LIGHT STABILITY AND THE EFFECT OF TEMPERATURE ON
MECHANICAL PROPERTIES OF
POLYPROPYLENE / POLY(ETHYLENE-VINYL-ACETATE) BLENDS

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LIGHT STABILITY AND THE EFFECT OF TEMPERATURE ON MECHANICAL PROPERTIES OF POLYPROPYLENE [PP] / POLY(ETHYLENE-VINYL-ACETATE) [EVA] BLENDS

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ABSTRACT

LIGHT STABILITY AND THE EFFECT OF TEMPERATURE ON MECHANICAL PROPERTIES OF POLYPROPYLENE / POLY(ETHYLENE-VINYL-ACETATE) BLENDS

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The variation in properties of Polypropylene (PP) / Ethylene Vinyl Acetate (EVA) blends upon EVA content, temperature, and light stability were followed by using tensile testing, impact testing, and differential scanning calorimetry (DSC).

Young's modulus of the blends decreased with increasing drawing temperature and EVA content. The stress at break values of the blends slightly increased with EVA whereas decreased with drawing temperature. The percent strain at break values of the blends were found to increase abruptly by increasing EVA content and drawing temperature. These changes in the mechanical properties are the indication of compatibility.

The impact tests were performed only at 0°C, 25°C and the impact strength increased with the temperature and EVA content, but none of the samples were broken at higher testing temperatures.

The effect of stabilizer was very obvious because stabilizer-free samples failed after 400 hours whereas, the samples with stabilizer resisted up to 750 hours.

Elongation values of the samples decreased because of increasing brittleness by UV irradiation. We also observed chain stiffening effect by crosslinking in all samples upon UV irradiation.

Thermal analysis of the blends of the drawn samples showed an increasing trend of crsytallinity with increasing drawing temperature. Increasing drawing temperature made polymer chains more flexible because of the increasing chain mobility. These flexible chains were then oriented in one direction during tensile testing and therefore uniaxial crystallization occurred.

The morphology of impact and tensile tests samples were also analyzed by scanning electron microscope (SEM). The fibrillation of pure PP is higher than the fibrillation of the blends.

ÖZ

POLİPROPİLEN / POLİ(ETİLEN-VİNİL-ASETAT) KARIŞIMLARININ IŞIĞA KARŞI DAYANIMI VE SICAKLIĞIN MEKANİK ÖZELLİKLER ÜZERİNE ETKİSİ

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Polipropilen (PP) / Etilen Vinil Asetat (EVA) karışımlarının; EVA miktarı, sıcaklık ve ışık dayanımına göre değişen özellikleri; çekme testi, çarpma direnci testi ve diferansiyel taramalı kalorimetri (DSC) ile incelenmiştir.

Karışımların elastik modulusları artan çekme sıcaklığı ve artan EVA miktarına bağlı olarak düşmüştür. Karışımların kopma noktasındaki gerilim değerleri EVA miktarına göre hafifçe artmıştır fakat artan çekme sıcaklığına bağlı olarak düşmüştür. Kopma noktasındaki yüzde uzama değerleri artan EVA ve çekme sıcaklığına bağlı olarak ani artış göstermiştir. Mekanik özelliklerdeki bu değişimler karışımların uyumunu göstermektedir.

Çarpma direnci testleri sadece 0°C ve 25°C'de yapılmıştır, çarpma direnci EVA miktarı ve sıcaklıkla artış göstermiştir, ayrıca yüksek sıcaklıklarda hiçbir örnek kırılmamıştır.

Karışımlardaki katkı maddesinin etkisi açıkça görülmektedir çünkü katkısız örnekler 400 saat dayanırken katkılı örnekler 750 saate kadar dayanmıştır.

Kopmada uzama artan kırılganlık nedeniyle hızla düşmektedir. Öte yandan tüm örneklerde capraz bağlanma nedeniyle oluşan zincir sertleşmesi gözlenmiştir.

Çekilen karışımların termal analizleri artan çekme sıcaklığına bağlı olarak artan kristallenme göstermiştir. Artan sıcaklık, zincirlerdeki hareketliliği arttırarak zincirlerin esnek bir yapıya kavuşmasını sağlamıştır. Bu esnek zincirler çekme testinde tek dogrultuda yönlenince tekyönlü kristallenme oluşmuştur.

Çarpma direnci ve çekme testlerinin morfoloji analizleri taramalı elektron mikroskop (SEM) ile yapılmıştır. Saf polipropilenin fibrilleşmesinin karışımlarınkinden daha fazla olduğu görülmüştür.

Anahtar Kelimeler: Polipropilen, Etilen Vinil Asetat, Karışımlar, Işık Dayanımı, Mekanik Özelliklere sıcaklığın etkisi.

To My Family

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TABLES AND EQUATIONS

ABBREVATIONS

PP   : Polypropylene

EVA   : Poly(Ethylene-Vinyl-Acetate)

VA   : Vinyl Acetate

DSC   : Differential Scanning Calorimetry

SEM   : Scanning Electron Misroscope

UV   : Ultraviolet Light

IPP   : Isotactic Polypropylene

Mw   : Molecular Weight

Tg   : Glass Transition Temperature

CHAPTER 1

INTRODUCTION

The chemical name and formula of Polypropylene (PP) is poly (1-methylene) and $(C_3H_6)_n$, respectively. PP is known as a linear hydrocarbon polymer also it can be defined as a polyolefin or a saturated polymer. PP can be used as a plastic and as a fiber [1].

The properties of the polymer blends are closely related to their phase morphology, composition ratio, viscosity, interfacial tension. And many other factors have effects to obtain polymeric materials with the desired properties [2].

The blending or mixing of polymers is an inexpensive way to modify the polymer properties. In the recent years, the use of PP is extensively enlarged by improving its properties by blending with suitable polymers. Among these polymers, ethylene vinyl acetate (EVA) occupies an important place. Because EVA has the acetate groups as active sites, by this property it is possible to develop fibers with good mechanical properties also for improving adhesive properties to PP fibers [3].

1.1 Importance of Blends

Physical mixing with another polymer can extensively modify the properties of polymers. The properties of the resulting polymer blend depend on the physical state of each component at the temperature of application, composition and processing conditions of the blend [4].

The resulting molecular weight (M_w) is slightly smaller than the theoretical M_w of simple blends. This indicates that the mixing process used for the preparation of blends affects the M_w [5]. This is especially very important in processing sensitive polymers that degrades by chain scission. PP and EVA are these kinds but it depends on processing temperature, shear rate, and molecular weight.

1.1.1 Miscibility & Compatibility

Miscible blends are homogeneous to the polymer segmental level, and most physical properties will be at least as good as the composition weighted average of the pure components. In many ways, miscible blends are the physical equivalent of random copolymers. When the intramolecular interaction is strongly repulsive, some copolymer compositions may prove to be miscible for systems where all homopolymer pairs are immiscible. Strong intermolecular attraction can also lead to miscibility. Even though two polymers may be miscible at low temperatures, they often have phase seperation on heating because of a lower critical solution temperature [6].

The term compatibility is used to describe materials with enhanced mechanical properties after mixing the components. The term miscibility is used to describe mixtures of polymers that are expected to from a single phase system. In this case, miscibility implies homogeneity within the mixture at a scale similar in dimensions to the size of the segmental movement responsible for glass transition temperature (T_g). Compatibility in mixtures of polymers can also be discussed in terms of glass transition [7].

The most important factors, determining the physical properties of polymer blends are the degree of compatibility between the respective components and their morphology. Even in the case of completely incompatible polymers, such

as PP and EVA, an interface layer can be created that affects the mechanical properties of the blends [8].

1.1.2 Morphology

The design of new polymer blends of required properties is related to the control of the morphology [9].

The particles of dispersed phase are usually distributed randomly in a polymer matrix. This morphology is very typical in the binary polymer blends. The morphological parameters include particle size, particle size distribution, particle volume fraction, configuration of particles in matrix and matrix ligament thickness. The influences of these parameters on the impact toughness of polymer blends also coexist [10].

1.1.3 Mechanical Properties

The mechanical properties of blends can be determined by the properties of the crystalline phases, overall crystallinity, crystalline morphology, the sizes of crystallites, and their aggregates such as spherulites. The mean size of spherulites in the blends is a very important factor influencing their mechanical properties like the yield stress and ultimate strength of the material [4].

Toughness is one of the most important properties of polymeric materials. The impact toughness of polymer blends can be influenced by many factors, such as morphology, interfacial adhesion, physical and mechanical properties of each component, also with frequency and temperature of deformation. These factors are usually interrelated [10].

1.2 Polypropylene

PP is one of the most widely used polymers all over the world. The useage variations of PP help us to use it for many application areas. Now we are focusing on PP in some detail.

1.2.1 Physical Properties

PP has various physical properties such as resistance to fatigue, light weight, resistant to staining, toughness, heat resistance, semi-rigidity, high tensile strength, impact resistance, easy fabrication, stiffness, flexibility, and high compressive strength [11].

1.2.2 Chemical Properties

PP has excellent resistance to acids, bases, alcohols, organic solvents and electrolytic attack; also, PP has excellent dielectric properties, low moisture absorption, non-toxic, high heat resistance. However, poor resistance to aromatic, aliphatic and chlorinated solvents [12].

1.2.3 Synthesis of Polypropylene

Polymerization of PP is achieved at low temperature and pressure [11], generally by two ways, Ziegler-Natta and Kaminsky catalysts.

Ziegler-Natta catalyst is able to control the incoming monomers to add them to the polymer chain for the desired orientation. Generally, PP is synthesized by titanium chloride catalysts, which produce mostly isotactic polypropylene (IPP) [13].

On the otherhand, Kaminsky catalyst is used to achieve a much greater level of control. Based on metallocene molecules, this catalyst uses organic groups to control the monomers being added, so that a proper choice of catalyst can produce isotactic, syndiotactic or atactic PP, or even a combination of these [13].

1.2.4 Crystallinity

In Figure 1.1, the regions that molecules are arranged in regular order are called crystalline regions. In between these ordered regions there are unarranged parts called amorphous regions.
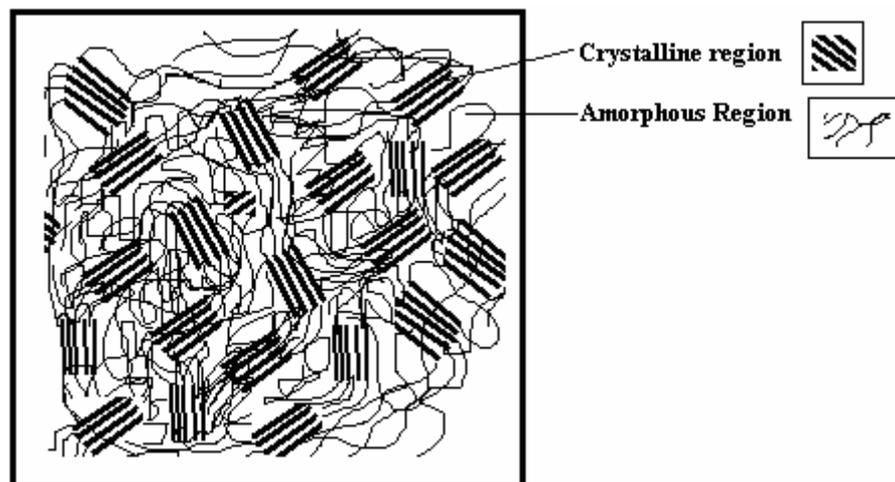
Figure1.1 Crystalline and amorphous regions in a polymer chain [14]

The tacticity of polymers influences their ability to crystallize. Stereoregular polymers are often highly crystalline [15]. Tacticities of %100 are ideal, but not

reached in practice. Crystallization of either isotactic or syndiotactic chains can result in high tacticity, which implies the presence of long, uninterrupted, stereospecific sequences along the chain. As the tacticity along the polymer chain is reduced the crystallinity decreases [16].

The density of PP differs according to the crystallinity of the structure [13]. The basic units of semicrystalline polymer morphology consist of chain-folded lamellae radiating outward from a nucleation site to form a spherulite [7]. The methyl groups tend to coil into a helical shape, these helices then line up next to one another to form the crystals that give PP its strength [13].

Isotactic chains result from the head-to-tail addition of propylene monomer units. Syndiotactic chains result from the same head-to-tail addition of monomer units with the same direction. Atactic chains do not have any certain placement of the methyl groups [16].

IPP crystallizes in three different crystalline forms, α (monoclinic), β (hexagonal) and γ (triclinic). These can be obtained as a function of crystallization temperature [7].

