

SYNTHESIS of 3-in-1 TYPE CO-CORESHELL REINFORCER-TOUGHENER-
COMPATIBILIZER for RIGID MATRICES via GRAFTING APPROACH

by

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*To my lovely husband who is always there –on the sidelines- cheering me on,
repeating over and over again that I am capable of greatness...*

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ABSTRACT

SYNTHESIS of 3-in-1 TYPE CO-CORESHELL REINFORCER-TOUGHENER-COMPATIBILIZER for RIGID MATRICES via GRAFTING APPROACH

In this project, synthesis and characterization of 3-in-1 type co-coreshell structured reinforcer-toughener-compatible for rigid polymer matrices were conducted to provide enhanced mechanical properties and thermal stability to polystyrene by obtaining optimal dispersion of P(AN-co-VAc) nanospheres in the matrix.

Crystalline poly(ethylene oxide) blocks (PEO) were synthetically grafted onto maleic anhydride grafted polystyrene-*b*-poly(ethylene/butylene)-*b*-polystyrene (SEBS-g-MA). The grafting efficiency was investigated by ¹H NMR and FTIR spectroscopic techniques and the thermal characterizations were conducted by TGA and DSC to analyse particularly the thermal stability and phase behaviors of graft copolymer. High shear mixing technique was used to provide better dispersion of P(AN-co-VAc) nanospheres in the graft copolymers having suitable polar sides to surround the nanospheres by hydrogen bond and dipole-dipole interactions. Effect of expanded P(AN-co-VAc) on dispersion quality was particularly discussed. In situ synthesis of polystyrene nanocomposites in the presence of obtained co-coreshell structures were carried out and resultant nanocomposites were inspected in terms of morphology, mechanical and impact strength as well as thermal properties. It has been found that , compared to neat PS, PS / SEBS-g-PEO 1% XP(AN-co-VAc) exhibited not only the highest toughness but also increased thermal stability and flame retardancy .

It is confirmed by this study that, covalently bonded bridges between each layers via grafting inhibited the extensive phase separation which then resulting in both stable co-coreshell structures and extra simultaneous benefits particularly on reinforcing, toughening and compatibilizing issues of rigid polymers.

ÖZET

AŞILAMA YAKLAŞIMIYLA SERT MATRİSLER İÇİN EŞ ÇEKİRDEK KABUK YAPISINDA, ÜÇÜ BİR ARADA GÜÇLENDİRİCİ-TOKLAŞTIRICI-UYUMLAŞTIRICI SENTEZİ

Bu projede sert polimer matrisler için eş çekirdek kabuk yapısında, üçü bir arada güçlendirici-toklaştırmacı-uyumlaştırmacı sentezi ve karakterizasyonu yapılmıştır. Bu yapı ile P(AN-co-VAc) nano kürelerin polistiren matrise ideal dağılımı sağlanmış ve mekanik dayanımları ile ısı kararlılıkları artırılmıştır.

Maleik anhidrit aşılı polistiren-b-poli(etilen/bütlen)-b-polistiren (SEBS-g-MA) kristal yapıdaki poli(etilenoksit) blokları (PEO) ile sentetik olarak aşılansmıştır. Aşılama verimliliği ¹H NMR ve FTIR spektroskopi teknikleri kullanarak incelenmiştir. Isıl karakterizasyonlar TGA ve DSC kullanarak ısı kararlılık ve faz geçişlerinin analiz edilmesi ile gerçekleştirilmiştir. Uygun polar kısımları bulunan ve hidrojen bağları ile dipol-dipol etkileşimleri sayesinde P(AN-co-VAc) nano kürelerin etrafını sarabilecek aşılı kopolimerler kullanılmıştır ve yüksek parçalayıcı karıştırıcı sayesinde iyi dağılım elde edilmiştir. Genişletilmiş P(AN-co-VAc) nano kürelerin kullanımının dağılıma olan etkisi özellikle irdelenmiştir. Elde edilen eş çekirdek kabuk yapılarının varlığında polistiren nanokompozit sentezi gerçekleştirilmiş ve sonuç nanokompozitler, morfoloji mekanik ve darbe dayanımı ile ısı özellikleri bakımından incelenmiştir. Saf PS ile karşılaştırıldığında, PS / SEBS-g-PEO 1% XP(AN-co-VAc) nanokompozitin en iyi mekanik dayanım sağladığı, yanı sıra ısı dayanım ve alevlenme geciktirici özelliklerini de arttırdığı gözlemlenmiştir.

Bu çalışmayla sert polimerlerde, aşılansmayla oluşmuş katmanlar arasındaki kovalent bağlı köprülerin faz ayrımını engellediği, sonucunda da hem kararlı eş çekirdek kabuk yapıları oluştuğu hem de güçlendirme, toklaştırma ve uyumlaştırma konularında eş zamanlı fayda sağlandığı doğrulanmıştır.

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LIST OF SYMBOLS

a_0	Atomic Spacing
cm	Centimeter
DP _n	Degree of Polymerization
E	Young's Modulus
g	Gram
J	Joule
L	Length
MHz	Megahertz
mL	Milliliter
M _n	Number Average Molecular Weight
MPa	Megapascal
N	Newton
rpm	Revolutions per Minute
T _g	Glass Transition Temperature
T _m	Melting Temperature
T _{onset}	Onset Temperature
UV	Ultra-violet
V _f	Volume Fraction
$\sigma_{\max}$	Theoretical Tensile Strength
%	Percentage
ΔH	Change in Enthalpy
°C	Centigrade Degree

