosan stearic acid grafted polymer (Ch-Sa)

Ch-Sa was synthesized in a three necked 250 ml round bottom flask sealed with rubber septa and equipped with magnetic stirrer, condenser and dropping funnel under Ar atmosphere in dry condition. Dried Ch (1.0 g) was weighted in reaction flask and purged for 30 minutes with Ar to remove moisture and create positive inert atmosphere. Reaction flask was placed in an ice bath and 50 ml of dry chloroform was added with continuous stirring and purging with Ar for 15 minutes. To this mixture, 5 ml of TEA was added. A separate solution of 2.5 g of stearoyl chloride in 50 ml chloroform was prepared and added dropwise within 30 minutes with vigorously stirring. After additional 30 minutes stirring at 0 °C the reaction mixture was allowed to slowly warm up to room temperature and was stirred 3 days at room temperature. Then the mixture was filtered and the yellowish filtrate was washed with 15 wt% aqueous HCl solution for three times and further washed with NaOH solution (pH:9) to remove the HCl-TEA

complex and unreacted stearic acid, respectively. Solvent was partly evaporated and clear solution poured into large amount of IPA. The precipitated pale yellow polymer was dried under vacuum at room temperature for a 5 days. The reaction setup is shown in Figure 2.5 and reaction mechanism is given in Figure 2.6.

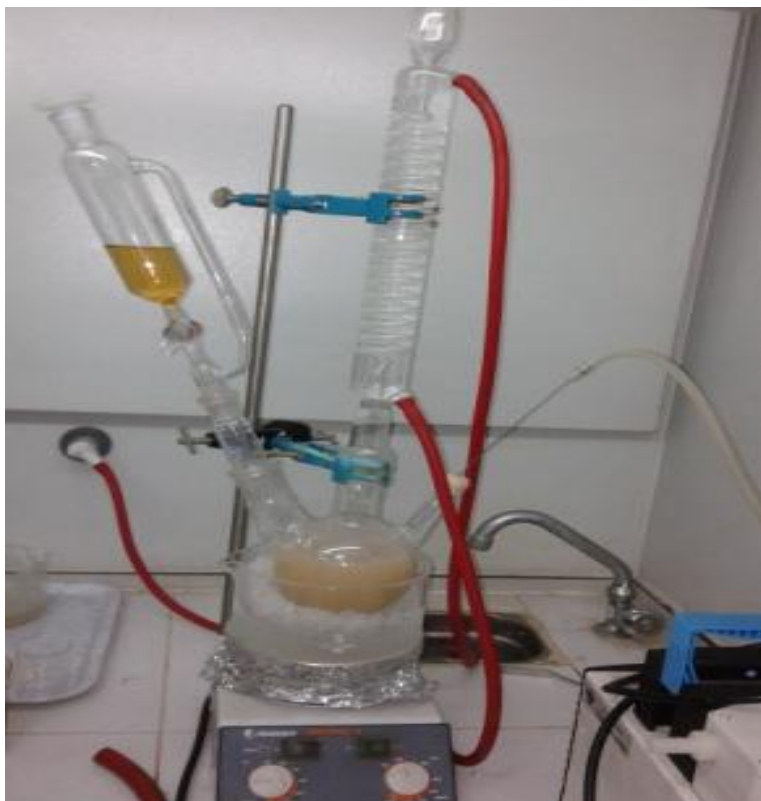


Figure 2.5. The setup of reaction

2.3.1.1. Reaction mechanism

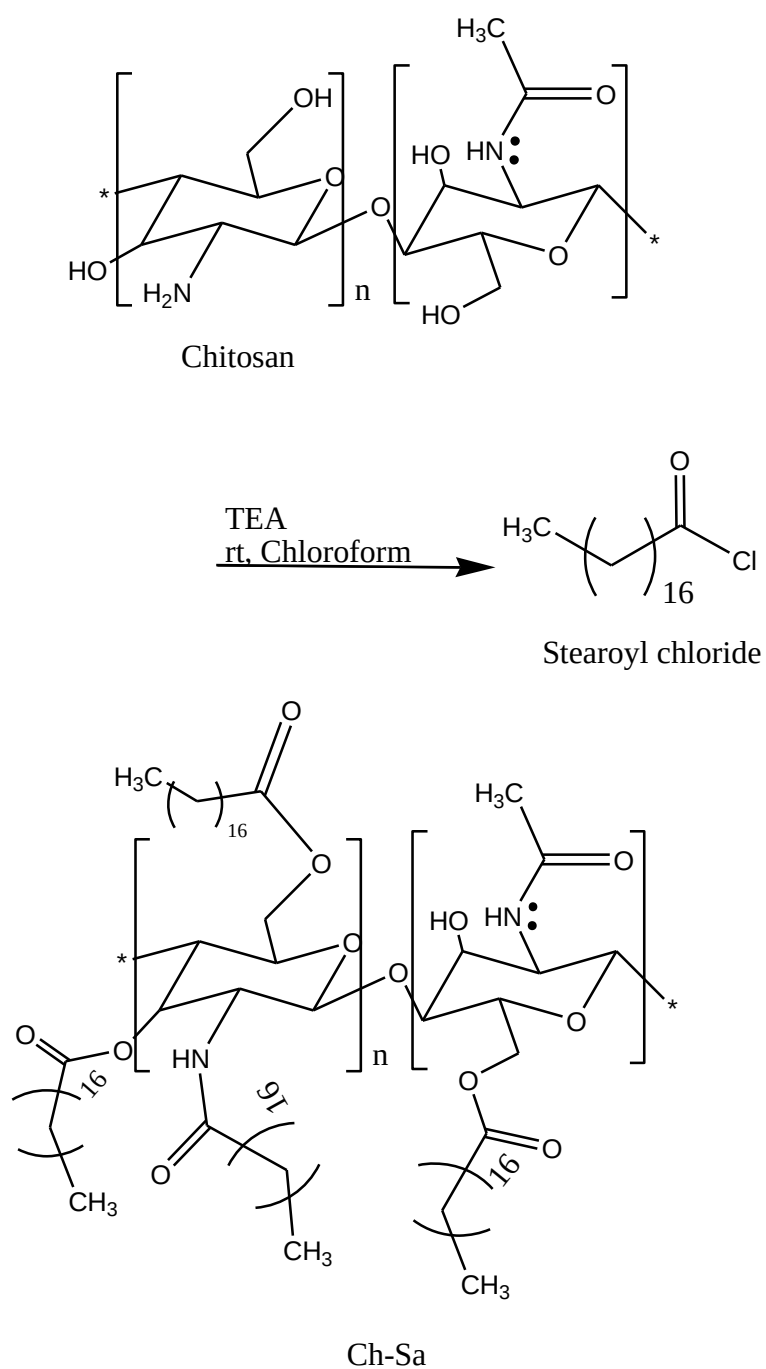


Figure 2.6. Reaction mechanism

2.3.2. Preparation of blend systems

Five different blend films were prepared from the stock solutions of Ch-Sa and EVA in chloroform. The solutions were mixed in predetermined proportions and mixed for 12 hours at room temperature. After degassing to remove air bubbles polymer solutions were poured into 100 mm diameter glass Petri dishes. To prevent bubble formation, solvent was slowly evaporated at room temperature and the films were kept in vacuum oven at room temperature to remove trace of chloroform. Thickness of the dry blend films was measured to be in the range of 70 ± 5 μm which were referred as EVA/Ch-Sa and the number at the end of the blend name is assigned as percentage of Ch-Sa. Composition of the blend films are given in Table 2.1

Table 2.1. Compositions of the blend films

Sample Name	EVA /Ch-Sa
EVA	100/0
EVA /Ch-Sa05	95/5
EVA/Ch-Sa10	90/10
EVA/Ch-Sa20	80/20
EVA/Ch-Sa40	60/40

2.3.2.1. Characterization of the blend films

Blend films were characterized by using FT-IR, DSC, TGA, DMA, SEM and one liquid contact angle measurement techniques.

FT-IR measurements

The spectroscopic characterization of pure components and the blend films were performed in transmission mode using a Thermo Scientific Nicolet 6700 model FT-IR equipped with a Smart Orbit high performance diamond attenuated total reflectance (ATR) accessory. Measurement range was $4000\text{--}400$ cm^{-1} .

TGA

The dynamic weight loss curves of pure components and the blend films (sample weights were between 8-10 mg) were recorded on a Perkin Elmer Pyris 6 model thermogravimetry between 25-800 °C temperature ranges. Data were evaluated using Pyris TA software. TGA measurements were performed at a heating rate of 10 °C/min under Ar atmosphere (20 ml/min). Temperature calibration was performed according to Curie temperatures of perk alloy, alumel and iron.