1.2.4.1 α-form

The α-form is the most stable form and can be easily obtained by crystallization from the melt or solution [17]. α structure is the typical arrangement in crystals of all isotactic polymers with sufficiently large side groups [18]. The melting point of α-form of IPP is strongly dependent on tacticity and thermal history [16]. The typical melting point of α-form is 159°C.

1.2.4.2 β-form

β-form is occasionally found in commercial IPP, usually at low levels [17]. The crystals formed with rich or pure in β-form are prepared through rapid quenching or by certain nucleating agent [19], the presence of the β crystalline spherulites is generally a second order effect in terms of the morphology properties [16]. β-form melts at the temperature of 170°C.

1.2.4.3 γ-form

γ-form can be observed in low molecular weight IPP [20] and takes place in high pressure crystallized IPP [18].

1.2.5 Crosslinking

PP contains three kinds of H atoms with various bond dissociation energies, but every monomeric unit of PP contains a tertiary H atom having the lowest C-H bond energy. In most of the degradation reactions of PP, these tertiary H atoms are the reaction sites [15]. For crosslinking, the reaction site is the one that is not on the polymer backbone.

Suitable crosslinking is favorable for improving the properties of polymeric materials, whereas excessive crosslinking makes them brittle and make lose the value of their industrial application [21].

1.2.6 Processing of Polypropylene

PP can be processed by all thermoplastic processing methods [11]. Important processing parameters are melt-processing conditions, orientation, thermal history, addition of nucleators and additives [16].

Molten polymer is injected into a cold mold cavity with geometry of desired shape. The final morphology of the molded part is a direct result of flow process during mold filling and solidification [16].

Flow conditions affect the morphology. To stabilize the morphology, copolymers are frequently added [9]. Additional factors such as packing, dependence of pressure, crystallization temperature, and cooling rate are also important [16].

1.3 Ethylene Vinyl Acetate

EVA is regarded as a copolymer of ethylene and vinyl acetate (VA) where the weight percentage of ethylene in the polymer molecule exceeds that of the VA [22]. Solvent resistance of EVA decreases with increasing VA content [23].

EVA should be kept under 80ºC otherwise, it will begin to degrade. Its low crystallinity gives it a low melting point and excellent low temperature toughness [24].

The VA content and the molecular weight range influence adhesive properties. The higher the ethylene content, the better the specific adhesion to non-polar substrates, such as polyolefins. On the otherhand samples higher in VA, show improved adhesion to polar substrates [22].

Higher VA content yields higher permeability to oxygen, nitrogen, carbon dioxide, and moisture vapor. EVA copolymers are all flexible with a high flex life and good film clarity [24].

EVA can be processed like other thermoplastics, and has good gloss, barrier properties, stress-crack resistance, resistance to UV radiation and ozone. Also

EVA has no odor and is competitive with rubber and vinyl products in many electrical applications [25].

1.4 Polypropylene / Poly (ethylene-vinyl-acetate) Blends

The use of PP is limited in some industrially important fields because of the lack of chemical functionalities, sensitivity to photo or thermal oxidation, low surface energy, extremely poor hygroscopicity, low sticking temperature and inadequate compatibility with other synthetic polymers [7].

The improvement of PP can be achieved with chemical modification by functional groups into macromolecules by copolymerization of propylene with polar monomers [7].

PP presents brittleness, low mechanical performance, and low impact resistance at temperatures below or around its T_g. This is the reason to make PP blends with elastomeric compounds [26].

Interactions between EVA and PP are important in modifying the original copolymer structure. In PP/EVA blends, EVA is basically introduced as an impact modifier for PP and it is dispersed as fine particles. Upon cooling, the molten EVA copolymer flows towards the free volume generated during the PP crystallization, leading to a phase interlocking between the two polymers. Compatibility in PP/EVA blends is due not only to local interfacial interactions but also to changes in the phase morphology [5].

1.5 Aim of the Study

In this study the light stability and the effect of temperature on mechanical properties of PP/EVA blends were investigated. In order to detect this; several

percentages of PP/EVA blends were prepared and studied. The change of the mechanical and thermal properties of the blends were studied at several temperatures.

CHAPTER 2

EXPERIMENTAL

2.1. Materials

Polypropylene used in this study is an isotactic homopolymer, MH 418 PP supplied by Turkish Petrochemical Industry (Petkim). It has a melt flow rate of (2.16 kg, 230°C) 4-6 g/10min according to ASTM D-1238. The density of PP is 0.905 g/cm^3. Melting point is 160ºC.

Poly (ethylene-vinyl-acetate) is a random copolymer, PA 461 supplied by Alcudia$^®$ having a melt flow rate of (2.16 kg, 190ºC) 45 g/10min. The VA content of EVA is 33% (w/w). The density of EVA at room temperature (23ºC) is 0.956 g/cm^3 and has a melting point of 60ºC.

Chimassorb 944 LD (a hindered amine light stabilizer) was used to protect the blends against UV irradiation. The molecular formula and melting point of Chimassorb 944 LD are $(C_{35}H_{68}N_8)_n$ and 140ºC, respectively. In order to detect the effect of Chimassorb, two different weight percantages (0.75% and 0.5%) were added to the blends by dissolving it in acetone and treating the blends by this solution, i.e by solvent absorption method.

The Chemical structures of PP, EVA, Chimassorb are given as chemical equation numbers 1, 2, 3. For Chimassorb n changes from 8 to 10.
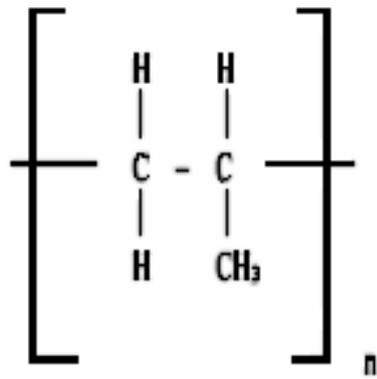
C.E # 2.1 Chemical structure of PP
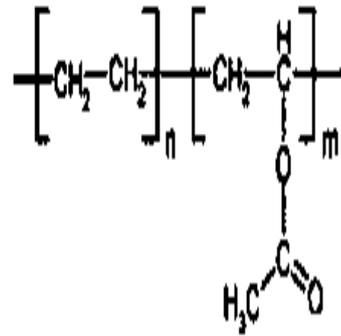
C.E # 2.2 Chemical structure of EVA

C.E # 2.3 Chemical structure of Chimassorb 944 LD
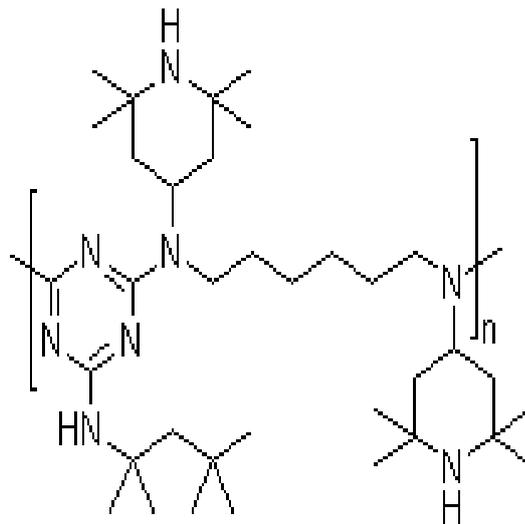
12

2.2 Preparation of Blends

2.2.1 Blending Extrusion

PP/EVA blends were prepared with a Thermoprism Twin Screw Extuder L/D=24 (TSE) with the weight percentages of 0, 3, 5, 10, 15, 20 of EVA. The processing temperature of twin screw extruder was ranged from 165°C (entrance), 180, 200, 200, to 210°C (die) temperature. The rotor speed was 150 rpm. About 2 min of mixing time was required for complete dispersion of the blend and then the molten blend dropped quickly into cold water to quench.

2.2.2 Film Extrusion

Thin films were prepared by Plasti-Corder® Brabender GNF 106/2 single screw extruder, the processing temperature of single screw extruder was ranged from 160°C (entrance), 200, 190, to 210°C (die) temperature. The rotor speed was 90 rpm. The average thickness was 200 micron. These films were then cutted into dogbone samples and UV irradiated.

2.2.3 Injection Molding

The blends were injection molded in dogbone shapes for the tensile tests. Bar shape samples were also injection molded for the impact tests with Arburg Allrounder 220-90-350 type. The barrel temperature was ranged from 180°C (entrance), 230, 250, to 270°C (die) temperature.

2.3 UV Irradiation

The samples were exposed to UV irradiation at room temperature and the changes in mechanical properties caused by UV irradiation were followed for

exposure times up to 750 hours. The UV lamp was a mercury high pressure lamp with a 36 $\mu W/cm^2$x100x10 power at a distance of 25 cm.

2.4 Mechanical Testing

2.4.1 Tensile Testing

The tensile testing was carried out in Instron TM1102 type. All tensile tests were carried out with the draw rate of 5 cm/min. The drawing temperature was ranged from 0°C, 20, 40, 60, to 80°C, to follow the temperature effect on the mechanical behavior of the blends.

2.4.2 Impact Testing

Bar shaped samples prepared in injection molding machine were used for the impact tests. The dimensions of the bar shaped samples were 6cm x 0,2cm x 0,7cm. Unnotched charpy tests were carried out with Pendulum Impact Tester of Coesfeld.

2.5 Morphological Analysis

Tensile and impact fractured samples were investigated by JEOL, JSM 6400 Scanning Electron Microscopy (SEM). The morphologies and fiber properties of the blends were compared according to the drawing temperatures at tensile tests, also with EVA percantages and the temperatures that impact tests were carried out. SEM images of drawn samples were taken from the break points of the blends and by peeling off the surface of the blends in draw direction.

In order to see the fractured surfaces clearly under SEM, chloroform was used in a water bath system to remove EVA from the blends.

2.6 Thermal Analysis

Calorimetric investigations were carried out with TA Instruments Differential Scanning Calorimetry (DSC) 910S. DSC was calibrated according to the melting peak of indium. DSC samples of 2-3 mg were set into aluminum DSC pans. Samples were heated from -20ºC to 300ºC under nitrogen atmosphere with a heating rate of 20 ºC/min. The accuracy of the transition temperature was estimated to be ± 2°C.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Tensile Properties of PP/EVA Blends

The tensile properties of PP/EVA blends were studied with respect to the EVA content (by weight) and drawing temperature.

3.1.1 The Effect of EVA on Tensile Properties

Although PP and EVA are immiscible polymers, it has been proposed that partial miscibility between these two polymers occurs in the molten state. In injection molding process, EVA flows into the free volume of PP matrix. During solidification, adhesion occurs between PP and EVA by affecting the mechanical properties [15].

High stiffness and brittleness are the characteristic physical properties of PP. PP was blended with EVA to increase the flexibility and to decrease the rigidity of the material in order to enhance the end use properties. The effect of EVA on tensile properties was investigated with three parameters. These are Young's modulus, stress at break and percent strain at break.

Young's modulus is a measure of the stiffness of a given material and is the ratio of the tensile stress by the tensile strain. It can be determined from the slope of a stress-strain curve.