LIST OF ACRONYMS / ABBREVIATIONS

¹ H-NMR	Hydrogen - Nuclear Magnetic Resonance
AIBN	Azobisisobutyronitrile
BMI	Bismaleimide
CCTP	Catalytic Chain Transfer Polymerization
CN	Cyanide
DGEBA	Diglycidyl Ether of Bis-phenol A
DMA	Dynamic Mechanical Analyses
DSC	Differential Scanning Calorimeter
DTGA	Derivative Thermogravimetric Analyses
EPDM	Ethylene Propylene Diene Monomers
EPR	Ethylene Propylene Rubber
ETPB	Epoxy Terminated Polybutadiene
FTIR	Fourier Transform Infrared Spectroscopy
GP-PS	General Purpose - Polystyrene
HIPS	High Impact Polystyrene
iPP	Isotactic Polypropylene
MA	Maleic Anhydride
NMR	Nuclear Magnetic Resonance
P(AN-co-VAc)	Poly(acrylonitrile Vinylacetate Copolymer)
PA	Polyamide
PAN	Polyacrylonitrile
PB-g-PS	Polybutadiene Grafted
PE	Polyethylene
PEO	Poly(ethylene oxide)
PET	Polyethylene Terephthalate
PMMA	Poly(methyl methacrylate)
PP	Polypropylene
PPE	Poly(phenylene ether)

PPhO	Poly(phenylene oxide)
PPO	Poly(propylene oxide)
PS	Polystyrene
PTFE	Polytetrafluoroethylene
SBM	Styrene-block-polybutadiene-block-poly(methylmethacrylate)triblock terpolymer
S-B-S	Styrene-Butadiene-Styrene
SEBS	Styrene-Ethylene-Butadiene-Styrene Copolymer
SEBS-g-MA	Maleic anhydride grafted Styrene-Ethylene-Butadiene-Styrene Copolymer
SEBS-g-PEO	Poly(ethylene oxide) grafted Styrene-Ethylene-Butadiene-Styrene Copolymer
SEM	Scanning Electron Microscope
SI-PMMA	Nano-silica surface grafted Poly(methyl methacrylate)
S-I-S	Styrene- Isoprene-Styrene
STEM	Scanning Transmission Electron Microscope
TGA	Thermogravimetric Analyses
TGMDA	Tetra-glycidylmethylenedianiline
THF	Tetrahydrofuran
XP(AN-co-VAc)	Expanded Polyacrylonitrile Vinyl Acetate Copolymer

1. INTRODUCTION

Polymers can be classified in many different ways such as polymer structure, reaction mechanism, preparation technique, or the origin of the polymer such as natural or synthetic. On the other hand, polymers may also be classified as fiber, flexible/rigid plastic, or elastomeric materials [1-3]. In this study we generally focused on the rigid polymers, elastomeric materials and preparation of rigid matrices containing additive with grafting technique.

1.1. Rigid Polymers

Classification of the polymers by taking into consideration of the chain rigidity or flexibility is beneficial for confirming the use of polymers and in this perspective fibers, flexible/rigid plastics or elastomers are the main titles [4], [5].

Rigid polymers are the polymers which have high elastic modulus and low elongation at break. It means that they are hard to deform, but due to their low elongation capability, they will have tendency to fail in a brittle manner after a small amount of deformation. This is why rigid polymers have low impact toughness, which is the total amount of energy a material can absorb through deformation until failure. Even though they are hard to deform, they cannot withstand large deformations. This is why toughener (impact modifier) additives are used to add flexible chains to the rigid matrix and improve the materials elongation capability.

Polymer chains are generally rigid when the cyclic structures are in the main polymer chains and generally crystallinity, mechanical properties and thermal transitions such as crystalline melting temperature (T_m) and glass transition temperature (T_g) are affected by the rigidity of the polymer chains [6]. Rigid polymers which have cyclic structures located in the polymer chain for example, cellulose and PET are difficult to crystallize. They have excess chain rigidity because there are extensive crosslinking similar to the phenol-formaldehyde and urea-formaldehyde resins and this prevents crystallization [5]. T_m and T_g of the polymers are also affected by the rigidity of the macromolecule chain

because thermal behavior of the polymers are directly related with chain mobility. The crystalline melting temperature is defined as the melting temperature of the crystalline regions of a polymer sample and the glass transition temperature is the temperature which affects the characteristic properties of the polymer such as glassy state brittleness, stiffness and rigidity. In general, rigid polymers such as poly(ethylene terephthalate) have high T_g (61°C) and T_m (270°C) values. On the other hand, the highly flexible polydimethylsiloxane results in very low values of T_g (-127°C) and T_m (-40°C) [5], [7]. In other words, decreasing the mobility of polymer chains, increases the chain rigidity, and high T_g are found where the chains are substituted with several substituents such as PMMA and PTFE or with bulky substituents such as polystyrene. The T_m values of crystalline polymers will also be affected from rigid chains and high T_m value can be expected in these structures [5].

Considering the mechanical properties can also be useful for evaluating the chain rigidity of polymers. The mechanical behavior of a polymer can be evaluated by using stress–strain properties. This test involves examining the behavior of a polymer using tension stress and elongation (strain) data points. The results are shown as a plot of the stress versus elongation (strain). The stress is usually expressed in Newton per square centimeter (N/cm^2) and the strain is the fractional increase in the length of the polymer sample, for example $\Delta L/L$ where L is the original, unstretched sample length. Stress-strain plots for rigid plastic, fiber, flexible plastic and elastomers are given in Figure 1.1. comparatively [5].