DSC

The glass transition temperatures and melting temperatures of pure components and the blend films were determined using Perkin Elmer Jade DSC. Data was evaluated using Pyris TA software. DSC was calibrated with metallic indium (99.9% purity). All samples were tested in crimped aluminum pans at a heating rate of 10 °C/min under dry Ar atmosphere (20 mL/min) over a temperature range of 25-250 °C. Melting temperature was taken as the peak of the melting endotherm.

DMA

Storage modulus (E'), loss modulus (E'') and loss-tangent ($\tan\delta$) values of the blend films were recorded in the range of -70°C, 50 °C. Measurements were conducted using Diamond model Dynamic Mechanical Analyzer (DMA) supplied by PerkinElmer-Seiko (Japan) in tensile mode at a heating rate of 4 °C/min under Ar atmosphere at multi-frequency mode (0.5, 1, 2, 5 and 10 Hz). The test specimens were in rectangular shape (50 x 10 x 0.07 mm³). For each sample, the initial grip separation was set to 20 mm and liquid nitrogen was used for cooling the system.

Contact angle measurement

The contact angles of water, methylene iodide, ethylene glycol, formamide on the blend films were measured using Model G-III Contact Angle Meter (Kernco Instrument Co. Inc., El Paso, TX, USA). The one-liquid contact angle method (air-liquid drop-polymer system) was used at room temperature and humidity. Measurements were performed by deposition of liquid drops using micro-liter syringe onto the blend surfaces. All contact angle values were the average of ten measurements with a standard deviation of ± 2 .

SEM

To assess the biodegradability of the blend films, they were buried for 3 months and then their SEM images were taken. Comparison of the surface morphologies of weathered and non-weathered samples were examined using Jeol JSM-5910 LV model SEM after sputter coating in vacuum with a thin layer of gold.

3. RESULTS AND DISCUSSION

3.1. FT-IR Results

FT-IR spectroscopy is widely used for quantitative and qualitative analysis of chemicals and compounds having absorbance in IR region. For polymers and their blends this technique provides valuable information regarding their morphology, composition and miscibility. In polymer blends any shift observed in absorbance frequency of a functional group to lower values compared to corresponding individual polymer chains is evidence of energetic interactions and therefore miscibility of the polymers.

In FT-IR spectrum of Ch a broad band between 3500-3300 cm^{-1} is due to the –OH and N-H stretching (Figure 3.1). The characteristics bands observed at 1646 cm^{-1} and 1588 and 1324 cm^{-1} are due to the vibrational absorption of C=O groups of amide I, N-H bending vibration of –NH₂ (amide II) and N-H bending vibration amide III respectively. The strong absorption peaks at 1076, 1021, 972 and 842 cm^{-1} are assigned to C-O-C bonds of glucose rings and glycosidic linkages of Ch [76].

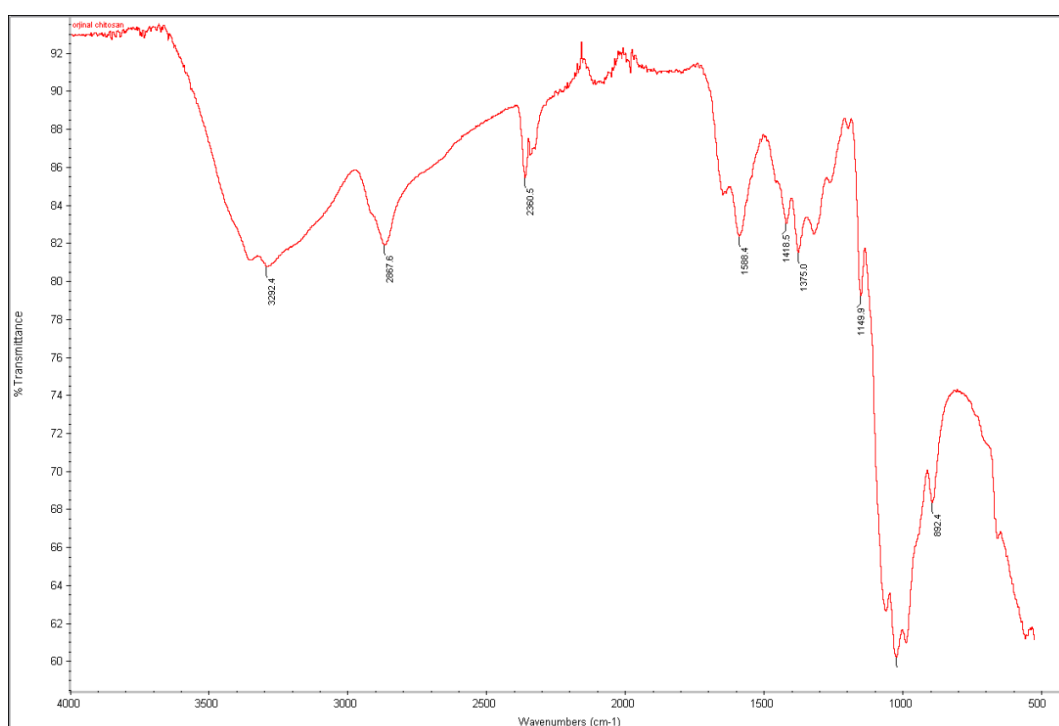


Figure 3.1. FT-IR spectrum of Ch

Figure 3.2 shows the FT-IR spectra of Ch-Sa. Compared to FT-IR spectrum of Ch disappearance of N-H and –OH peaks of Ch at between 3500-3300 cm^{-1} and 1588 cm^{-1} is an evidence that all –OH and N-H groups are reacted with stearoyl chloride to form Ch-Sa. The new peaks appeared at 1860, 1846 and 1721 cm^{-1} are due to the –C=O groups of different ester linkages formed in grafting reaction. In this spectrum the strong absorption peak observed at 1467 cm^{-1} is assigned to the C-H vibrational absorption of Ch and Sa groups. Characteristic C-O-C absorption bands of Ch are observed between 26-1061 cm^{-1} which indicates that Ch ring remained unchanged.

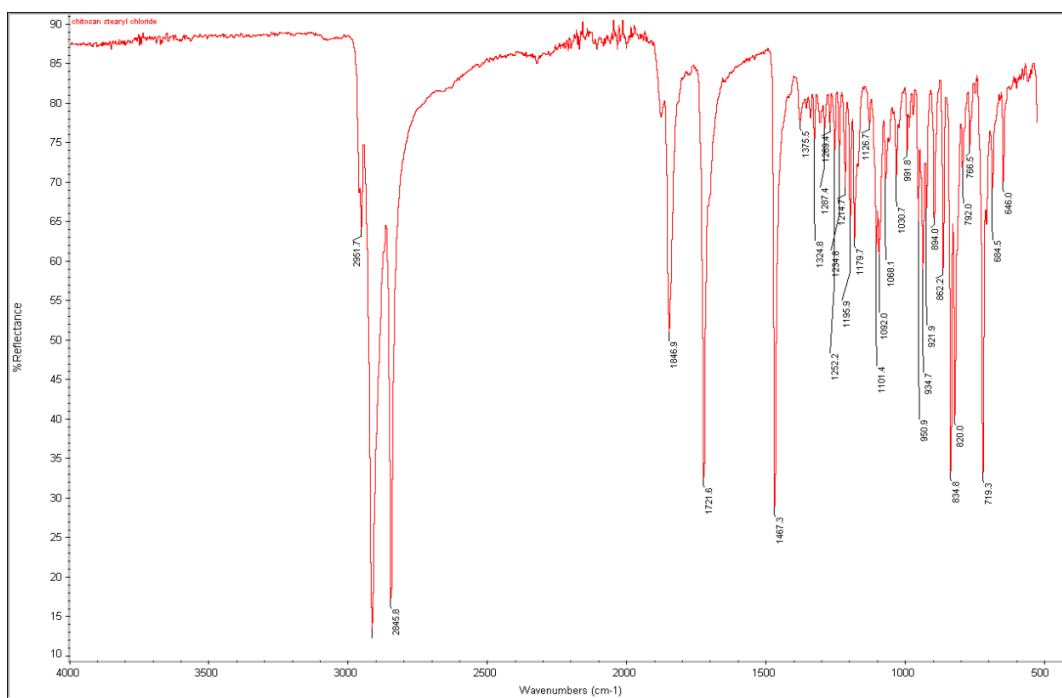


Figure 3.2. FT-IR spectrum of Ch-Sa

In FT-IR spectrum of EVA (Figure 3.3) strong absorption peaks at 2848 cm^{-1} and 2916 cm^{-1} are due to the CH and CH_2 groups of ethylene and VA segments of EVA. The bands appeared at 1735 cm^{-1} for asymmetric –COO stretching vibration and at 1637 cm^{-1} for symmetric –COO stretching vibration of acetate groups, respectively. The bands between 1300-1500 cm^{-1} are due to the CH, CH_2 and CH_3 bending vibration of ethylene and VA segments of EVA.