The effect of EVA on Young's modulus of the blends is given in Figure 3.1. This figure represents the change in Young's modulus of PP/EVA blends drawn at room temperature. The brittleness of the material decreased by increasing EVA content and as a result the Young's modulus decreased.
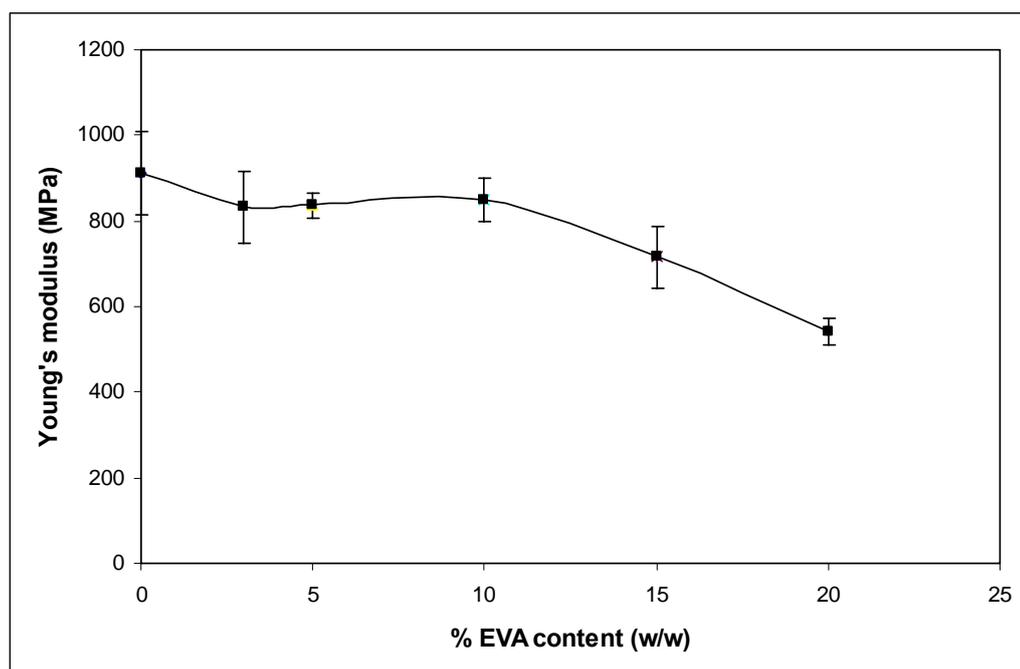

Figure 3.1 The variation of Young's modulus in PP/EVA blends with respect to EVA content

The stress at break of a material is the measure of the tensile strength just at the failure. The tensile testing results that were drawn at room temperature are given in Figure 3.2. It can be seen from the figure that the stress at break of the blends slightly increased with EVA content, but this increase is not very effective, it seems almost constant within the experimental error limits. Therefore, we can

say that EVA even up to 20% by weight did not greatly affect stress at break value of PP very much.
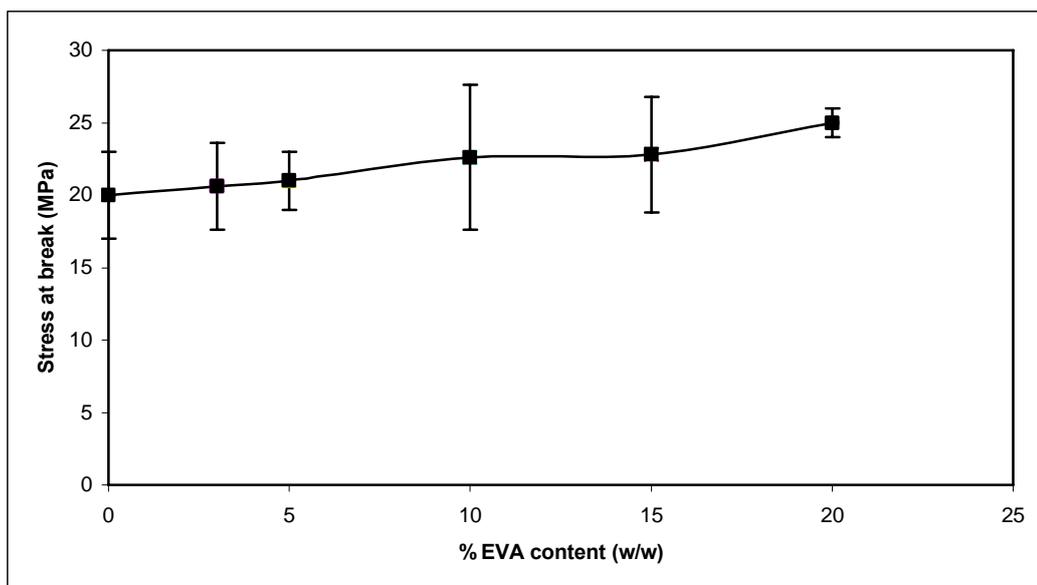

Figure 3.2 The variation of stress at break in PP/EVA blends with respect to EVA content

The percent strain at break is the measure of elongation of the material during tensile test. In Figure 3.3 the elongation at break values of the blends are given. Since the material becomes flexible because of soft EVA, the elongation values increased with EVA. In the same way Ramirez-Vargas et al. [27] reported that the elongation shows a remarkable increase with increasing EVA of the blends because of the changes in morphology.
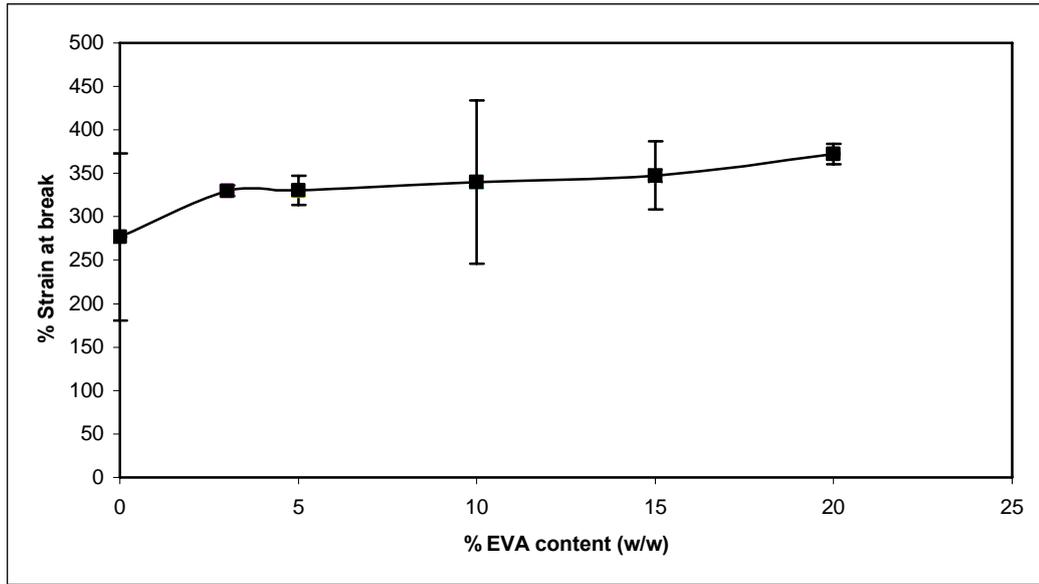
Figure 3.3 The variation of percent strain in PP/EVA blends with respect to EVA content

According to the study of Ramirez-Vargas et al. [28], results indicated a transition toward compatibility between both components and highly affected the morphological and mechanical properties by increasing EVA content.

The summary of Young's modulus, stress at break, and percent strain at break values of the blends are given with their standard deviations in Table 3.1.

Table 3.1 Tensile Testing Results of the Blends

%EVA	Young's modulus (MPa)	Stress at break (MPa)	Percent strain at break
0	911 ± 98	20.0 ± 3.4	277 ± 96
3	832 ± 85	20.6 ± 3.0	330 ± 7
5	836 ± 30	22.6 ± 2.9	331 ± 18
10	849 ± 50	22.6 ± 5.2	340 ± 95
15	715 ± 73	22.8 ± 4.9	347 ± 40
20	541 ± 32	25.0 ± 1.4	372 ± 13

3.1.2 The Effect of Temperature on Tensile Properties

Mobility of the polymer chains are affected in cooperation with the increasing temperature. Therefore the tensile testing results (Young's modulus, tensile strength, and percent strain at break) were highly affected by the change in temperature.

The effect of drawing temperature on Young's modulus with respect to the addition of EVA were presented for 0°C and 20°C in Figure 3.4, and for 40°C, 60°C, 80°C in Figure 3.5.

As expected, the Young's modulus of the blends decreased with increasing drawing temperature. Temperature affected the materials by decreasing the hardness. It is obvious that Young's modulus decreased dramatically at 40°C and afterwards Young's modulus values were found to be low. Note that EVA copolymer has a low melting point (60°C) than PP homopolymer (160°C), therefore this component starts to flow at higher temperatures producing free volume for PP to orient.
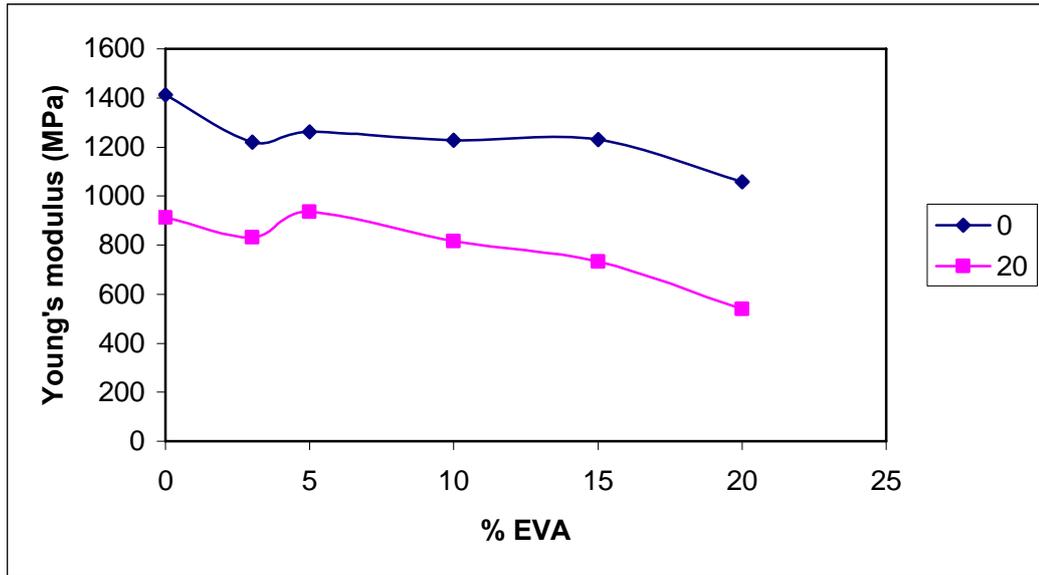
Figure 3.4 Effect of drawing temperature (0°C and 20°C) on Young's modulus of the blends and pure PP
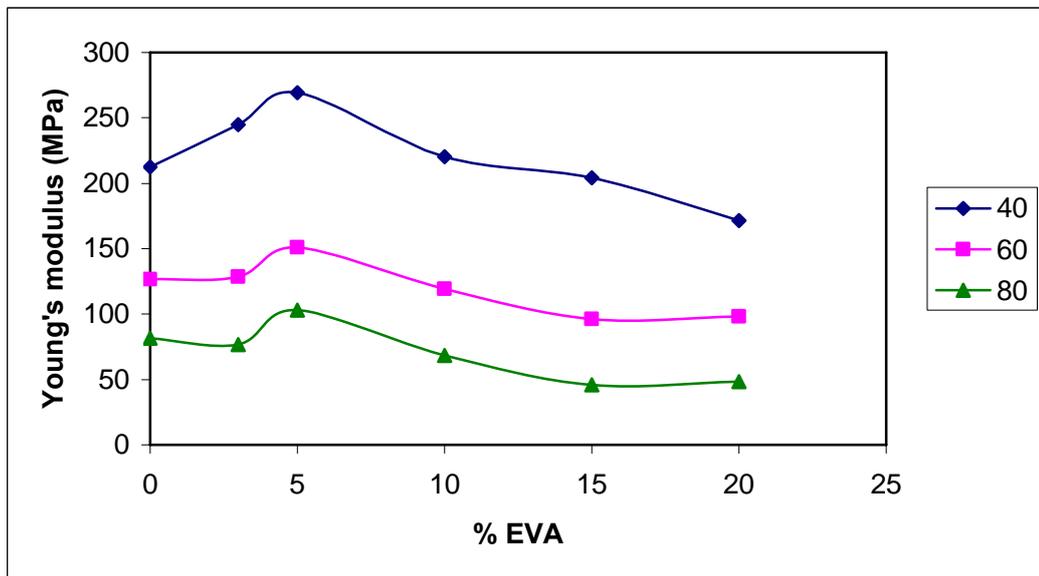

Figure 3.5 Effect of drawing temperature (40°C, 60°C and 80°C) on Young's modulus of the blends and pure PP

The effect of drawing temperature on stress at break with respect to the addition of EVA were presented for 0°C and 20°C in Figure 3.6 and for 40°C, 60°C, 80°C in Figure 3.7.