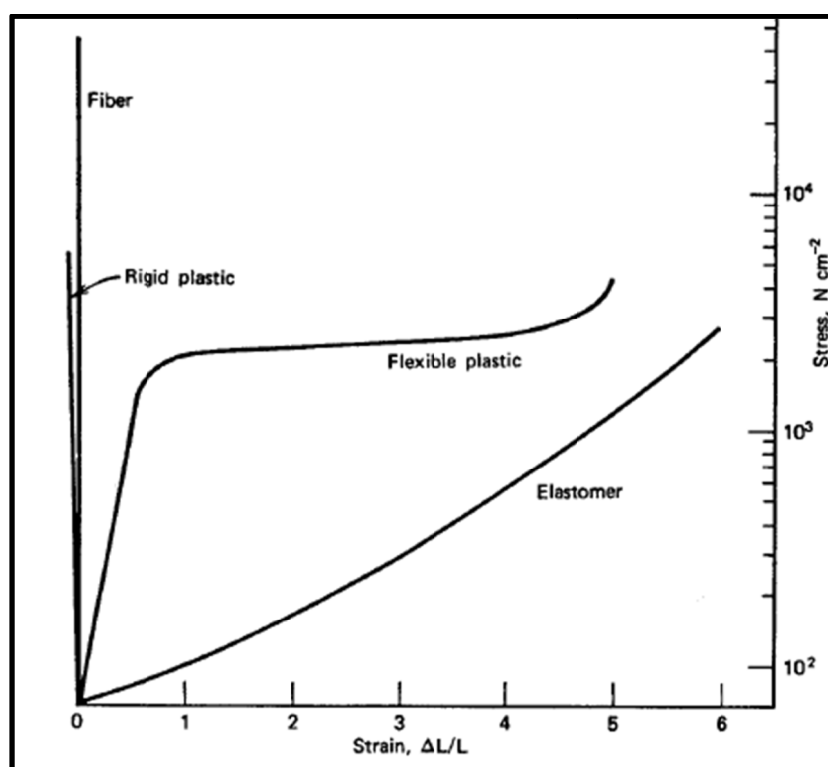


Figure 1.1. Stress versus strain curve for a usual rigid plastic, flexible plastic, elastomer, and fiber.[5].

Figure 1.1. shows the dissimilarities between plastics, fibers, and elastomers. Plastics represent a large group of polymers. Mechanical behaviors of these polymers are in between the properties of elastomers and fibers. Flexible plastics and rigid plastics are the two types of plastics. The flexible plastics have moderate toughness and they have a large variety of T_m and T_g values. They have moderate to high moduli (15000-350000 N/cm^2), tensile strengths (1500-7000 N/cm^2), and ultimate elongations (20-800%). On the other hand, rigid polymers are rather dissimilar from the flexible polymers. Characterization of rigid polymers which contain high amounts of rigid chains can be performed by evaluating the deformation resistance. They have high moduli (70000-350000 N/cm^2) and moderate to high tensile strengths (3000-8500 N/cm^2), but more importantly, they undergo very small elongations (<0.5-3%) before fracturing. An example for these polymers can be amorphous rigid polymers. Extensive crosslinking can be the reason for high chain rigidity and phenol-formaldehyde, urea-formaldehyde, and melamine-formaldehyde resins are the examples of this situation. In other polymers, high T_g values are resulted by the high rigidity of polymer due to bulky side groups on its chains for instance poly(methyl methacrylate) ($T_g = 105^\circ C$) and polystyrene ($T_g = 100^\circ C$) [5].

1.1.1. Polystyrene

Polystyrene is one of the most widely used and common example of rigid thermoplastics. Polystyrene is made from styrene (vinyl benzene) monomer and this monomer is obtained from the reaction of benzene and ethylene. In one process, ethylene is passed into liquid benzene under pressure, in the presence of aluminum chloride catalyst. The resulting ethylbenzene is dehydrogenated to styrene by passing it over an iron oxide or magnesium oxide catalyst at about 600°C. The styrene is then refined by distillation [4]. Chemical structure of the polystyrene is shown in Figure 1.2.

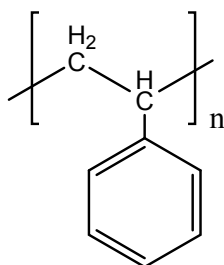


Figure 1.2. Chemical structure of polystyrene.

Polystyrene is a rigid polymer whose main characteristics include transparency, ease of coloring and processing as well as low cost. It can be available in general-purpose or crystal (GP-PS), high impact (HIPS) and expanded grades and forms. In addition, copolymerization of styrene with other vinyl containing monomers can be useful in many applications. Commercial atactic polystyrene is made by free radical bulk, solution, emulsion or suspension polymerization of styrene monomer by using thermal initiators [3].

Polystyrene is a linear polymer and it can be produced in isotactic, syndiotactic and atactic forms. Atactic form is used as general-purpose or commercial product and as such amorphous; compare to atactic form, processing isotactic polystyrene is more difficult due to its brittle structure and consequently isotactic form is not commercial. On the other hand, commercial polystyrene is a transparent, rigid polymer that is in comparison chemically inert. Polystyrene, as produced, has superior flow characteristics and therefore its processing is very easy. It has outstanding optical properties, also high refractive index and these characteristics make it beneficial in optical applications. However general purpose (crystal) polystyrene has various limitations such as its brittleness, low heat

deflection temperature, poor UV resistance and sensitivity to attack by a sort of solvents. Therefore, polystyrene is sensitive to foods with high fat or oil content and it crazes and its color turns to yellow in the open air exposure. Many of the problems associated with general purpose crystal polystyrene can be lessened, or at least minimized, through copolymerization of styrene with another monomer, blending or proper formulation. For example, blending polystyrene with butadiene rubber enhances impact resistance and toughness compare to neat polystyrene [3]. Another example, the addition of ultraviolet light absorbers improves the light stability of polystyrene enough to make it useful in lighting fixtures such as fluorescent-light diffusers. Flame retardant polystyrenes have also been developed with additives [4]. Emulsion polymerization is used to obtain high impact polystyrene commercially by using styrene monomer containing the polybutadiene and SBR dispersing agents. The end product contains a glassy PS matrix including dispersed small domains of polybutadiene in it. The impact strength of HIPS depends on the distribution, size, and concentration of the polybutadiene particles. Stereochemistry of polybutadiene influence this situation and optimal properties are obtained using 36% cis-1,4 polybutadiene ingredients [3].