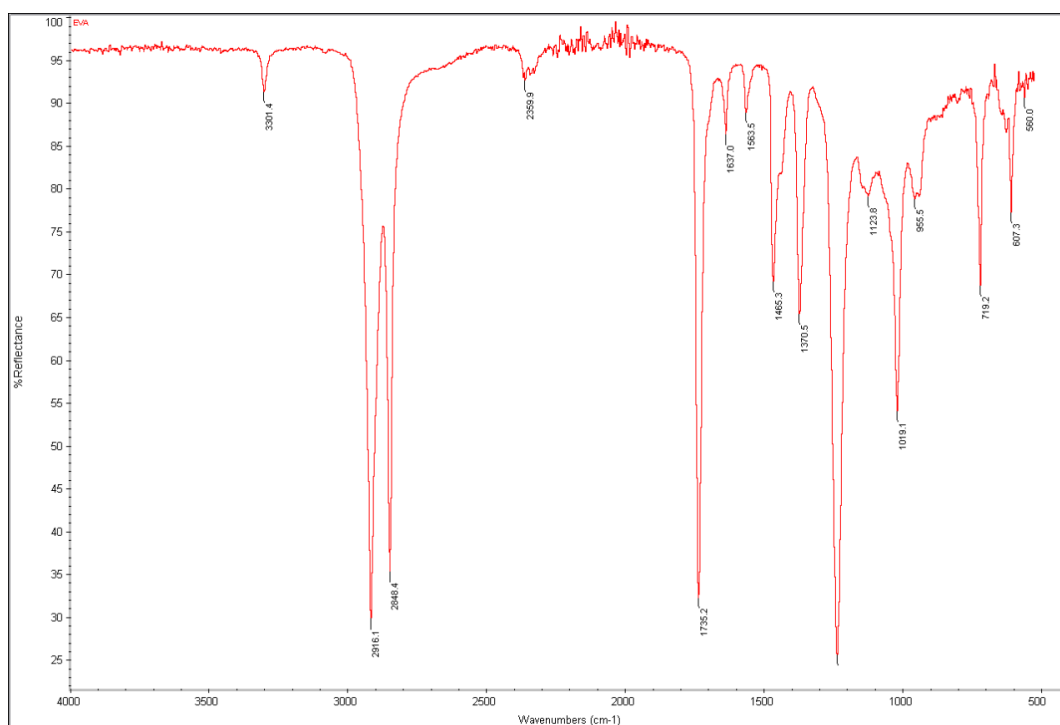


Figure 3.3. FT-IR spectrum of EVA

Figures 3.4 and 3.5 show FTIR spectra of the blends at the EVA/Ch-Sa05 and EVA/Ch-Sa10 compositions taken in the range of 4000-400 cm^{-1} , respectively. The spectra of blend films were characterized by the presence of the characteristic absorption bands of blend components at varying intensities. Figure 3.6 shows the FTIR spectra of blend components and the blends at EVA/Ch-Sa05 and EVA/Ch-Sa10 compositions in the range of 1800-1300 cm^{-1} . Acetate groups of EVA interact with Ch-Sa indicated with the decrease in C=O band intensity of VA which shifted to lower values with increasing Ch-Sa proportion. This is an evidence of the interaction between blend components.