The stress at break values decreased with increasing temperature. In Figures 3.6 and 3.7, it can be seen that, the effect of temperature on the stress at break is more than that of the EVA content in the blends. A sudden decrease observed in the stress at break after 40°C of drawing temperature, and therefore in order to asses this dramatic change, Figure 3.7 presents the drawn values of 40°C, 60°C, 80°C.
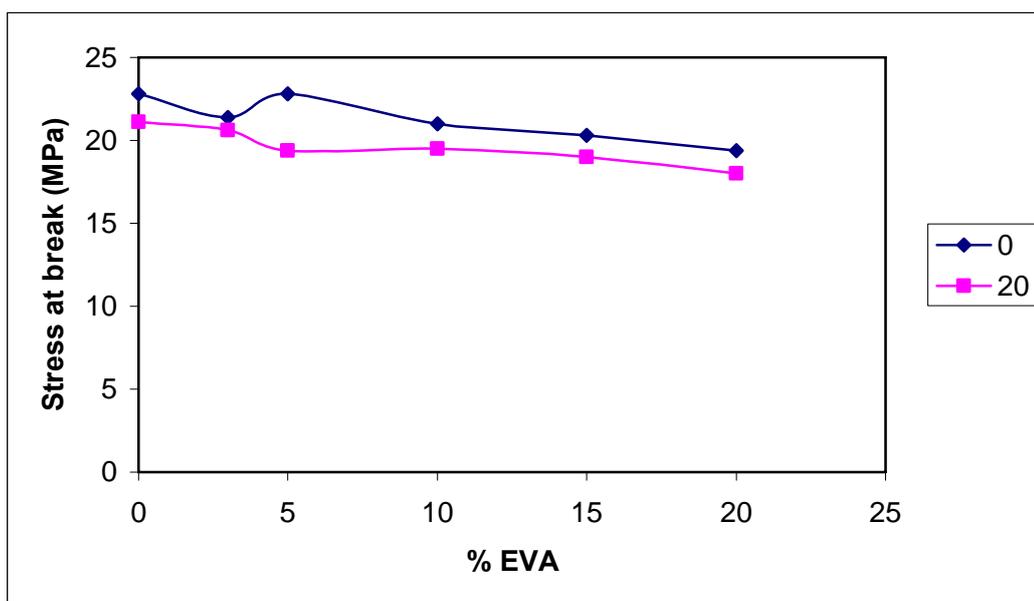

Figure 3.6 Effect of drawing temperature (0°C and 20°C) on stress at break values of the blends and pure PP
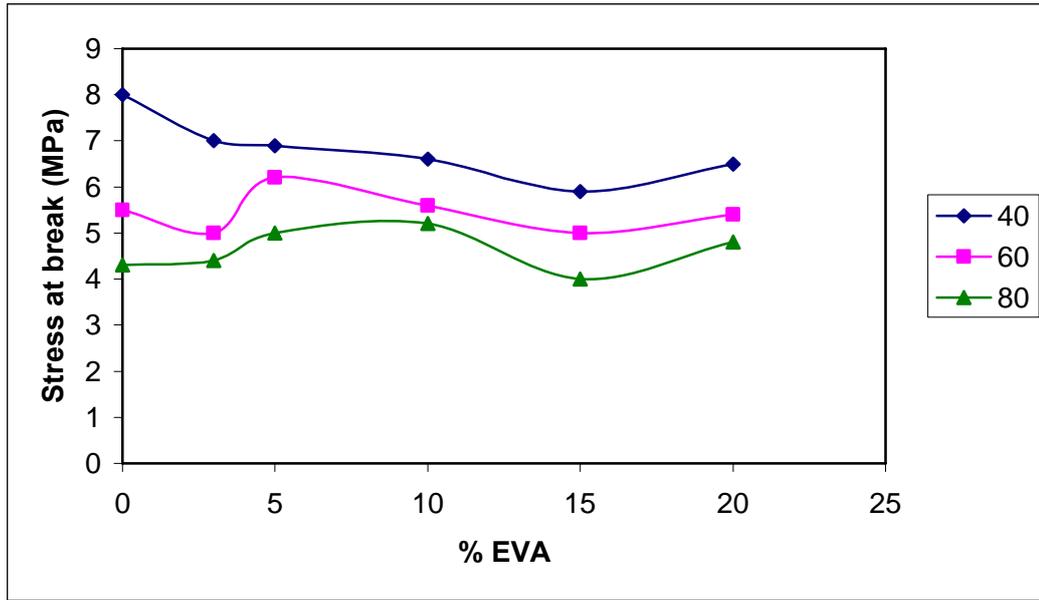
Figure 3.7 Effect of drawing temperature (40°C, 60°C and 80°C) on stress at break values of the blends and pure PP

The percent strain at break values of the blends were found to increase from 10% to 900% for 0°C to 80°C. This was reasoned by the flexible property of the blends, because the mobility of the polymer chains has increased according to the increasing temperature. The results presented here is parallel with Zhang et al. [29].
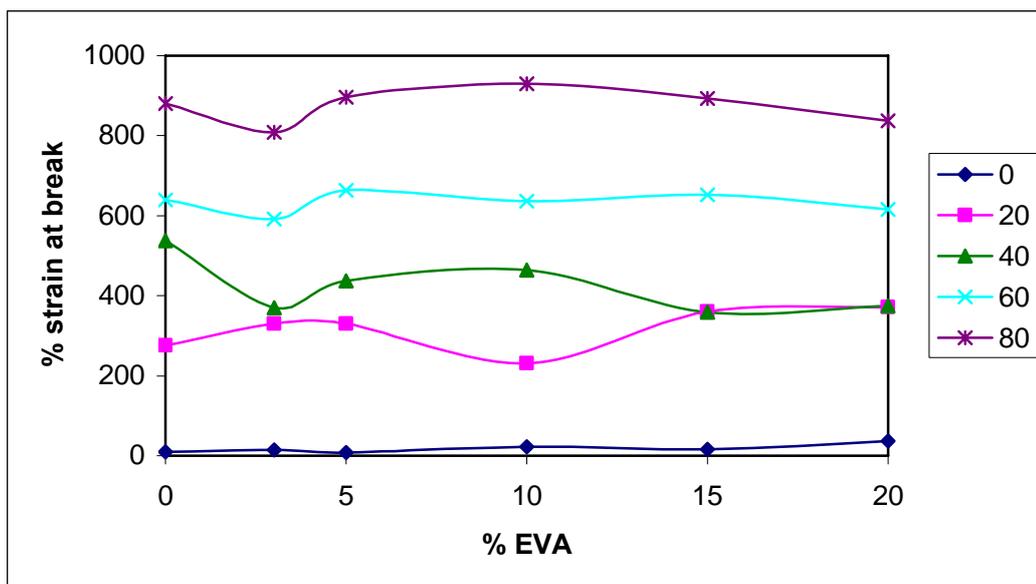
Figure 3.8 Effect of drawing temperature on percent strain at break values of the blends and pure PP

Increasing EVA content favors melting point depression, increase in strain at break, and high flexibility. These changes are due to the partial miscibility between PP and EVA. The results indicate compatibility of PP/EVA blends in the amorphous region [21]. This is also consistent with the study of Ramirez-Vargas et al. [30] that the compatibility in PP/EVA blends has been determined in the amorphous regions of the blends.

3.2 Impact Strength of PP/EVA Blends

Charpy impact test determines the amount of energy absorbed by a material during fracture. It is considered as an indication of toughness of the material.

3.2.1 The Effect of EVA and Importance on Impact Properties

EVA copolymer has been introduced as an impact modifier for PP for a long time [5]. As EVA content of the blends was increased, the impact strength increased. This was due to the decreasing brittleness of the blends and increasing ability of absorbing impact energy.

3.2.2 The Effect of Temperature on Impact Properties

Temperature has an important effect on the impact strength of the blends. In Figure 3.9, the impact values of the blends increased when the temperature was at 25ºC because the material lost its brittleness and gained flexibility. On the otherhand when the temperature was decreased to 0ºC the mobility of the polymer chains decreased and the material became more brittle with decreasing impact absorbing capacity.

In Figure 3.9, at both temperatures the impact absorbing capacity increased according to the increasing EVA content. The impact values of 15% and 20% EVA at 25°C, and 20% EVA at 0°C could not be recorded. At high temperatures, no impact strength was available because none of the samples were broken.
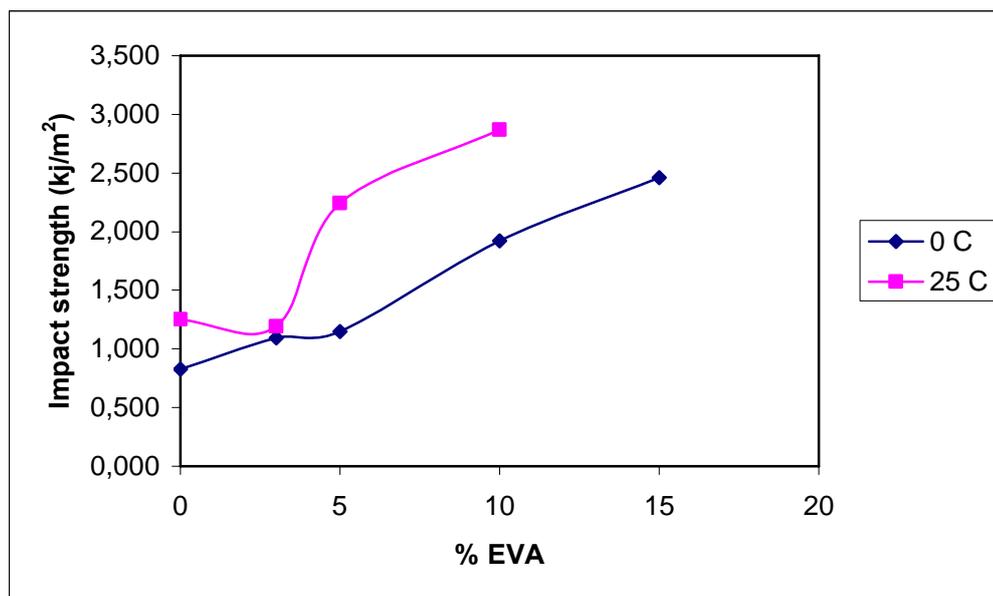
Figure 3.9 Effect of temperature and EVA on impact strength

The increase in the amount of EVA made the distribution within the matrix more easy and homogeneous therefore, strong adhesion between PP matrix and EVA increased the impact strength. This was due to the fact that EVA is an impact modifier in PP/EVA blends in the amorphous region [7].

It is obvious that blending PP with EVA produces greater improvement on the impact strength of PP by the flexible property of vinyl acetate [31].

Avila-Orta et al. [32], have reported the interfacial interactions in amorphous zones of the blends. At EVA concentrations up to 20%, the impact strength of the system has increased.

3.3 Thermal Properties of PP/EVA Blends

The thermal characterization of polymers was extensively done by DSC. In addition, the percent crystallinity of PP could be calculated from DSC thermograms by the formula;

Percent crystallinity = $(\Delta H_{blend} / \Delta H_{PP})$ x 100

ΔH_{blend} is the actual heat of fusion of the blends, ΔH_{PP} is the heat of crystallization of 100% crystalline PP accepted as 209 J/g [33]. Percent crystallinity is an indication of amount of crystalline region in polymer with respect to amorphous content. Furthermore, crystallinity influences the properties of polymers such as; hardness, Young's modulus, stress at break and melting point.

Table 3.2 presents the change in percent crystallinity of PP in the PP/EVA blends. All these samples were the undrawn blends. Since EVA is an amorphous copolymer (but very low crystallinity), the crystallinity of PP has decreased with increasing EVA content. The major changes have seen just after addition of 3% EVA and 20% EVA.

Table 3.2 Percent crystallinity of PP in PP/EVA blends

% EVA	% Crystallinity	J/g (from DSC software)
0	39.47	82.49
3	37.83	79.06
5	36.22	75.7
10	37.47	78.31
15	37.23	77.81
20	34.34	71.77

T_m values of PP from DSC thermograms according to EVA concentration can be seen in Figure 3.10. A decrease in T_m values can be explained by the partial miscibility [21]. And also Ramirez-Vergas et al. [36], reported the presence partial miscibility in amorphous regions of the blends.
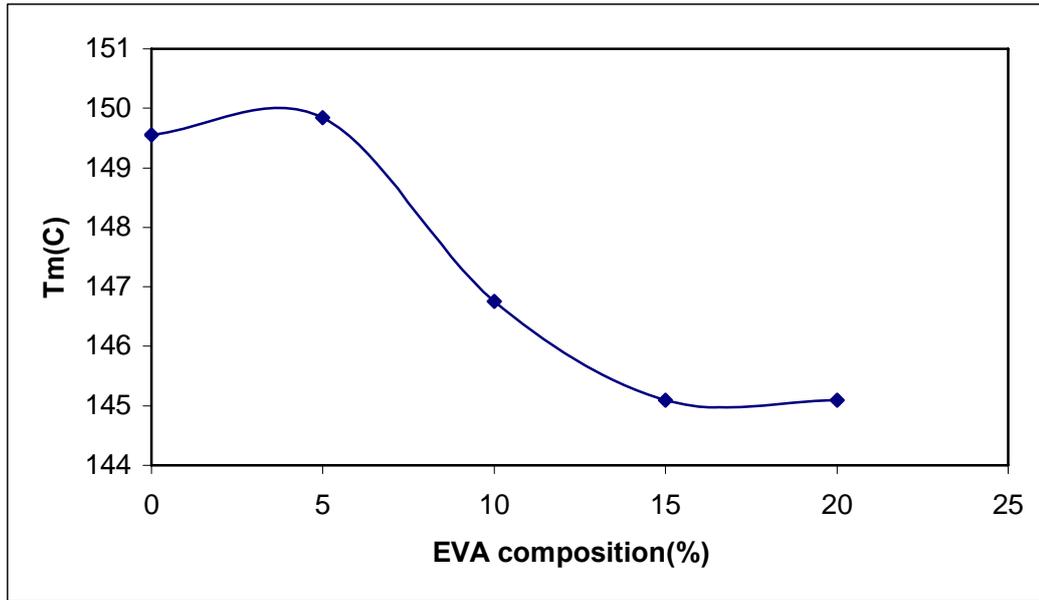
Figure 3.10 T_m values of PP from DSC Thermograms of undrawn samples