Applications of polystyrene can be classified in terms of processing method. Polystyrene which is processed with extrusion can be used in containers, tubs and trays for food packaging, mirror and picture frames, refrigerator breaker strips, room dividers, shower doors, glazing and lighting products. Polystyrene which is processed with thermoforming can be used in refrigerator door lines, signs, horticultural trays, luggage, furniture panels, glove compartment boxes, meat, poultry, and egg containers, blister packs, container lids, cookie, candy, pastry and other food packages. Polystyrene which is processed with injection molding can be used in packaging and non-packaging disposables, air conditioner grilles, refrigerator and freezer components and small appliance housings. Consequently, the applications for all grades of polystyrene include packaging, housewares, toys and recreational products, electronics, appliances, furniture, building and construction insulation [3].

1.2. Thermoplastic elastomers

The term thermoplastic elastomer is currently used to describe a wide variety of materials that have elastomeric properties at medium temperature, but are processed like thermoplastics, obviating the need for the vulcanization step to enhance typical rubberlike elasticity [4]. Thermoplastic elastomers were introduced in the 1960s. Softness, flexibility and resilience are some physical properties of thermoplastic elastomers similar to rubbers but they are processed as thermoplastics in contrast to classical rubbers. Rubbers must be cross-linked to give useful properties. Vulcanization is a thermosetting process which usually is carried out using sulfur in the polymer industry. This process is slow and irreversible. It takes place upon heating, similar to the other thermosetting processes. With thermoplastic elastomers, on the other hand, the transition from a melt to a solid, rubber-like object is rapid and reversible and takes place upon cooling. Injection molding and extrusion are the conventional plastic techniques for processing the thermoplastic elastomers however scrap is usually recycled. Most of thermoplastic elastomers have multiphase compositions with intimately dispersed phases for example block copolymers of styrene with a suitable elastomer. Block or graft copolymerization is a technique to bonding the phases chemically in many cases. In others, a fine dispersion is apparently enough. In these multiphase systems, there is a hard phase and soft phase at room temperature. The hard phase melts by heating, the softer phase is rubber-like. A–B–A block copolymer as a simple structure and in this structure A denote the hard phase and B denote an elastomer, for example, poly (styrene-*b*-elastomer-*b*-styrene). Most of polymer blends are thermodynamically incompatible and phase separation occurs in time. Even it is sustainable when the polymeric species are part of the same molecule, as in these block copolymers [8]. Poly (styrene-*b*-elastomer-*b*-styrene) copolymers, in which the elastomer is the main constituent, should have a structure as shown in Figure 1.3.

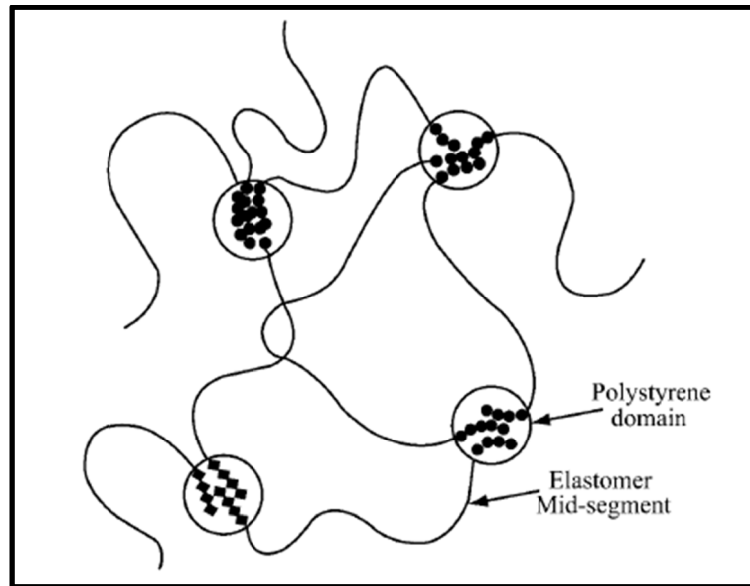


Figure 1.3. Phase arrangement in styrene based block copolymers [8].

The most widely used thermoplastic elastomers, to which the name originally applied, are block copolymers of styrene (S) with butadiene (B) or isoprene (I) with the block structure S-B-S or S-I-S [4]. Block copolymers are very attractive materials in consideration of their technological applications. It is well known that early enhancements were based upon the thermoplastic behavior which results when a glassy component is linked to a rubbery material [9].