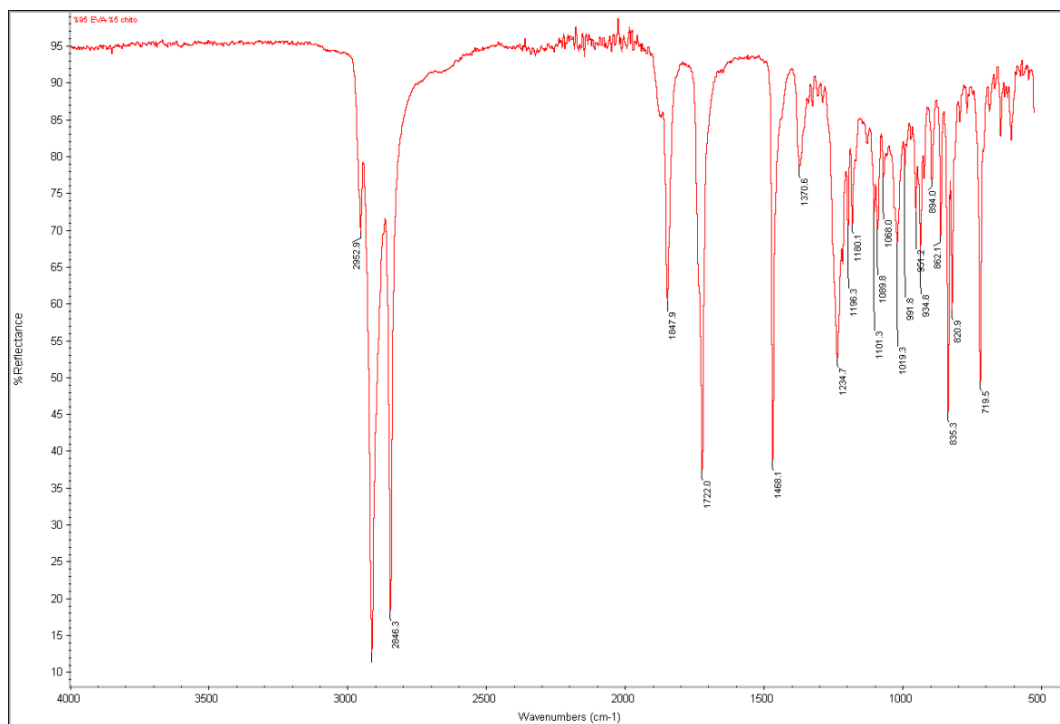


Figure 3.4. FT-IR spectrum of EVA/Ch-Sa05

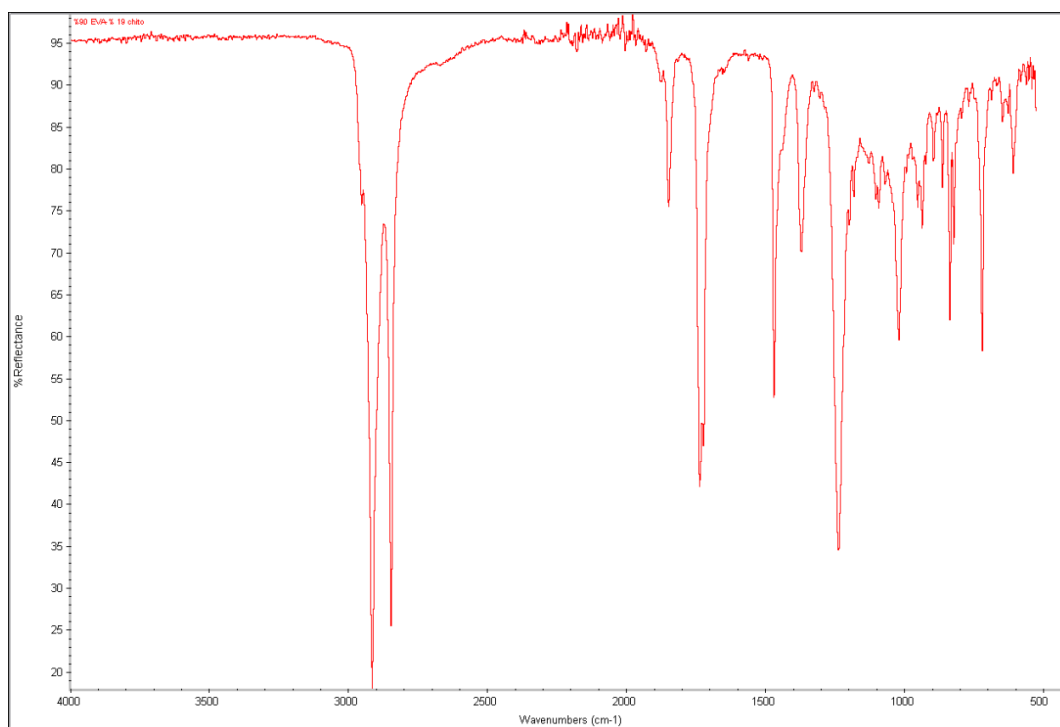


Figure 3.5. FT-IR result of EVA/Ch-Sa10

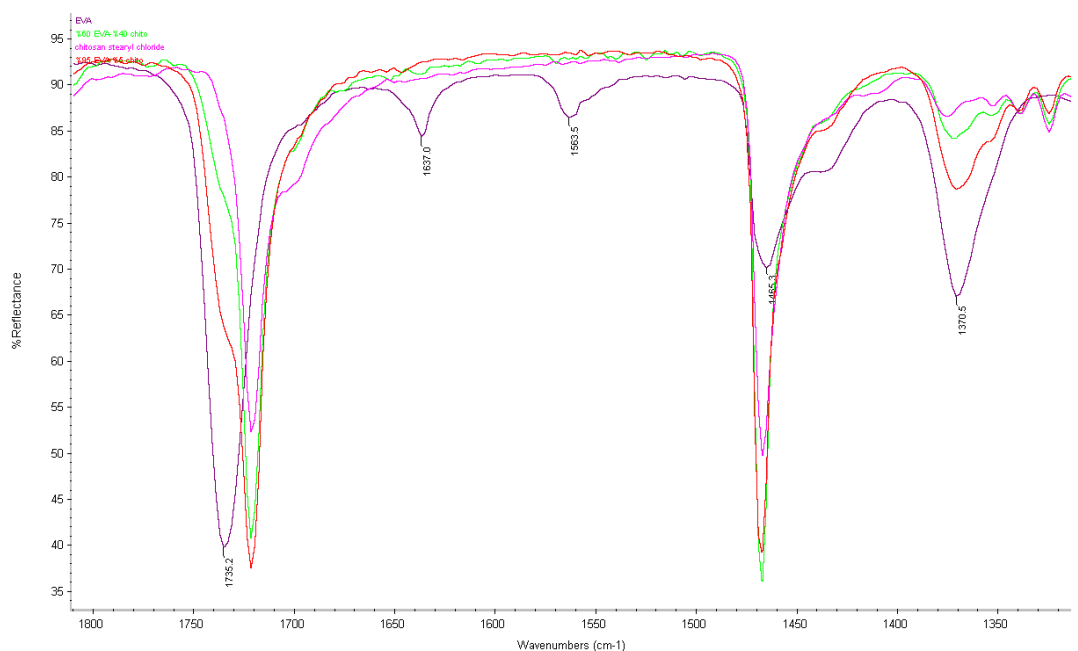


Figure 3.6. FT-IR spectra of blend components and blends in the range of 1800-1300 cm^{-1}

3.2. TGA Results

TGA technique provides useful information regarding the composition of polymer blends if components have distinguishable thermal behavior. Typical TGA curves of Ch, Ch-Sa and EVA are shown in Figure 3.7. From the TG curves initial and final decomposition temperatures were determined. As shown in Figure 3.7 a and b, Ch and Ch-Sa have quite different thermal behavior from EVA. In TG curve of Ch (Figure 3.7, a) while the first weight-loss step within 220-400 $^{\circ}\text{C}$ corresponding to 60 % weight-loss is due to the decomposition of glucose ring, the second weight-loss step observed at higher temperatures than 400 $^{\circ}\text{C}$ is due to the decomposition of remaining more thermally stable carbonized structure of Ch. Thermal decomposition of Ch-Sa include two weight-loss steps as well. The first weight-loss step of Ch-Sa starts at nearly the same temperature with that of Ch and ends at much higher temperature than that of Ch (471 $^{\circ}\text{C}$) which corresponds to 95% weight-loss. This result implies that stearic acid grafting gave extra thermal stability to Ch which is result of the more intermolecular interaction of stearic acid pendant groups. This can be taken as a proof of the presence of the stearic acid groups attached to Ch (Figure 3.7.b). Thermal decomposition of EVA takes places in two main weight-loss steps (Figure 3.7.c) The first step corresponding to

20% weight-loss starts at 330 °C and ends at around 386 °C. Second step corresponding to 80% weight-loss starts at 386 °C and ends at 502 °C. In this thermogram the first step corresponds to quantitative elimination of acetic acid from VA portion of EVA and the second step corresponds to remaining poly(ethylene) portion of EVA. From the first stage decomposition the amount of VA in EVA was calculated as 29%.

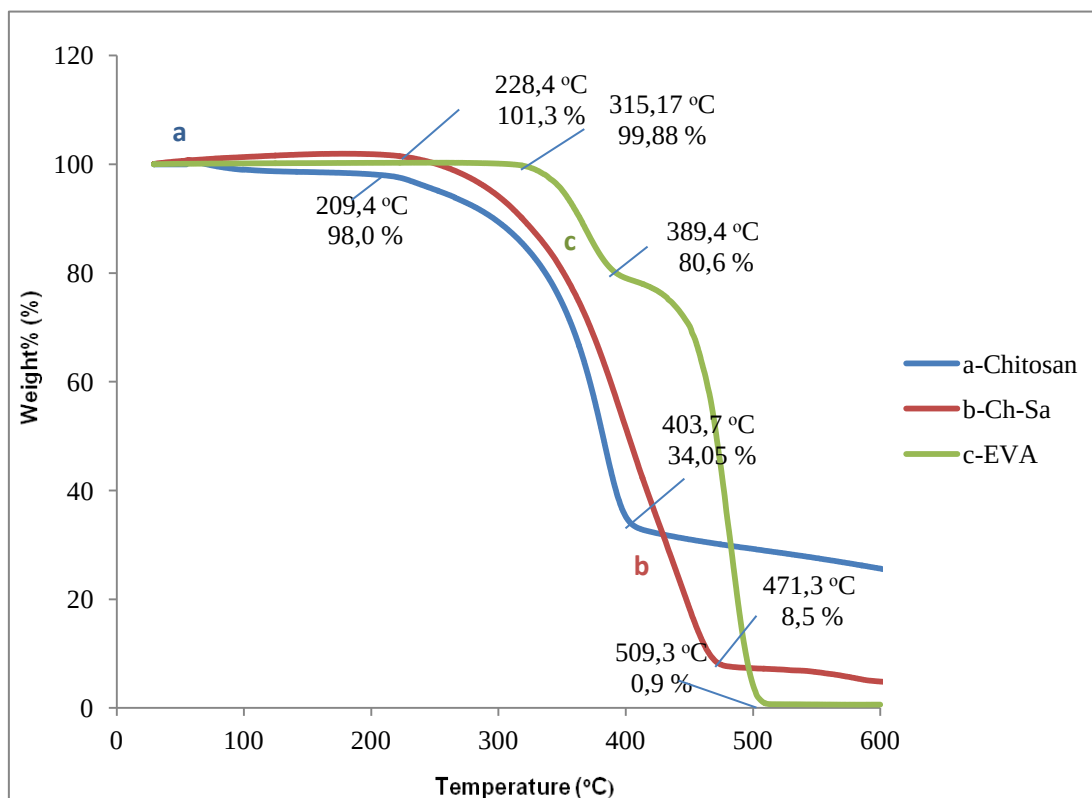


Figure 3.7. TGA curves of Ch and the blend components. a:Ch, b:Ch-Sa, c:EVA

Figure 3.8 shows TGA curves of the blends at different EVA/Ch-Sa ratios. While thermal behavior of the blends containing 5% and 10% Ch-Sa are quite similar with that of pure EVA, which is due to the more compatibility of Ch-Sa with EVA, above these concentrations phase separation was observed and thermal behavior of the blends becomes similar to that of Ch-Sa. It is worth noting that the below the EVA/Ch-Sa10 concentrations blends films were more homogenous and therefore more useful for biodegradable packaging film applications.

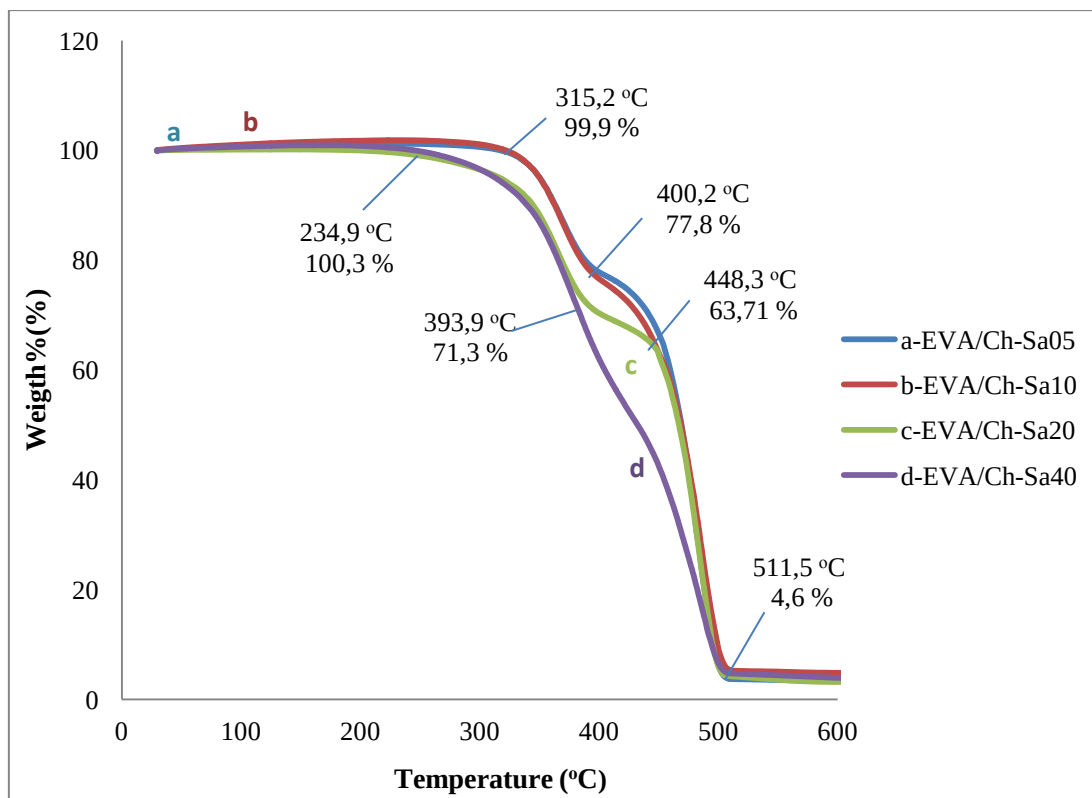


Figure 3.8. TGA thermograms of the blend films. a: EVA/Ch-Sa05, b: EVA/Ch-Sa10, c: EVA/Ch-Sa20, d: EVA/Ch-Sa40