The orientation of polymers depends on drawing rate and drawing temperature. Crystallinity influences the mechanical properties of polymers. In Figure 3.11, the theoretical development of crystalline phases during tensile tests and uniaxial orientation was illustrated.
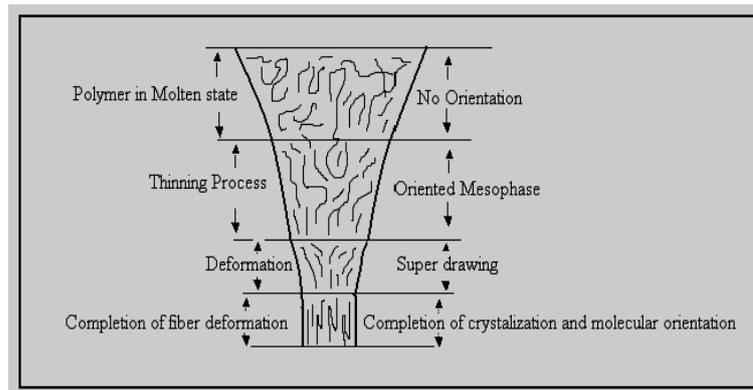
Figure 3.11 Development of crystallinity at high temperature tensile test [34,35]

Table 3.3 represents the variation of percent crystallinity of PP in the blends of drawn samples at different temperatures. According to this table there is an increasing trend of crsytallinity with increasing drawing temperature. This increase was not continued at 80°C drawing temperature. The results indicate increasing crystallinity with increasing drawing temperature. Increasing temperature made polymer chains, especially PP, more flexible because of the increasing chain mobility. These flexible chains were then oriented in one direction during tensile testing and therefore uniaxial crystallization occurred. This result is consistent with Moore [16]. And we observed some irregularities from the increasing trend. This can be due to measurement and sampling errors.

Table 3.3 Percent crystallinity of PP in the blends of drawn samples

Drawing Temperature→	0°C	20°C	40°C	60°C	80°C
Pure PP	34.35	39.32	42.16	48.85	28.34
3% EVA	37.42	39.08	51.05	42.23	46.28
5% EVA	38.89	39.60	49.90	46.81	46.20
10% EVA	37.90	32.78	41.09	63.01	38.70
15% EVA	32.89	37.80	31.51	47.76	39.59
20% EVA	30.17	31.05	37.00	32.48	36.59

Figure 3.12 shows the DSC analysis of pure PP done for the drawn samples starting from 0°C to 80°C. We did not observe any important changes in the T_m values of PP at different drawing temperature limits. This indicates that the melting point of PP was not affected by the temperature up to 80°C. The melting point of pure PP is 160°C and the results are consistent with the literature.
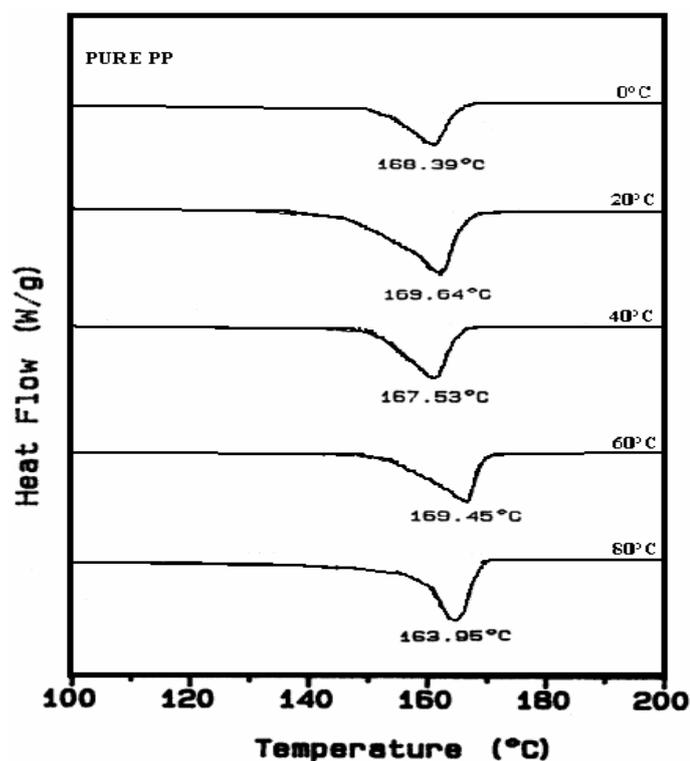
Figure 3.12 DSC Thermograms of drawn samples of pure PP at various
temperatures

However, DSC analysis of the blends of the drawn samples showed two distinct
endothermic peaks of PP at 60°C and 80°C.

The β-phase of PP is well known to be thermodynamically unstable and this
phase can melt and recrystallize into the more stable monoclinic α-phase. The
shoulder that occured in the DSC thermograms of 60°C and 80°C drawn
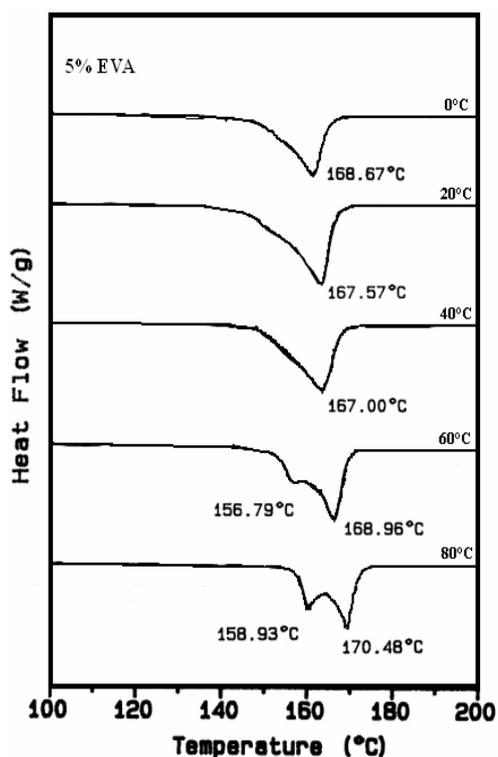samples is the indication of the transformation of β-phase to α-phase [37,38,39].

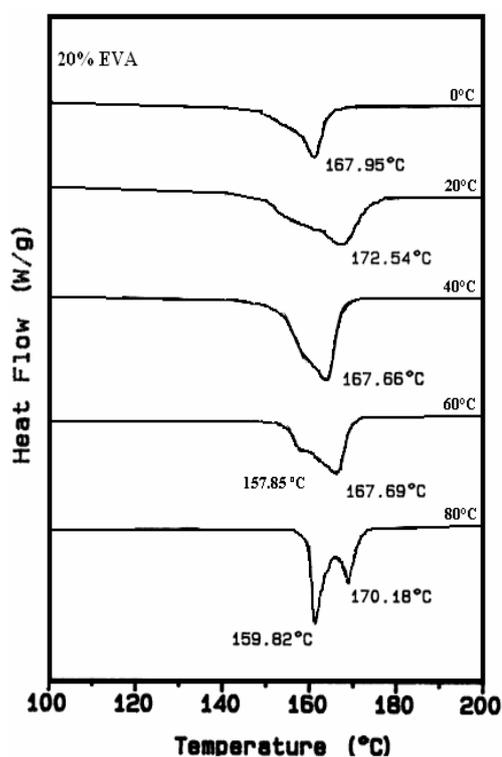**Figure 3.13** DSC Thermograms of 5% EVA drawn at various temperatures

Figure 3.14 DSC Thermograms of 20% EVA drawn at various temperatures

3.4 Morphological Properties of PP/EVA Blends

3.4.1 The Effect of EVA on Morphology

The effect of EVA on morphology was studied on the impact fractured surfaces of the blends. In Figure 3.15 SEM Photograph of the impact fracture surface of pure PP is given. The surface of pure PP is smooth relative to the fracture surfaces of the blends that are given in Figures 3.16, 3.17 and 3.18. In Figure 3.16 the surface of 20% EVA was given, the surface seems to be not dispersed

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as 3% or 15% EVA. It can be said that the impact resistance of 20% EVA blends are higher than pure PP and other blends that contain less EVA content. The presence of EVA has provided a fine distribution and appears to adhere well in the PP matrix [31].
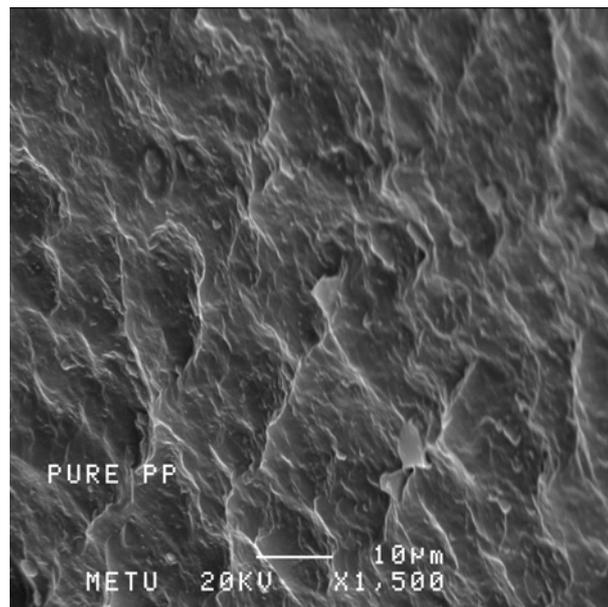

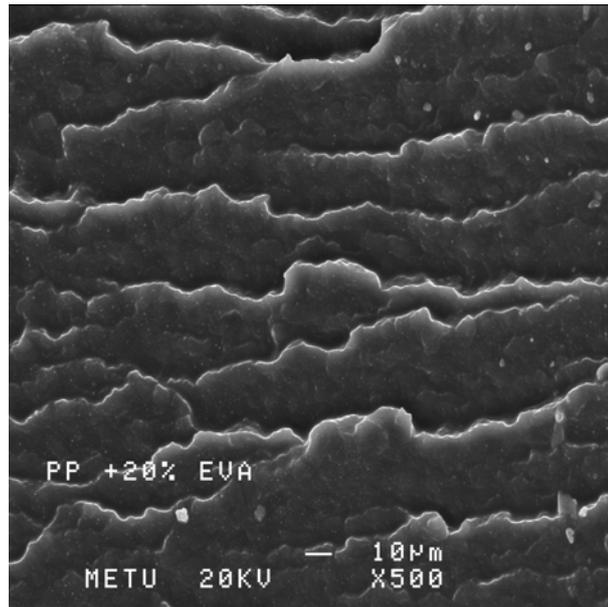**Figure 3.15** SEM Photograph of the impact fractured surface of pure PP

Figure 3.16 SEM Photograph of the impact fractured surface of 20% EVA
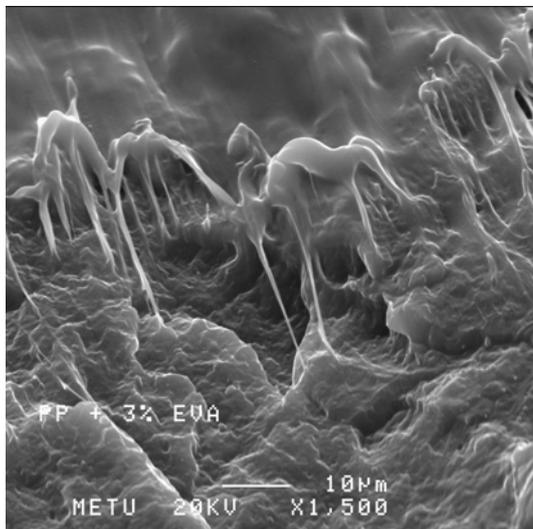

Figure 3.17 SEM Photograph of
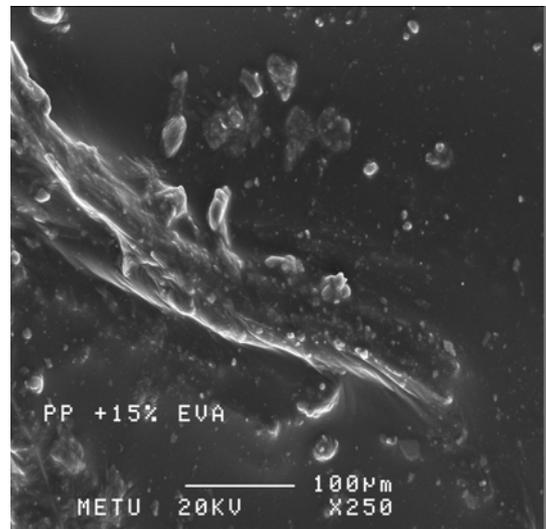the impact fractured surface of 3%
EVA

Figure 3.18 SEM Photograph of the
impact fractured surface of 15%
EVA

The impact fractured surfaces of the blends were treated with chloroform to remove EVA content from the matrix in order to see the fracture surfaces clearly under SEM. When EVA removed from the PP matrix the remaining surface was not smooth as expected. So we observed dispersed fracture surfaces by the removal of EVA.