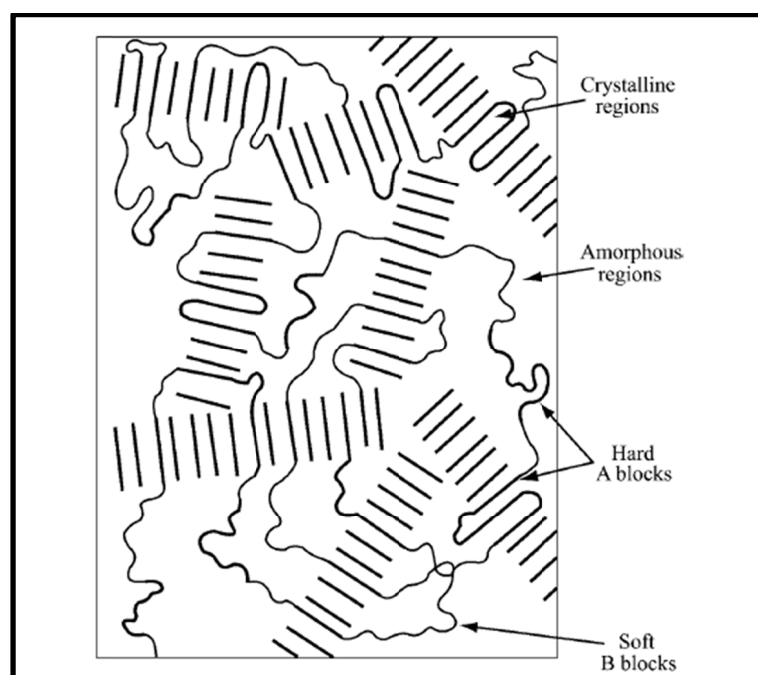


Figure 1.4. Phase arrangement in crystalline block copolymers [8].

Defining the thermoplastic elastomers, in general, A can refer to any hard thermoplastic polymer, for example, polystyrene, polyethylene, or polypropylene, and B can refer to any elastomeric polymer, for example, polyisoprene, polybutadiene, poly(ethylene-propylene), or polydimethylsiloxane. A–B or B–A–B is a block copolymer but they do not show thermoplastic elastomer properties, both ends of the elastomer segment must be immobilized in the hard domains to provide a continuous network. Instead, these are much weaker materials looking like conventional unvulcanised synthetic rubbers (Figure 1.3.) [8].

In recent years, new materials have been developed in, in order to provide higher thermal and ultraviolet degradation resistance by hydrogenation of the poly(butadiene) blocks. Poly(styrene-co-ethylene-co-butylene-co-styrene) (SEBS) block copolymer (Figure 1.5.) is a widely used thermoplastic elastomer and it is the most popular example for this situation.

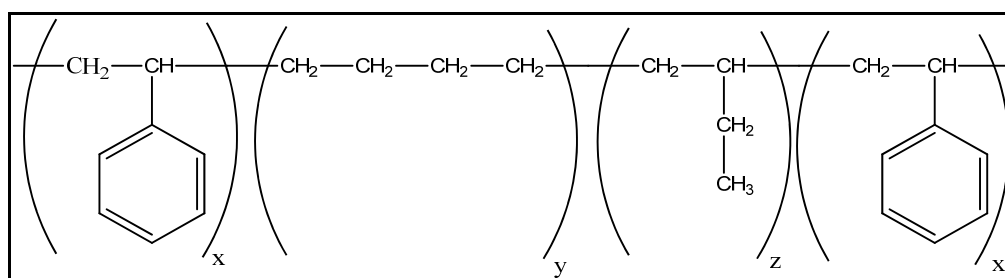


Figure 1.5. Chemical structure of the SEBS triblock copolymer.

These hydrogenated block copolymers present an elastomeric block consisting of a copolymer of ethylene and butylene. Anionic polymerization is used to produce the precursor polybutadiene-styrene and this polymer is used for the resulting poly(styrene-b-ethylene-co-butylene-b-styrene) triblock copolymer (SEBS) and the ratio of these two structures can be controlled in the process of 1,4 or 1,2 addition. Therefore, butylene units are accurately defined after hydrogenation. In any case, phase separation into domains of polystyrene in a matrix of the ethylene-butylene central block occurs due to immiscible blocks in the structure [9]. It exhibits both processibility and elasticity in balanced, and also enhanced thermal, oxidation and weather stability. Such triblock copolymers can exhibit characteristics of crosslinked rubber at low temperature whereas can flow at high temperature because at low temperature polystyrene dispersed micro domains are formed

by end blocks [10]. The ethylene–butylene midblocks form a rubbery co-continuous matrix phase. SEBS polymers are compatible with PP, PS and PE and they have outstanding weather and oxidation resistance since they don't have a double bond in their structure. They exhibit very good processibility in extrusion and molding operations, and improve impact resistance upon blending with impact-deficient polymers [11].

Table 1.1. Glass transition and crystal melting temperatures of some thermoplastic elastomers [8].

Thermoplastic Elastomer Type	Soft, Rubbery Phase T_g (°C)	Hard Phase T_g or T_m (°C)
S-B-S	-90	95 (T_g)
S-I-S	-60	95 (T_g)
SEBS	-60	95 (T_g)
Polyurethane/elastomer block copolymers	-40 to -60	190 (T_m)
Polyamide/elastomer block copolymers	-40 to -60	220 to 275 (T_m)
Polyethylene/poly(α -olefin) block copolymers	-50	70 (T_m)
Polypropylene/EPDM or EPR combinations	-50	165 (T_m)
Polypropylene/butyl rubber combinations	-60	165 (T_m)
Polypropylene/butyl rubber combinations	-60	165 (T_m)
Polypropylene/nitrile rubber combinations	-40	165 (T_m)

Thermoplastic elastomers have two transition phase temperatures. The lower transition temperature depends on the T_g of the elastomer phase whereas the upper phase transition temperature depends on the T_g or T_m of the hard phase. T_g and T_m values of the some commercially important thermoplastic elastomers with various phases are given in Table 1.1. As a result, type of the hard and soft phase of thermoplastic elastomers affect the properties of the end product [8].

1.3. Nanoparticles

Nanotechnology is the study of material behavior at the scale of 1 billionth of a meter and it is also the study of manipulating matter within the scale of atomic and molecular sizes.