3.3. DSC Results

DSC is an important quantitative technique in thermal characterization of polymers and blends. This technique allows us measuring heat absorption and release in the course of any thermal phenomenon such as phase change, thermal decomposition etc. The peak area obtained in DSC is a quantitative value of a phase transition. DSC curves of EVA, and Ch-Sa are shown in Figure 3.9 and heat of fusion values (ΔH_{fusion}) for EVA and each composition are summarized in Table 3.2. Heat of fusion values were calculated on the basis of heat absorbed for per gram of ethylene portion of EVA and Sa portion of Ch-Sa since both VA in EVA and Ch in Ch-Sa do not display any melting behavior in the DSC operation range (Figure 3.9) [77].

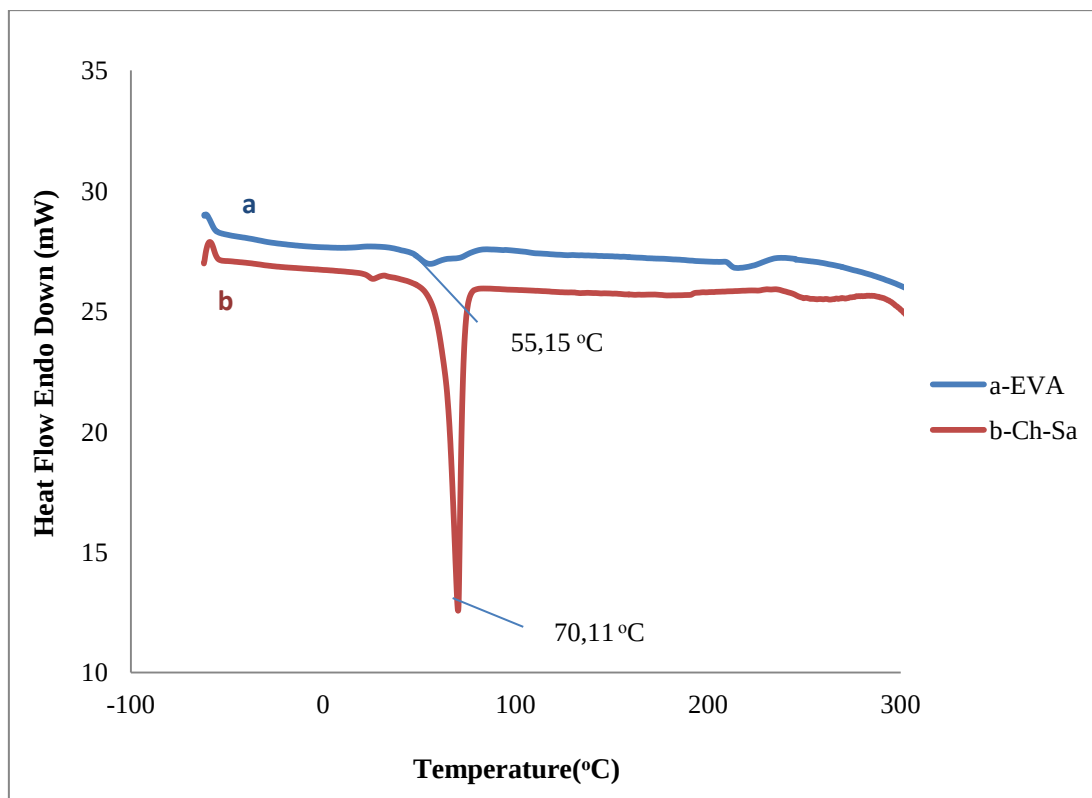


Figure 3.9. DSC curves of the blend components.

Table 3.1. Heat of fusion values of the blend films*.

Sample Name	EVA/Ch-Sa	$\Delta H_{\text{fusion}}(\text{J/g}_{\text{EVA+Ch-Sa}})$
EVA/Ch-Sa05	95/5	22,37
EVA/Ch-Sa10	90/10	20,42
EVA/Ch-Sa20	80/20	41,12
EVA/Ch-Sa40	60/40	55,85

*Heat of fusion value of EVA was measured by DSC as 41.4 J/g which belongs to PE portion of EVA. The literature value of heat of fusion for PE is 282 J/g,[78] and melting temperature is 110 °C, VA portion of EVA suppressed the crystallinity of PE in EVA leading to lower melting temperature.

Therefore heat of fusion values can be taken as a measure of crystallinity of the crystalline part of EVA and Ch-Sa which is directly proportional to the phase segregation in the blends such that low heat of fusion of a blend is more amorphous and therefore more homogeneous. While heat of fusion of blends containing 5 and 10% Ch-Sa have almost the same value, remarkable changes were noticed in heat of fusion of the blends containing more than 10% Ch-Sa. Change in heat of fusion values

of the blends with composition were quantitatively observed in their DSC curves (Figure 3.10). This result implies that the blend films became more homogeneous and less opaque up to EVA/Ch-Sa10 composition which contains 10% Ch-Sa. Over this percentage the opacity of blend films increased and the films become more brittle and more phase separation was observed.

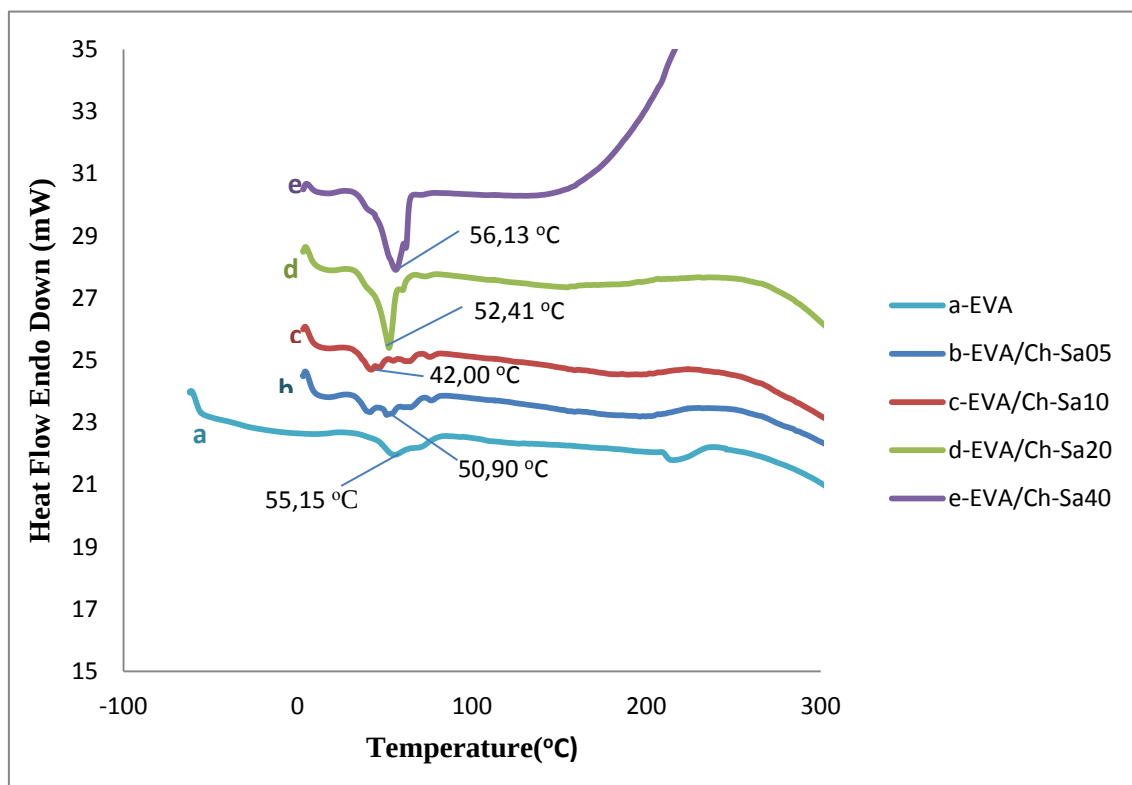


Figure 3.10. DSC curves of the blend films

3.4. DMA Results

Dynamic mechanical analysis (DMA) is used to analysis and characterize the dynamic mechanical response of a material such as storage modulus (stiffness, E'), loss modulus (E'') and loss tangent ($\tan \delta$) against an applied oscillating mechanical forces as a function of temperature and frequency. Thus, this is a useful technique for polymer blends to investigate the extent of miscibility and phase morphology. DMA also measure glass transition temperature of polymer films more sensitively than other thermal techniques like DSC [79, 80].