In Figures 3.19, 3.20, 3.21 the fractured surfaces after removal of EVA content are given. In Figures 3.19 and 3.20 the increase in dispersity of the surfaces can easily be seen. However in Figure 3.21 the surface is not broken as expected, this has occured because high EVA content did not permit a full break up on the surface.
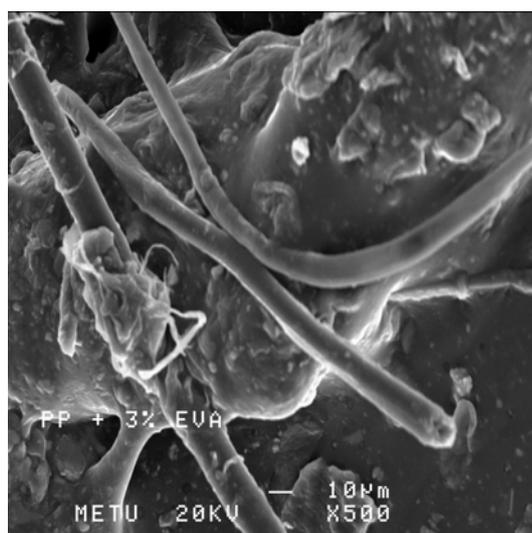

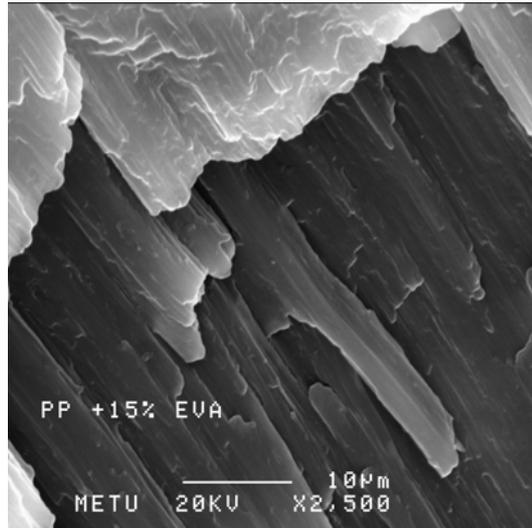**Figure 3.19** SEM Photograph of the impact fractured surface of 3% EVA treated with chloroform

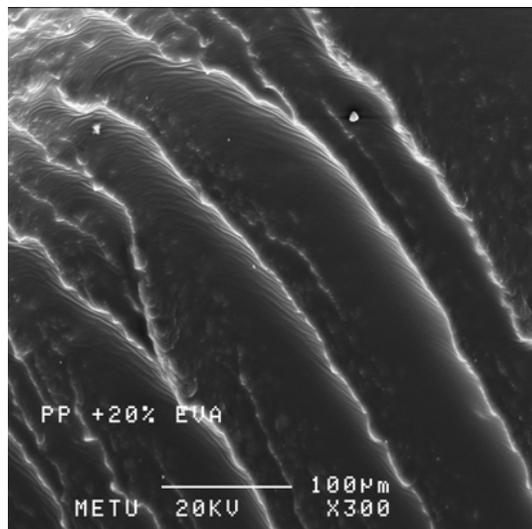**Figure 3.20** SEM Photograph of the impact fractured surface of 15% EVA treated with chloroform

Figure 3.21 SEM Photograph of the impact fractured surface 20% EVA treated with chloroform

3.4.2 The Effect of Drawing Temperature on Morphology

The effect of drawing temperature on morphology was studied on the tensile testing samples. Figures 3.22 and 3.24 are SEM Photographs of the samples that were drawn at 20°C. Figures 3.23 and 3.25 are SEM Photographs of the samples that were drawn at 80°C. The increase in the fibrillation can be seen easily.
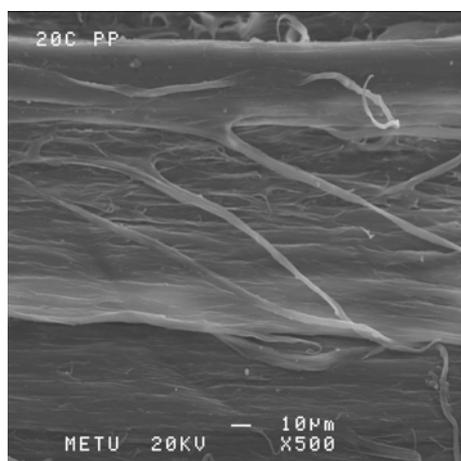

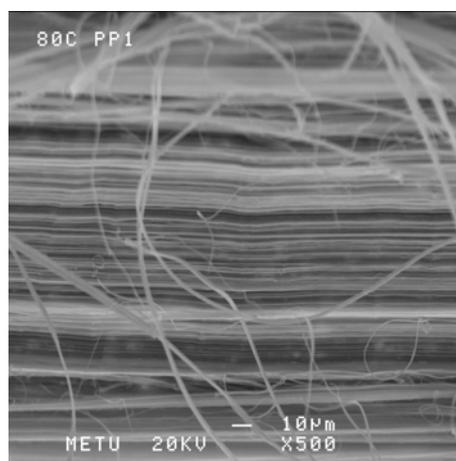**Figure 3.22** SEM Photograph of pure PP drawn at 20°C

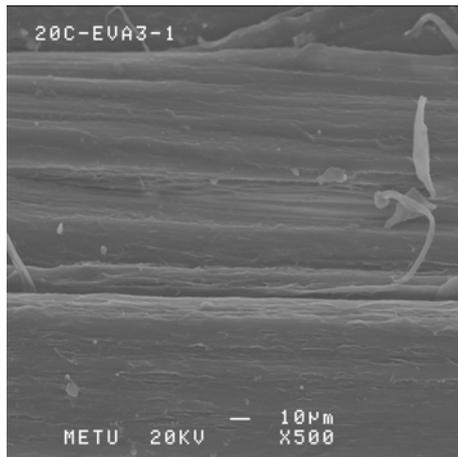**Figure 3.23** SEM Photograph of pure PP drawn at 80°C

Figure 3.24 SEM Photograph of 3% EVA drawn at 20°C

Figure 3.25 SEM Photograph of 3% EVA drawn at 80°C

Increasing temperature made the samples flexible by increasing the mobility of the chains. By this flexibility the elongation values increased. In Figures 3.23 and 3.25 we can see that the fibrillation of pure PP is higher than fibrillation of %20 EVA blend. This can be interpreted as the melting of EVA at high temperatures.

To analyze the morphology of the blends truely, the samples that were taken from orientation mesophose of the blends were also analyzed with SEM. Figures 3.26, 3.27 and 3.28 are SEM Photographs of these samples. All the samples were drawn at 80°C. Since EVA was highly affected from drawing temperature we could not observe a true fibrillation in the blends that contains 15% and 20% EVA. Temperature affected the fibrillation of the samples in reverse order.

Figure 3.26 SEM Photograph of
pure PP drawn at 80°C

Figure 3.27 SEM Photograph of
15% EVA drawn at 80°C
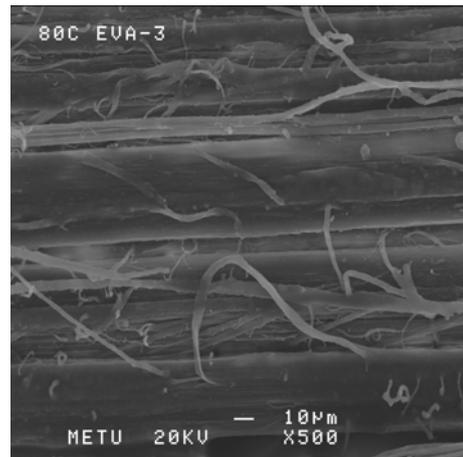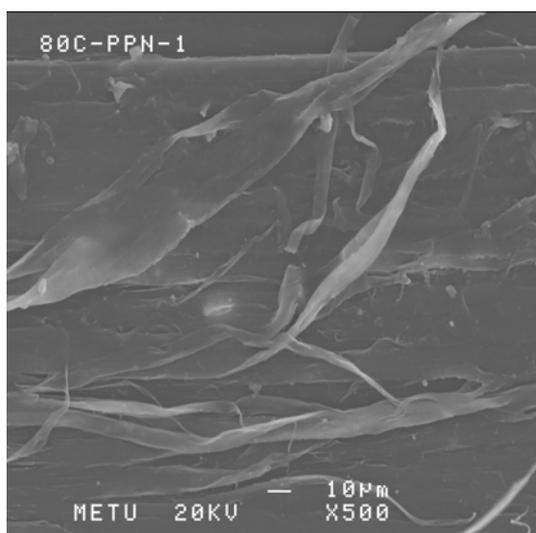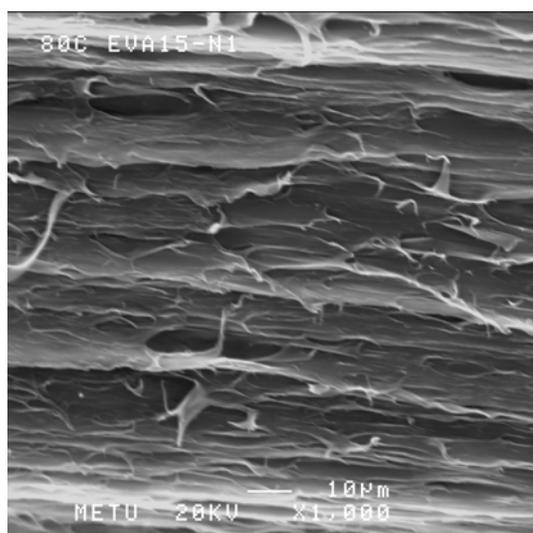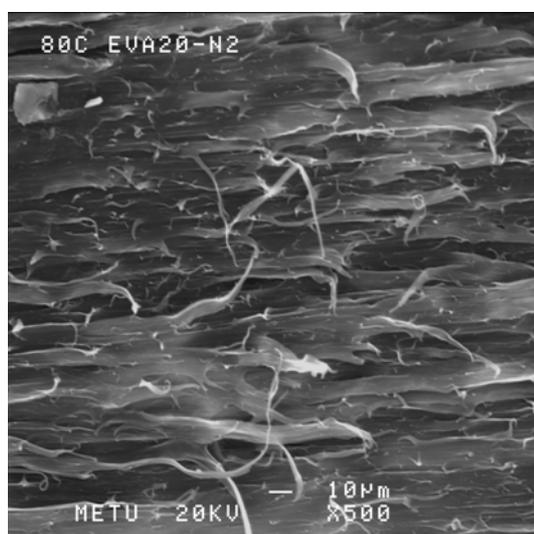

Figure 3.28 SEM Photograph of 20% EVA drawn at 80°C

3.5 Light Stability of PP/EVA Blends

PP is the most common commercial polymer of good mechanical and thermal properties however the polymer is degradable upon radiation processing. UV irradiation initiates the PP radicals that lead to undesired processes like chain scission, oxidative degradation or formation of oxygen containing polar groups. These reactions occur in the amorphous region because of the higher permeability to oxygen [40]. PP undergoes chain scission while EVA crosslinks at the initial stages of UV irradiation.

As mentioned in the introduction part, PP contains three kinds of hydrogen atoms with various bond dissociation energies, but every monomeric unit of PP contains a tertiary hydrogen atom having the lowest C-H bond energy of all. In most of the degradation reactions of PP, these tertiary hydrogen atoms will be the reaction sites [15].

Radiation influences the properties of polymeric materials. Suitable crosslinking is favorable to improve the properties and stiffening effects observed by UV irradiation, whereas excessive crosslinking makes polymeric materials brittle and cause losing the value of their industrial application [21].