1.3.1. Definition and Properties

A nanoparticle is the basic component in the nanostructure manufactured, and it is quite smaller compare to the daily life objects that are defined by Newton's laws of motion, however bigger than a simple molecule or an atom that are driven by quantum mechanics and it can be described as objects varying in size from 1-100 nm. Their properties may differ from the bulk material due to their size [12], [13]. In addition, metals, semiconductors and metal oxides are some examples of nanoparticles and they are applicable to a wide variety of industries in the field of medical, information, energy, and environmental technologies. They provide improved unique properties based fundamentally upon composition, structure and size along with their self-organized film structures [14]. Cosmetics, clothes, optical devices, catalytic, bactericidal, electronic, sensor technology, biological labelling and treatment of some cancers are some application fields of nanoparticles and they can be synthesized using chemical or biological techniques. Nanoparticles are also being used in a variety of purposes in energy industry such as solar and oxide fuel batteries. Gold, silver, alloy and magnetic are some metallic nanoparticles which can be applicable to these industries [13]. The addition of inorganic nanoparticles to polymers cause changes in the properties of both the nanoparticles and polymers and these phenomena is the widespread research field in this sector. Silica, magnetic nanoparticles (iron oxide), titanium dioxide, zinc oxide, alumina, magnesium hydroxide, gold, silver, gadolinium oxide, manganese oxide, cerium oxide, copper, platinum palladium and rhodium are the popular examples of nanoparticles used with polymers [15]. For example, silica nanoparticles have a broad excitation band and size-dependent optical emission, so they can be used for detection purposes. Due to the potential applications, the area of inorganic (silica)-organic (polymer) nanocomposites are extensively investigated in the literature [15]. For example, Lu *et al.*, synthesis of nano-silica surface-grafted poly(methyl methacrylate) (PMMA) (SI-PMMA) macromonomers by using CoBF as a chain transfer catalyst via CCTP. They pointed out that the molecular weight of the polymer decreases with increasing CoBF concentration [16].

Nanoparticles can be classified as zero-dimensional; which are nanoparticle droplets, one-dimensional nanoparticles that are nanorods or nanotubes, and two-dimensional such as plates which are shown in Figure 1.6.

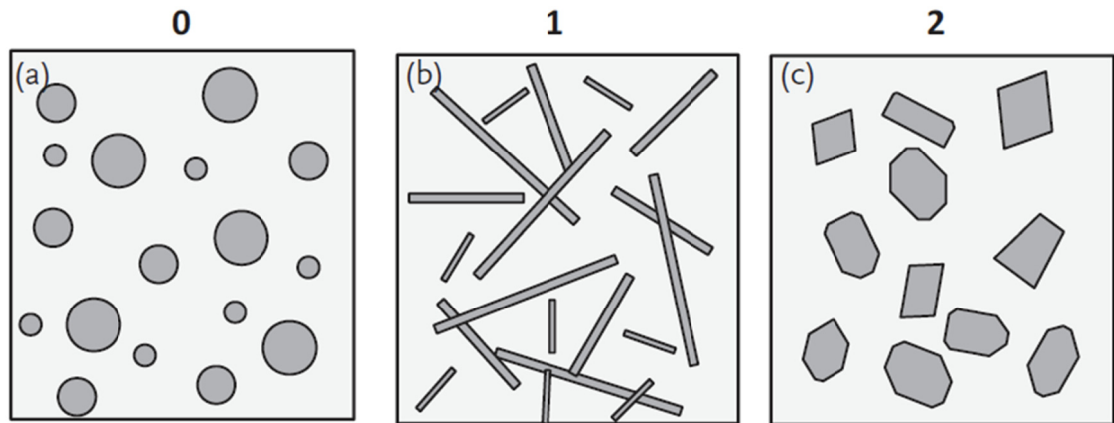


Figure 1.6. Dimensionality of nanocomposites. (a) Zero-dimensional particles in a matrix.
 (b) One-dimensional nanocomposite consisting of nanotubes or nanorods.
 (c) Two-dimensional nanocomposite consisting of platelets.[17].

The main problem related to nanoparticle usage in providing toughness is agglomeration. Nanoparticles have tendency to get together and create larger domains. It causes decreased toughness in polymer matrix and creates defect points which will lead to fracture starting from these points. Therefore good dispersion quality has ultimate importance in the use of nanoparticles. Coating nanoparticles is a way to increase dispersion quality and compatibility by preventing their interaction between each other. In this way co-coreshell structures can be obtained and dispersion becomes easier in the polymer matrix. On the other hand, different mechanical and physical properties can be achieved by these co-coreshell structures. For example elastomeric properties of the polymer can be increased by surrounding the nanoparticle with an elastomeric chain. A typical co-coreshell structure is shown in the Figure 1.7. [17]

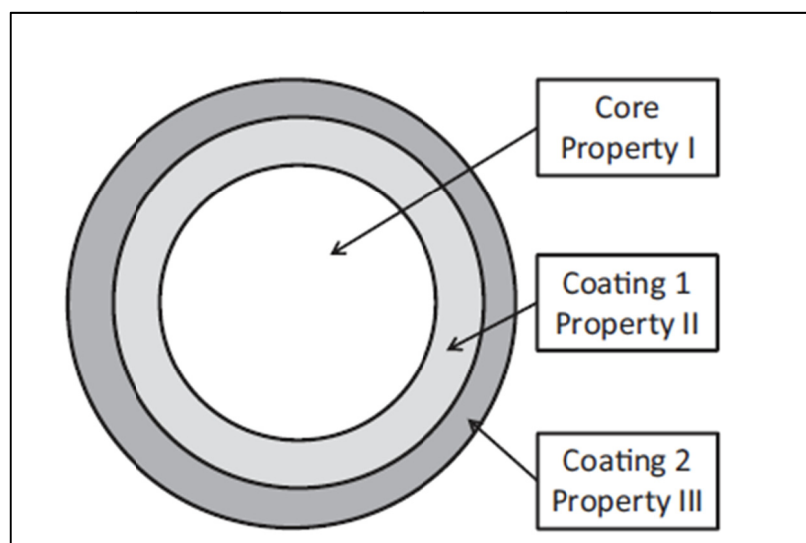


Figure 1.7. Typical design of a co-core-shell nanocomposite particle. [17].