The value of storage modulus (E') of a blend film is assigned as a quantitative measure of its stiffness. If a material is in glassy state where the segmental mobility is restricted

(below T_g) then it has high stiffness and therefore high storage modulus. When it is heated, a drastic decay in E' curve at T_g region with temperature is observed. This is due to the sudden increase in segmental mobility of the chains resulted from increasing internal energy and therefore rubbery region is observed. The change of storage modulus (E') of the blend films with temperature and blend ratio at a frequency of 10 Hz and 4 °C/min heating rate scanned between -80, +40 °C are given in the Figure 3.11. Measurements were conducted at 5 different frequency simultaneously (0.5, 1.0, 2.0, 5.0 and 10 Hz) but data obtained at 10 Hz were evaluated. The results indicated that at all temperatures, the E' values of the blend films increased regularly with increasing Ch-Sa proportion. This is due to the more stiff Ch and crystalline nature of Sa segment of Ch-Sa. Higher crystalline structure is result of more intermolecular interaction and therefore higher E' .

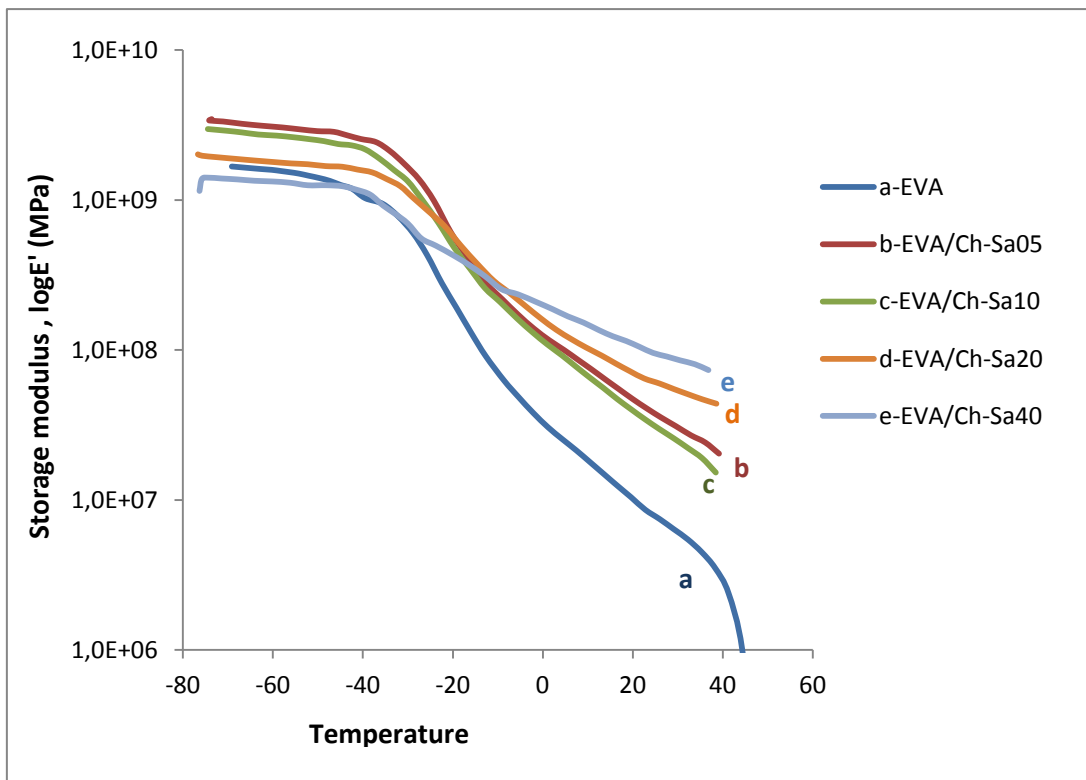


Figure 3.11. Storage modulus (E') curves as a function of temperature for the blend films.

Loss modulus is a quantitative measure of the heat dissipated per unit area resulted from segmental movements and frictions between polymer chains. Since minimum segmental motions are observed under T_g , minimum E'' values are observed. Therefore T_g is

determined temperature corresponding the peak value of E'' when plotted against temperature. The change of loss modulus (E'') of the blend films with temperature are given in Figure 3.12. The T_g of EVA was determined from this figure as $-28\text{ }^{\circ}\text{C}$ and for the blends containing 5%, 10% and 40 % of Ch-Sa T_g s were determined as -25 , -30 and $-35\text{ }^{\circ}\text{C}$, respectively. The decrease in T_g s with increasing Ch-Sa proportion of the blend films might be due to the T_g of Sa than EVA.

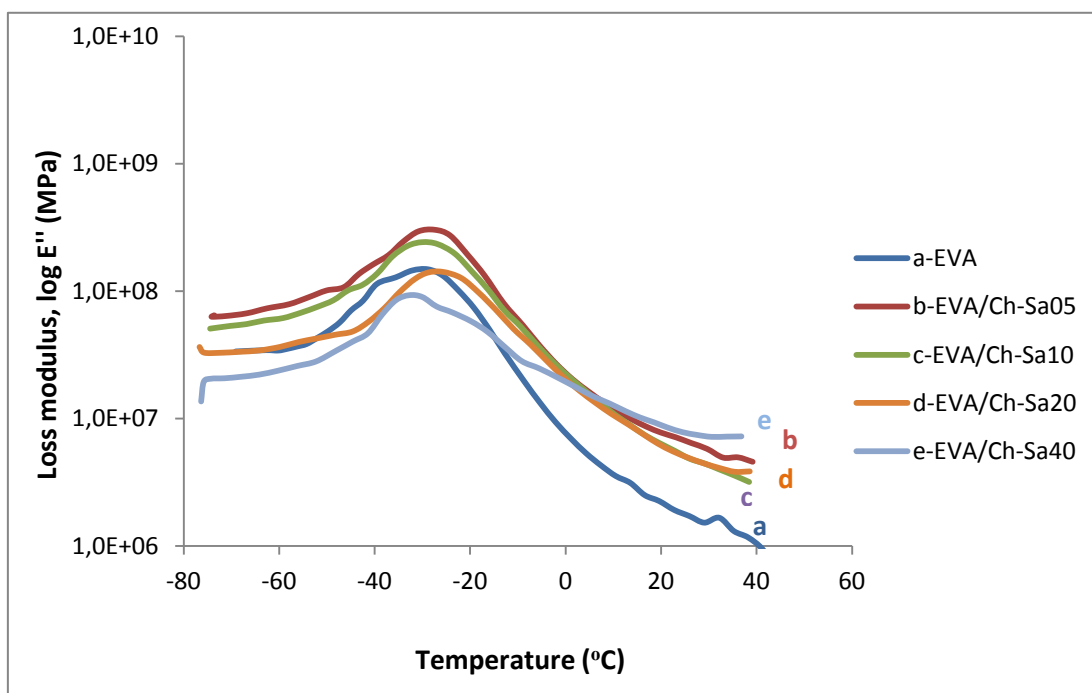


Figure 3.12. Loss modulus (E'') curves as a function of temperature for EVA and the blend films.

Glass transition temperature (T_g), the main relaxation process of a polymer film, is known as α -relaxation temperature. Generally, in a blend film, when the variation of $\tan(\delta)$ with temperature shows unique T_g damping peak between T_g s of corresponding blend components, they are compatible. Otherwise, they are incompatible and therefore shows phase segregation. Thus, the shape (broadening) and number of $\tan(\delta)$ peak in a damping curve give us an important information about compatibility of blend components. Figure 3.13 shows the change of $\tan(\delta)$ with temperature. Due to the high chain relaxation and rotational energy barrier of polysaccharide chains, T_g of Ch is well above the melting point of stearic acid and EVA. Therefore, $\tan(\delta)$ of the blend films were measured between -80 , $+55\text{ }^{\circ}\text{C}$. As shown in Figure 3.13, The T_g s of the blend films decreased with increasing Ch-Sa approaching toward the T_g of pure stearic acid

portion of Sa. It is worth noting that a single peak observed in $\tan(\delta)$ curves at all concentrations indicated the compatibility of components.