The degradation of pure PP and PP/EVA blends with the addition of Chimassorb 944 LD were followed by the mechanical property changes with respect to UV irradiation time. The amount of stabilizer-1 (st-1) was 0.75% (by weight) and the amount of stabilizer-2 (st-2) was 0.5% (by weight). The effect of these weight percentages were compared with the stabilizer-free (st-free) samples.

Tensile tests for the light stability of PP/EVA blends were performed by the film extruded samples so the results differed by the tensile test values of injection molded samples.

In Figures 3.29, 3.30 and 3.31 the changes of Young's modulus of pure PP, 10% EVA blend and 20% EVA blend were given for stabilized and unstabilized samples. In these figures, The Young's modulus values of the samples have increased in the time interval of 0-200 hours.

In Figure 3.29 we see the stiffening effect of UV irradiation up to 200 hours on pure PP. The Young's modulus values of the samples of st-1 slightly exceeded the st-2 and st-free samples. In this Figure the effect of stabilizer is obvious because st-free samples no longer existed after 400 hours of irradiation. St-1 samples resisted up to 500 hours and st-2 samples have the maximum resistance to UV irradiation.

When we looked at Figure 3.30 we saw the same increase up to 200 hours and decrease after that point. But here the Young's modulus values were slightly higher than pure PP samples. The stabilized samples again resisted to irradiation more than unstabilized samples that resisted up to 400 hours. Since the crosslinking occurs in the amorphous region, as the EVA content increases the ability of finding reaction sites of the free radicals also increase.

In Figure 3.31, because of excessive brittleness the Young's modulus values of 20% EVA blends of st-1 samples no longer existed. The samples of st-2 resisted up to 750 hours and unstabilized samples resisted only 400 hours of irradiation.

From the Figures 3.29, 3.30 and 3.31, it can be seen that st-2 samples resisted to UV irradition longer than the other samples. And even stabilized samples failed after 750 hours of irradiation.
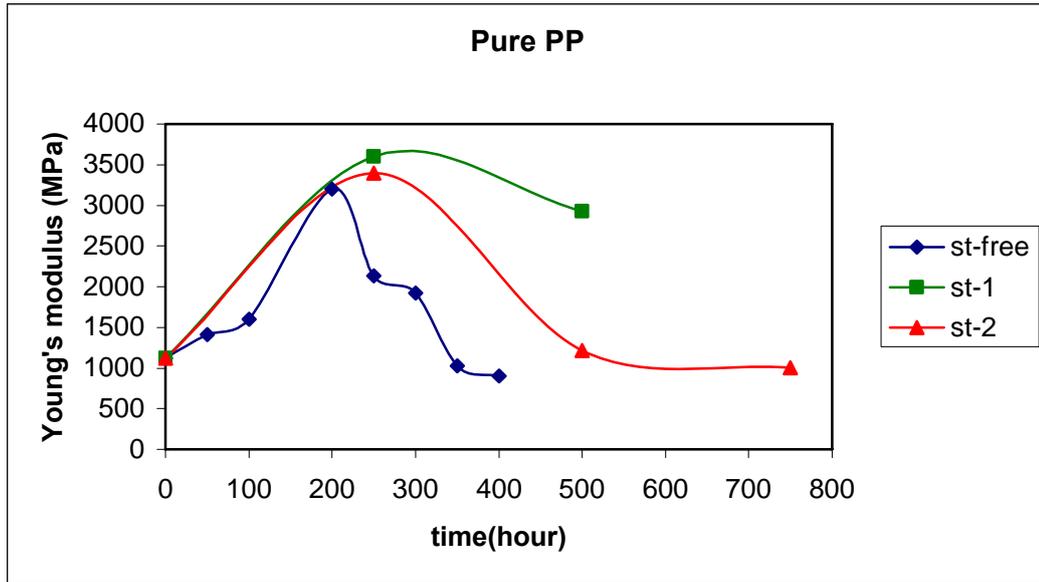
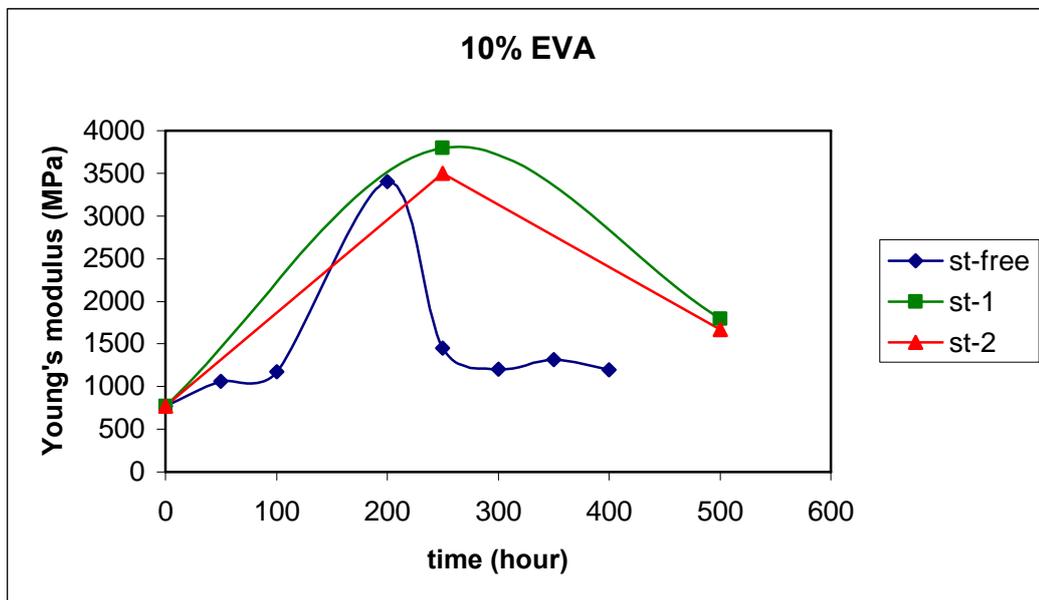**Figure 3.29** Effect of UV irradiation on Young's modulus of pure PP

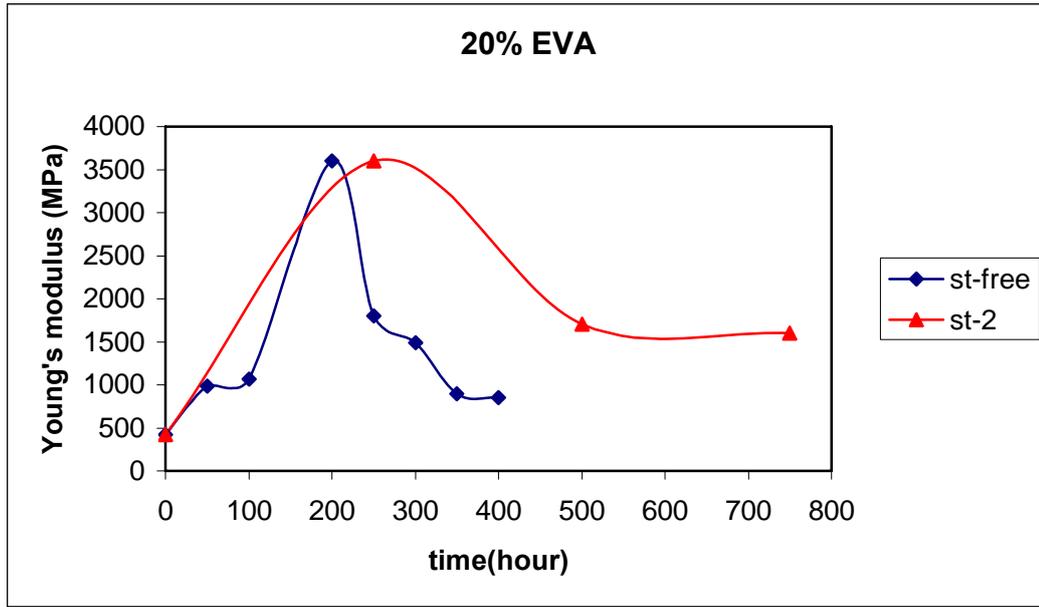**Figure 3.30** Effect of UV irradiation on Young's modulus of 10% EVA

Figure 3.31 Effect of UV irradiation on Young's modulus of 20% EVA

In Figures 3.32, 3.33 and 3.34 the changes of stress at break values of pure PP, 10% EVA blend and 20% EVA blend were given for stabilized and unstabilized samples. UV irradiation did not have much effect on the tensile strength of pure PP and blends.

The stress at break values of pure PP samples without stabilizer and pure PP samples with stabilizer remained almost constant upon UV irradiation in Figure 3.32. Here st-free samples resisted up to 400 hours of irradiation. St-1 samples resisted up to 500 hours and st-2 samples resisted up to 750 hours. On the otherhand we observed a slight increase in Figure 3.33 which can be reasoned by the increasing EVA content of the samples. Again it was observed that the the resistance of st-free samples was less than st-1 and st-2 samples. In Figure 3.34 the increase becomes obvious, especially for the st-2 samples, it reached to 35 MPa. St-free samples again failed at 400 hours. We could not take any data

from st-1 samples of 20% blends because the brittleness of the samples increased so much and unfortunately the sensitivity of the tensile testing machine could not record them.
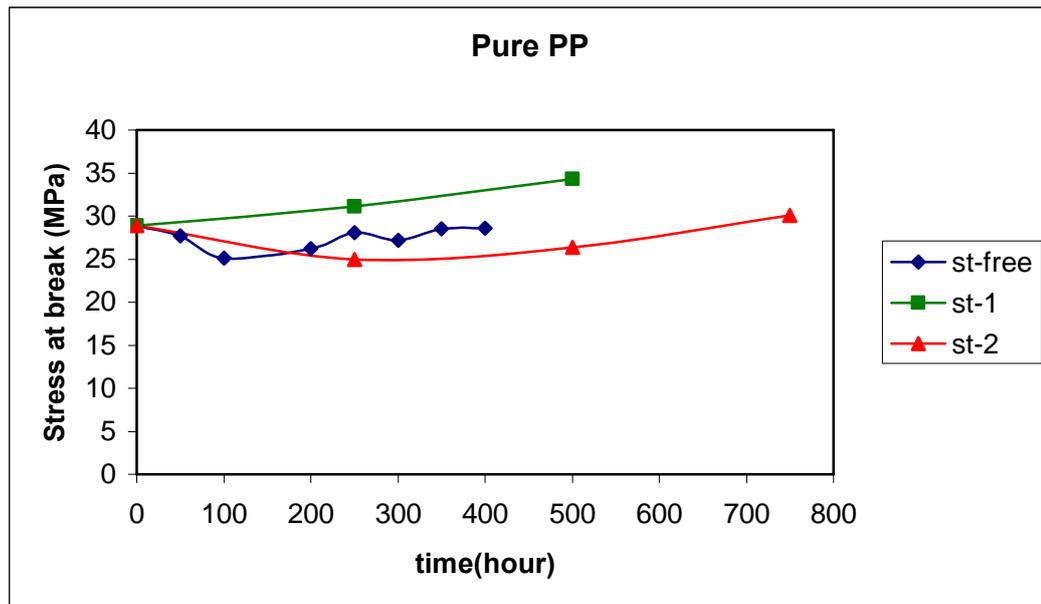

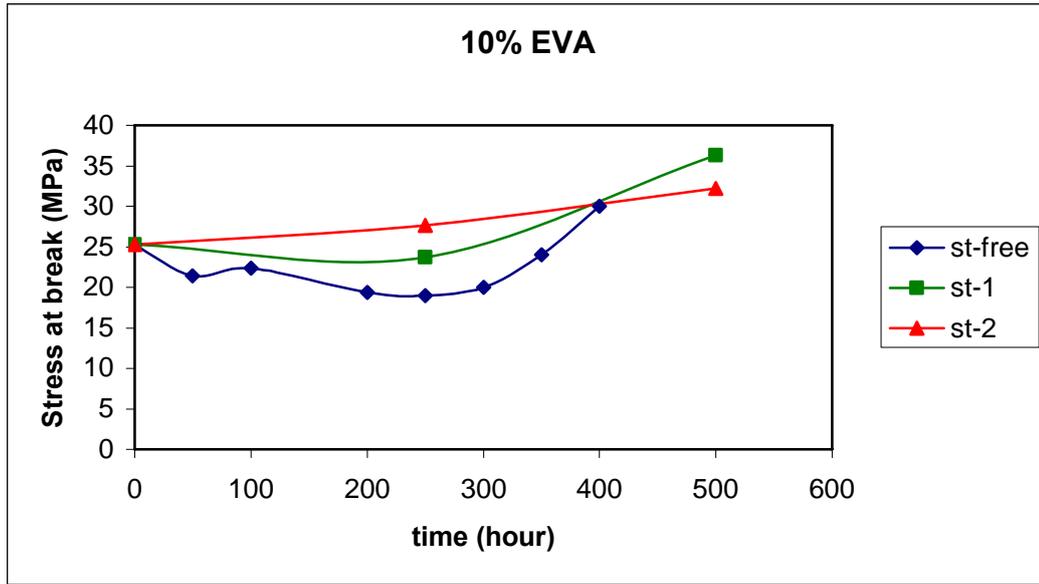**Figure 3.32** Effect of UV irradiation on stress at break of pure PP