1.3.2. Acrylonitrile/Vinyl Acetate Copolymer

Polyacrylonitrile (PAN) is a highly polar material due to strong interactions by CN groups in its structure. PAN is widely used in industry as a good starting material especially to produce synthetic fiber, but its degradation temperature is lower than its melting point due to its high polarity. This situation can be prevented by copolymerization of Acrylonitrile to decrease the polar interactions in PAN (Figure 1.8.) and main monomers that can be copolymerized with PAN are styrene, acrylates, methacrylates and vinyl acetates. Therefore, copolymerization of PAN with Vinyl acetate monomers will provide both thermal stability by increasing degradation temperature of PAN and improve its mechanical properties. [18]

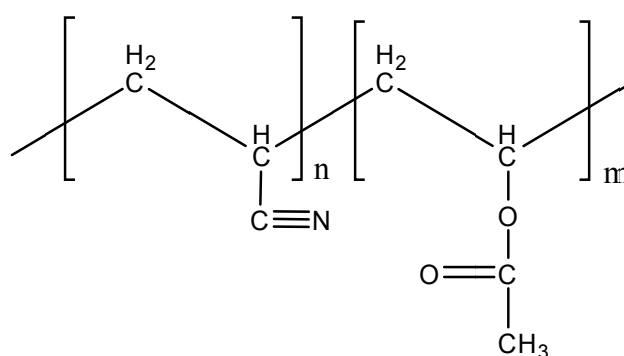


Figure 1.8. The structure of Poly(Acrylonitrile/Vinyl Acetate Copolymer)

Copolymerization can be done in many ways. Electrospinning after free radical polymerization is one way to make micro or nano sized copolymer fibers [18]. Also emulsion polymerization by creating micelles is another method to prepare spherical micro or nano sized copolymers [19]. Schematic representation of these example copolymerization methods are in Figure 1.9.

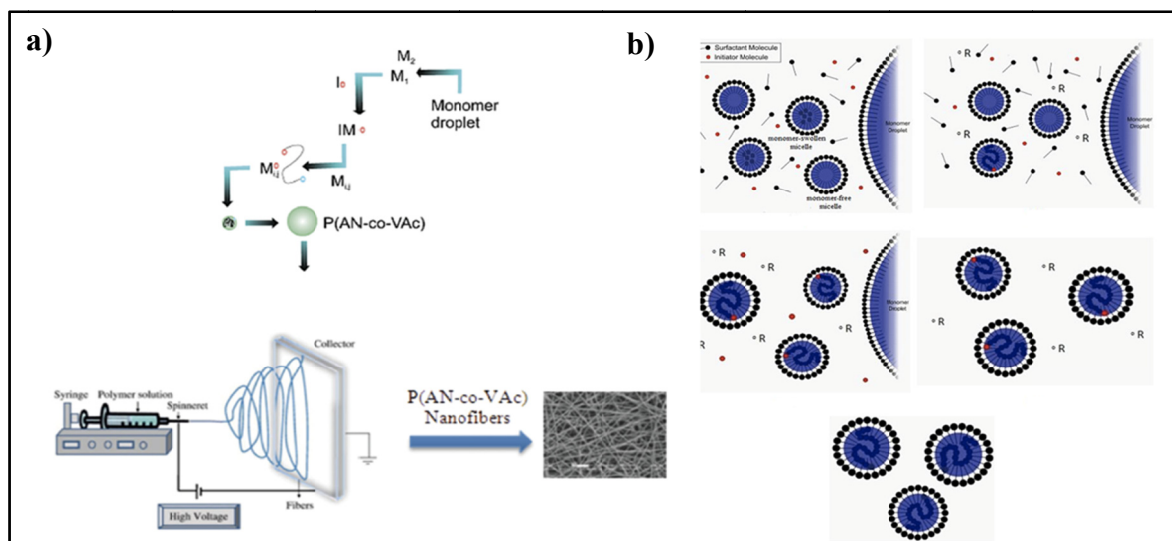


Figure 1.9. Schematic representation of copolymerization of P(AN-co-VAc) (a) nanofiber formation by free radical polymerization and electrospinning [18]. (b) nanosphere formation by emulsion polymerization [19].

1.4. Reinforcement - Compatibilizing - Toughening

Structural modification of polymers (for example, post-polymerization) often leads to significant property enhancement, most of the time, polymers are not used in their chemically pure form in industry. It is generally necessary to modify their behavior through blending of two or more polymers such as reinforcement to achieve improved mechanical properties. The need to meet challenging end-use requirements and simultaneously time reducing the costs is stimulating a extensive spectrum of product development involving the use of reinforcements and fillers to improve product performance. This method is usually preferred to the development of new and more expensive resins. Reinforced materials shows some advantages such as light weight, high strength, fatigue life and corrosion resistance, this is the reason that these materials are widely used in aerospace industry and in many industrial and consumer applications

instead of conventional materials. Recently, fiber reinforced materials play a big role in the development of engineering materials. Both thermoplastics, and thermosets can be reinforced with fibers to produce materials with entirely new kind of structure [3].

Strength of the reinforcement can be controlled by changing the dimension of the reinforcing material. For example, as shown in Figure 1.10, tensile strength of the composites decreases with the increase in the fiber diameter [8].