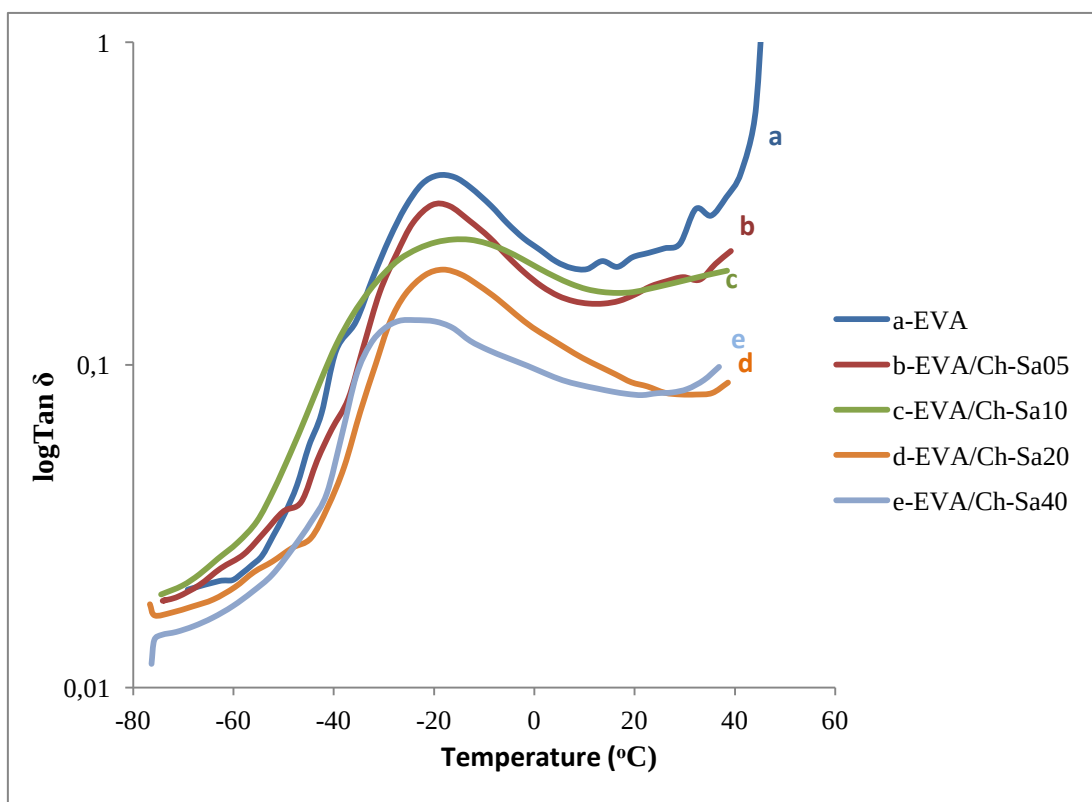


Figure 3.13. Loss tangent δ curves as a function of temperature for EVA and the blend films.

3.5. Surface Free Energy Analysis of the Blend Films

The surface free energy and its components (i.e. apolar Liftshitz-van der Waals, LW, and polar electron donor-electron acceptor interactions) of blend films were determined by contact angle measurements. For this purpose, sessile drop technique in one-liquid contact angle method was used. It is well known that the surface dynamics of polymers are considerable different from those of more rigid materials such as ceramics and metals due to the high mobility of macromolecules at the surface. Therefore the compositions of the polymer surfaces are considerably different from the bulk and also vary with depth from the surface. Depending on environmental condition, polymeric materials can have different surface configurations. In non-polar environment they minimize the density of the polar groups at the surface via the segmental rotation and movement. In polar environment, the surface enrichment of more energetic polar groups

is obtained. The essential advantage of the contact angle technique compared with other spectroscopic techniques such as electron spectroscopy for chemical analysis (ESCA), Auger electron spectroscopy (AES) and secondary ion mass spectroscopy (SIMS) is that while these techniques require ultra-high vacuum environment for analysis, contact angle technique provides us a quantitative evaluation of the surface dynamics of polymer solids under their application medium. Over the glass transition temperature, since polymers have substantial segmental rotations and movements, their surfaces have dynamic nature. In nonpolar environments such as air, the density of hydrophobic groups increases on the surface whereas in a polar environment the polar groups towards the surface and the surface becomes more energetic. The contact-angle values of water, ethylene glycol, formamide and methylene iodide drops on the blend film surfaces were collected in Table 3.2.

Table 3.2. Contact-angle results of the blend films

Sample Name	DI-Water	Methylene iodide	Ethylene glycol	Formamide
EVA	78.5	56.7	72.5	82.5
EVA/Ch-Sa05	114.5	64.7	70.7	112.5
EVA/Ch-Sa10	119.5	55.0	76.7	116.5
EVA/Ch-Sa20	109.3	55.5	74.0	105.5
EVA/Ch-Sa40	98.5	65.0	83.0	125.5

The surface free energy and its LW and electron-donor and electron-acceptor components (i.e. apolar Liftshitz-van der Waals, and polar interactions) of the blend films were calculated by using the following equation which is an expression of the one liquid contact angle theory [81].

$$\gamma_L (1+\cos\theta) = 2(\gamma_S^{LW} \gamma_L^{LW})^{1/2} + 2(\gamma_S^+ \gamma_L^-)^{1/2} + 2(\gamma_L^+ \gamma_S^-)^{1/2} \quad (3.1)$$

In this equation, subscripts *L* and *S* refer to liquid and solid respectively. θ is the contact angle of liquid drop on solid surface, γ_L is the surface free energy of liquid probe. γ_S^{LW} and γ_L^{LW} are the apolar Lifshitz–Van der Waals components of solid and liquid, respectively. γ_S^+ and γ_L^+ are the electron acceptor components of surface free energy of

solid and liquid, respectively. γ_s^- and γ_L^- are the electron donor components of surface free energy of solid and liquid, respectively. This equation is mainly based on Young-Dupre theory which was developed later by van Oss, Good and Chaudhury [82].

For an apolar liquid, $\gamma_L^+ = \gamma_L^- = 0$, which means $\gamma_L = \gamma_L^{LW}$. Hence, the Eq(1) can be rewritten as follows,

$$\gamma_s^{LW} = \gamma_L (1 + \cos\theta)^2 / 4 \quad (3.2)$$

Consequently, the γ_s^{LW} of a solid surface can be calculated using contact angle value of an apolar liquid probe. For a sample, this calculation was performed for apolar liquid (paraffin) and then the γ_s^{LW} value was calculated. By using the known γ_s^{LW} value in Eq.3.1, two unknown parameters (i.e. γ_s^+ and γ_s^-) were calculated for two liquid sets of water-formamide and water-glycerol. The results were averaged. The total surface energy of a solid (γ_s^{TOT}) and its relationship with dispersion (γ_s^{LW}) and acid-base (γ_s^{AB}) components are expressed as follows,

$$\gamma_s^{TOT} = \gamma_s^{LW} + \gamma_s^{AB} \quad (3.3)$$

$$\gamma_s^{AB} = 2(\gamma_s^+ \cdot \gamma_s^-)^{1/2} \quad (3.4)$$

The contact angle values of liquid probes on blend films surfaces and their calculated surface free energy components are collected in Table 3.3 and Table 3.4, respectively.

Table 3.3. Surface free-energy component values of the liquids used (mJ/m²)

Liquid	γ_L	γ_L^{LW}	γ_L^{AB}	γ_L^+	γ_L^-
Water	72.8	21.8	51.0	25.5	25.5
Ethylene Glycol	48.0	29.0	19.0	1.92	47.0
Formamide	58.0	39.0	19.0	2.28	39.6
Methylene iodide	50.8	50.8	0	0	0

Table 3.4. Surface free-energy components of blends (mJ/m²)

Samples	γ_s^{LW}	γ_s^-	γ_s^+	γ_L^{AB}	γ_s^{TOT}
EVA	30.5	6.23	1.26	2.8	33.3
EVA/Ch-Sa05	25.9	6.32	4.22	5.2	31.1
EVA/Ch-Sa10	31.4	4.05	6.16	4.3	32.7
EVA/Ch-Sa20	31.2	4.80	3.70	4.2	35.4
EVA/Ch-Sa40	32.7	5.47	3.6	4.5	36.2

At once, it will be useful to compare the γ_s^{LW} values of blend films. It is seen from Table 3.5. that γ_s^{LW} values first increased with Ch-Sa which was varied between 30.5 and 32.7 mJ/m². This result is an evidence of the surface enrichment of Ch-Sa on the film surface. This might be due to the hydrophobic and more dispersive stearate groups of Ch-Sa. In line with these results the surface basicity decreased with decrease of EVA which has large amount of basic C=O groups (electron rich groups) in acetate portion. It was calculated using contact angle data that acid contribution of the blend film surface increased as Ch-Sa groups increased.