Figure 3.33 Effect of UV irradiation on stress at break of 10% EVA
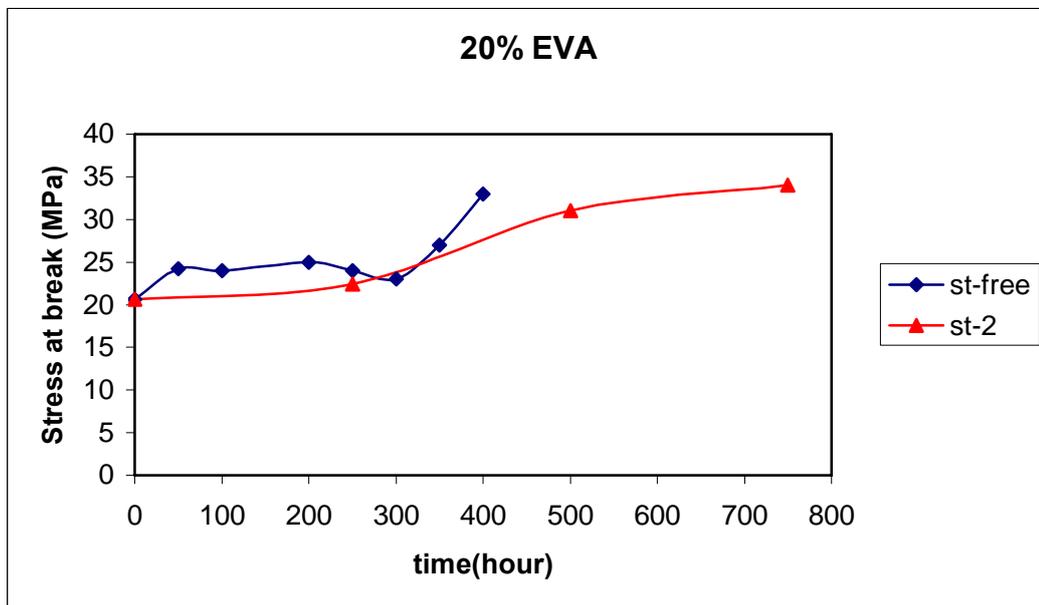

Figure 3.34 Effect of UV irradiation on stress at break of 20% EVA

Molecular alterations changed the elongation properties of the blends by the formation of flexible chain segments in the amorphous regions by UV irradiation.

In Figure 3.35 the change of strain at break value of pure PP with increasing UV irradiation time was given. UV irradiation decreased the elongation values of pure PP because of stiffening the samples. As expected st-free samples failed at 400 hours of irradiation. St-1 samples broken earlier than st-2 samples at 500 hours because of much stiffness. St-2 samples resisted up to 750 hours.

In Figure 3.36 the same decrease in strain at break values was observed. St-1 and st-2 samples of 10% EVA resisted to UV irradiation more than st-free samples of 10% EVA and failed at 500 hours.

Figure 3.37 represents the dramatic decrease of the percent strain at break values, here we also see the effect of EVA. The sudden decrease in the elongation values is due to the increasing brittleness of the samples with increasing EVA content, because the compatibility occurs in amorphous regions in the blends. St-free samples could resist up to 100 hours where st-2 samples resisted up to 250 hours of irradiation. Because of excessive brittleness of st-1 samples no data were taken from 20% EVA blends.

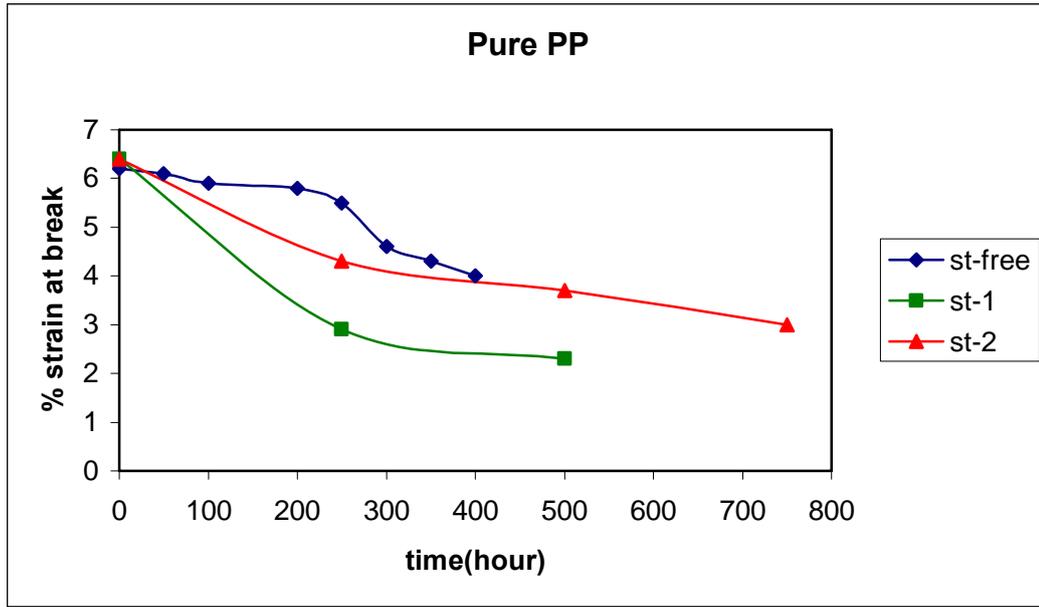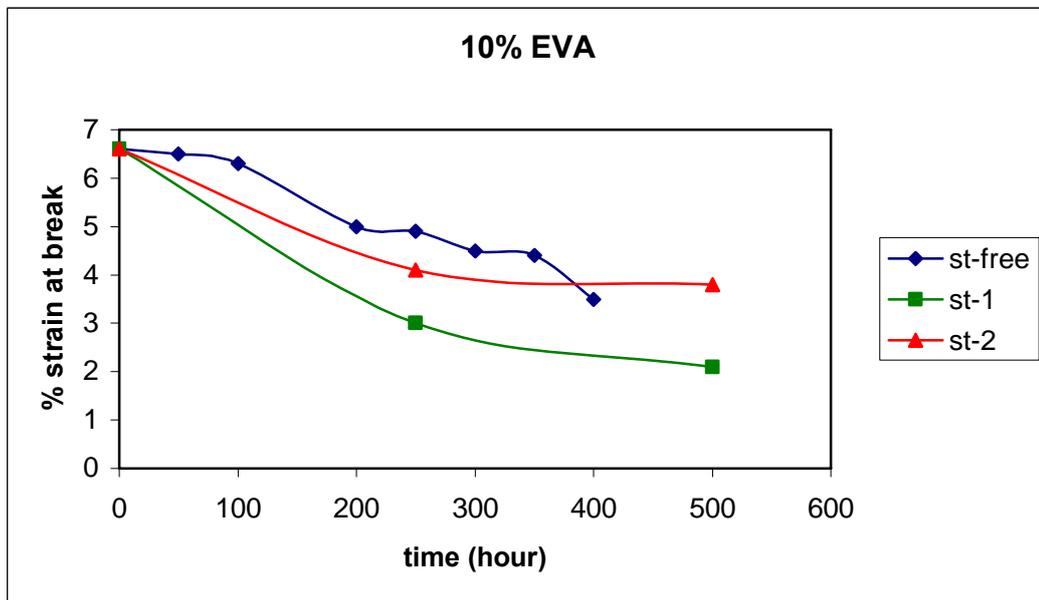**Figure 3.35** Effect of UV irradiation on elongation of pure PP

Figure 3.36 Effect of UV irradiation on elongation of 10% EVA
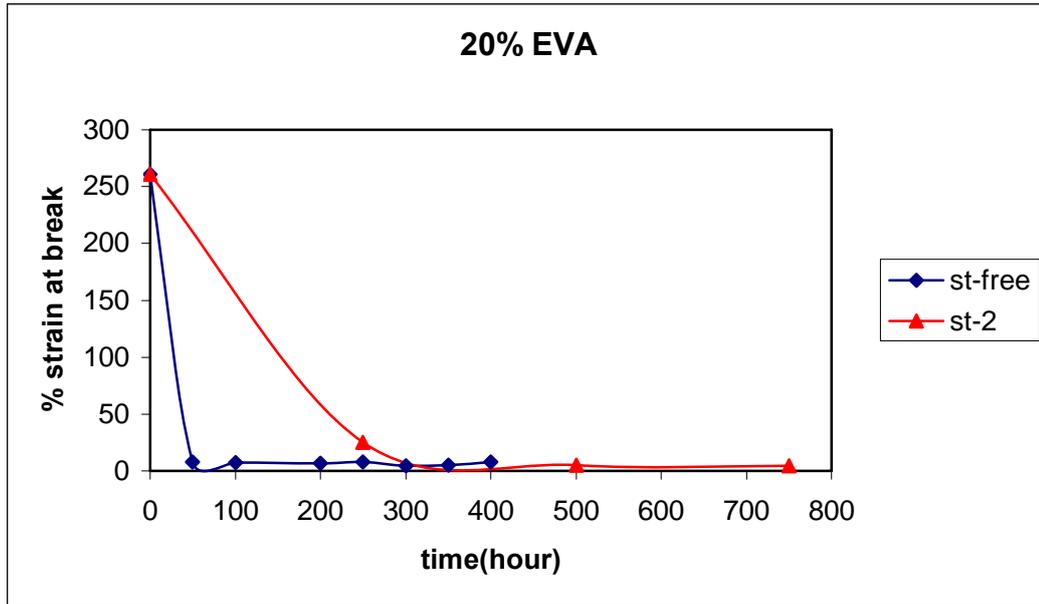
Figure 3.37 Effect of UV irradiation on elongation of 20% EVA

The stabilizer amount of st-2 was less than st-1 for pure PP and PP/EVA blends. Since the st-1 samples were failed because of excessive brittleness, st-2 samples well fitted with the desired tensile properties.

CHAPTER 4

CONCLUSIONS

PP was blended with EVA to increase the flexibility and to decrease the rigidity of the material in order to enhance the end use properties. The effects of temperature on tensile properties, and UV irradiation were investigated for the blends.

The Young's modulus of the blends decreased with increasing drawing temperature and EVA content. Temperature and EVA affected the materials by increasing chain mobility and decreasing hardness.

The stress at break values of the blends slightly increased with EVA and then remained almost constant for the same drawing temperature within the experimental error limits. EVA even up to 20% by weight in the blends did not greatly change stress at break values of PP/EVA blends. The stress at break values also decreased with increasing temperature. The effect of temperature on stress at break is more than that of EVA.

The percent strain at break values of the blends were found to increase with the presence of EVA. Also the mobility of the polymer chains are greatly affected with the temperature.

We see the stiffening effect of UV irradiation at the initial periods and followed by the loss of measured properties like Young's modulus, stress at break, percent strain at break. The effect of stabilizer is obvious because st-free samples no longer existed after 400 hours of irradiation. The decrease in the

elongation values of the blends was due to the increasing brittleness of the samples by UV irradiation.

The mobility of polymer chains has increased and the samples become more flexible by EVA and temperature. The impact values of the blends were high when the temperature was at 25ºC. On the otherhand when the temperature was decreased to 0ºC the mobility of the polymer chains decreased and the material become more brittle with lower impact strength.

DSC analysis of the drawn samples of 60°C and 80°C showed two distinct endothermic peaks. This is the indication of the transformation of β-phase to α-phase. In addition, the percent crystallinity of PP in the blends was calculated from DSC thermograms.

There is an increasing trend of crsytallinity with increasing drawing temperature. This increase was not continued to high temperature of 80°C. Increasing temperature made polymer chains, especially PP, more flexible because of the chain mobility. These flexible chains were then oriented in one direction during tensile testing and therefore uniaxial crystallization occurred.

According to SEM analysis it has been found that increasing temperature made the samples flexible by increasing the mobility of the chains. By this flexibility the elongation values increased and fibrillation occurred. The fibrillation of pure PP is higher than fibrillation of 20% EVA blend. This can be interpreted as the melting of EVA at high temperatures. Temperature affected the fibrillation of the blends in reverse order.

In conclusion, the mechanical test results indicated a transition toward compatibility between both components of the blends. St-2, i.e 0.5% stabilizer showed better stabilization and well fitted with the desired tensile properties.

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