3.6. SEM Results

The morphology of EVA/Ch-Sa05 blend film was examined by SEM. SEM images were taken before and after burying the blend film 3 months (Figure 3.14). SEM images revealed that morphology of the buried samples had considerable structural defects on surface caused by bacteria. This result was an evidence of the biodegradative contribution Ch-Sa to EVA. The use of Ch-Sa as biodegradable additive in EVA based blend formulations will be gained considerable advantage from the point of biodegradability.

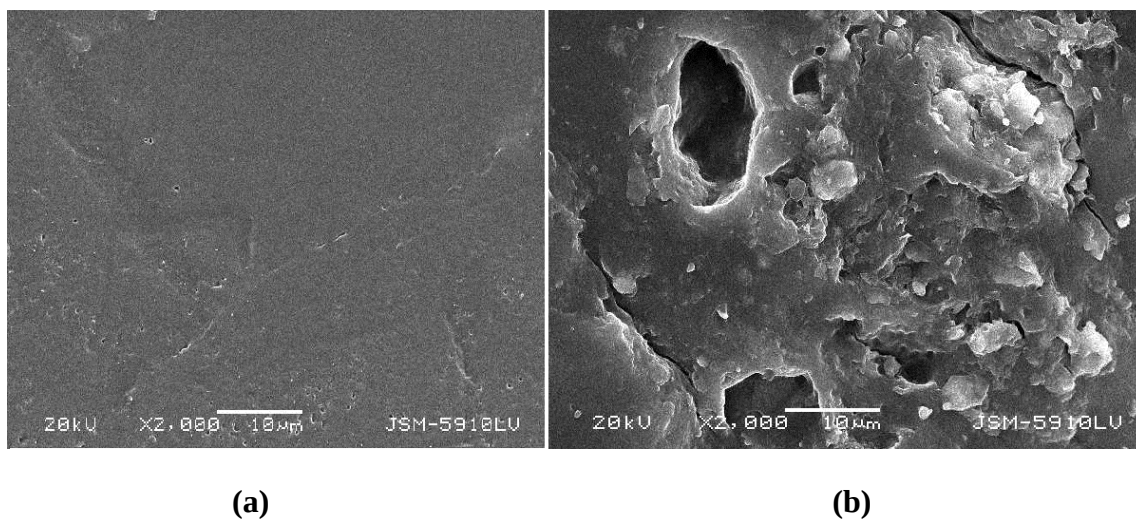


Figure 3.14. SEM views of EVA/Ch-Sa before (a) and after (b) degradation (X2000)

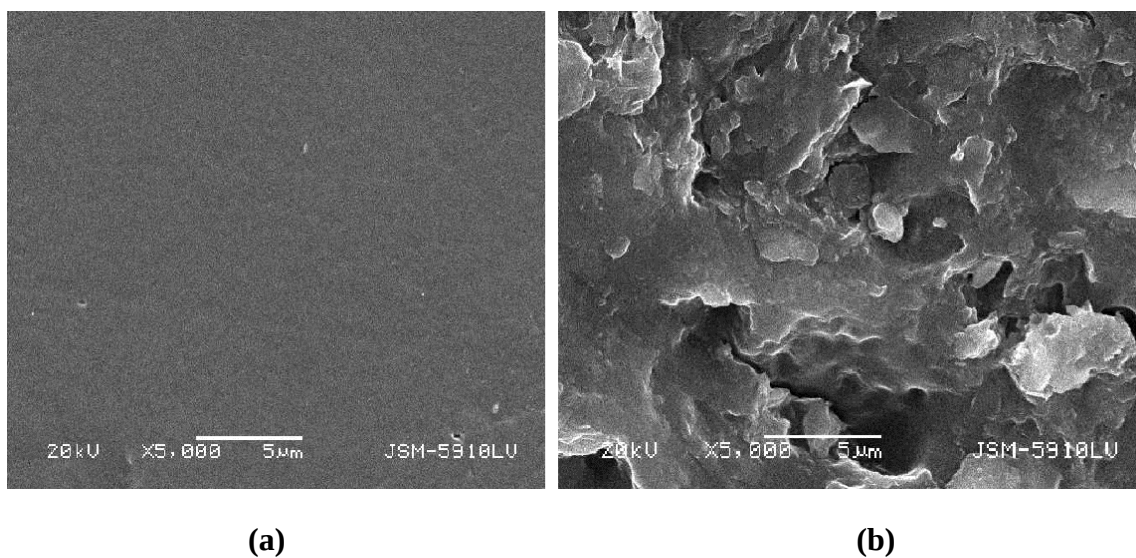


Figure 3.15. SEM views of EVA/Ch-Sa05 before (a) and after (b) degradation (X5000)

4. CONCLUSIONS

From the point of environmental pollution arising from plastic wastes the use of biodegradable polymers and additives have generated considerable interest. Nowadays, because of its excellent biodegradability, biocompatibility and bioactivity properties, Ch becomes significantly attractive in food industry and packaging material. In many cases, the relatively poor mechanical properties and film forming capability of Ch make some limitation in its use. These drawbacks have been partly overcome by some modification using its reactive groups and thus incorporated novel properties such as water solubility and compatibility with other polymers resulted in diversify of utilization.

EVA has better physical properties than most of the packaging materials but has less biodegradability. To increase biodegradability of EVA, the blend films containing biodegradable Ch were prepared. EVA and Ch are incompatible polymer pairs. To increase the compatibility with EVA, Ch-Sa was synthesized by the reaction of functional $-OH$ and $-NH_2$ groups with stearoylchloride. EVA blend films containing 5%, 10%, 20% and 40% Ch-Sa were prepared. The mechanical, thermal and surface characterization of the blend films were characterized by FT-IR, TGA, DSC, DMA, SEM, and contact angle measurements

The FT-IR revealed that all $-OH$ and $N-H$ groups are reacted with stearoyl chloride to form Ch-Sa and $-C=O$ groups of different ester linkages formed in grafting reaction. These results also indicate that Ch ring remained unchanged. From the FT-IR results of EVA/Ch-Sa blend films, it was observed that acetate groups of EVA interact with Ch-Sa which was convinced with the decrease in $C=O$ band intensity of VA shifted to lower values with increasing Ch-Sa proportion. This was an evidence of the interaction between blend components.

The TGA results showed that Sa grafting gave extra thermal stability to Ch which could be result of the more intermolecular interaction of Sa pendant groups. This can be taken as a proof of the presence of the Sa groups attached to Ch. While thermal behavior of the blends containing 5% and 10% Ch-Sa were quite similar with that of pure EVA, which was due to the more compatibility of Ch-Sa with EVA, above these concentrations phase separation was observed and thermal behavior of the blends became similar to that of Ch-Sa. It is worth noting that, below the EVA/Ch-Sa10

concentrations, blends films were more homogenous and therefore more useful for biodegradable packaging film applications

DSC results of the blend films revealed that the blend films became more homogeneous and less opaque up to EVA/Ch-Sa10 composition which contains 10% Ch-Sa. Over this percentage the opacity of blend films increased and the films became more brittle and more phase separation was observed.

DMA results indicated that at all temperatures, the E' values of the blend films increased regularly with increasing Ch-Sa proportion. This is due to the more stiff Ch and crystalline nature of Sa segment of Ch-Sa. Higher crystalline structure was result of more intermolecular interaction and therefore higher E' . From the E'' curves the T_g of EVA was determined as $-28\text{ }^{\circ}\text{C}$ and for the blends containing 5%, 10% and 40 % of Ch-Sa T_g s were determined as -25 , -30 and $-35\text{ }^{\circ}\text{C}$, respectively. The decrease in T_g s with increasing Ch-Sa proportion of the blend films might be due to the lower T_g of Sa than EVA. From loss tangent δ curves, it was observed that T_g s of the blend films decreased with increasing Ch-Sa approaching toward the T_g of pure Sa. It is worth noting that a single peak observed in $\tan(\delta)$ curves indicated the compatible of components.

The calculated γ_s^{LW} values increased with Ch-Sa which was varied between 30,5 and 32.7 mJ/m^2 . This result is an evidence of the surface enrichment of Ch-Sa on the film surface.

SEM images of the 3 months buried blend sample of EVA/Ch-Sa05 showed structural defects formed by bacteria. This result was an evidence of the biodegradative contribution Ch-Sa to EVA. The use of Ch-Sa as biodegradable additive in EVA based blend formulations will be gained considerable advantage from the point of biodegradability.

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