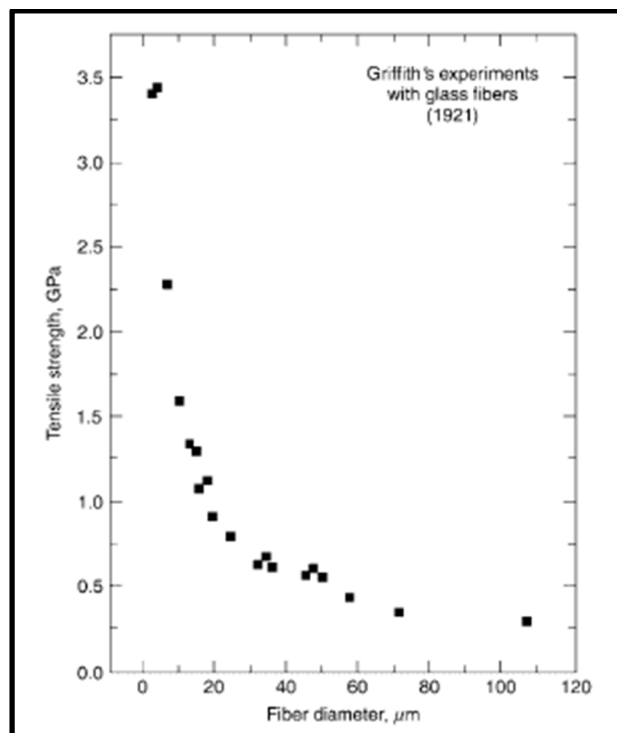


Figure 1.10. Plot demonstrating the effect of fiber diameter on the tensile strength [8].

In addition, strength of the reinforcement can be controlled by the type of the reinforcing material. It is possible to use mechanical material models to select suitable materials as reinforcements. The theoretical tensile strength $\sigma_{\max}$ of a solid can be given as; $\sigma_{\max} = (E\gamma/a_0)^{1/2}$, where E and γ are the Young's modulus and the surface energy of the solid, respectively, and a_0 is the atomic spacing. By considering strong solids, the main requirements for good reinforcement are as high surface energy, small atomic spacing and high elastic modulus. This situation suggests us that atoms with small atomic radii should be considered and beryllium, boron, carbon, nitrogen, oxygen, aluminum, and silicon are suitable and good candidates [8].

Adding fillers and reinforcements are traditional methods and effective for improving the materials properties however it has been insufficient for coping with the increasing performance requirements. Development of new resin systems to meet demands are very expensive, take too long time and require huge investments because it requires totally new technologies and plant facilities. An alternate way for new polymer development is the development of blends that are a physically combined two or more polymers to form a new material [3].

Single- phase systems are formed by compatible polymer blends and they have generally single property such as the glass transition temperature that is commonly the measured arithmetic average of blend components' T_g values. At certain compositions, some compatible polymer blends exhibit high level of thermodynamic compatibility due to strong intermolecular attractions. This situation provides excellent properties for those of the individual components alone. This blends show synergistic properties like modulus and tensile strength. Polystyrene (PS) modified poly(phenylene oxide) (PPO) and polystyrene (PS)-modified poly(phenylene ether) (PPE) are some of the most important engineering alloys and these polymers are commercially available. [3].

Blending of two or more polymers is an effective and low cost way to enhance properties of materials and has proven to be industrially relevant. But, improving the interfacial adhesion between the polymeric components by compatibilization is necessary because most of the polymers are immiscible [20]. Incompatible polymer blends are formed by heterogeneously mixed components and exhibit separate polymer phases and several glass transition temperatures corresponding to each component of the blend. Polymer blends containing completely incompatible components has restricted use due to the separation during processing. Due to inadequate interfacial adhesion, even though the material looks homogenous at first, phase separation will be observed in time for this kind of blends. Improvement of adhesion and addition of compatibilizers can be effective to overcome the immiscibility problem. Compatibilizing agents bring compatibility or miscibility permanently between otherwise immiscible or partially immiscible polymers creating homogeneous materials [3]. The most effective compatibilizing solutions are generally reactive polymers, copolymers such as block, random and graft copolymers, and nanoparticles [20-22]. For example, Walther *et al.*, evaluate the ability of nanoparticles

which have an amphiphilic anisotropic structure comprising two distinct hemispheres (Janus nanoparticles) to compatibilizer polymer blends. Organic nanoparticles were chosen based on polystyrene-block-polybutadiene-block-poly(methyl methacrylate) triblock terpolymer (SBM) to provide compatibility to polystyrene/poly(methyl methacrylate) (PS/PMMA) blends. Anionic polymerization with crosslinking of the polybutadiene core of SBM lamella process is a technique for obtaining SBM triblock polymeric nanoparticles. They showed that the Janus SBM segregate at the interface of a PS/PMMA blend and show themselves as better compatibilizers than conventional linear SBM copolymer [22], [20].

On the other hand, toughening is another terminology used for improving the polymer properties in terms of mechanical properties. For example, polystyrene can be toughened by blending with styrene-butadiene-styrene block copolymer (SBS), natural rubber, polypropylene, polyethylene and other rigid polymer components [23-26]. Explanations of toughening with several kinds of polymers and literature examples were given in detail in section 1.5.

Consequently, compatibilization of immiscible polymer blends is a very effective technique to transform usually poor multiphase blends into high performance compounds. The application of this strategy is very beneficial because it is applicable to the commercially available polymers and/or existing processing equipment. As a rule of thumb, industrial applicability of compatibilization techniques depends on many factors such as final performance, cost, biodegradability and recyclability [21].

1.5. Toughening mechanisms

Several methods have been employed to improve the toughness of polymers. Rigid-rigid polymer toughening method is one of them and this method can be applied to many different polymer systems including PPhO-modified BMI resins. It was found that PPhO could be utilized to greatly increase the toughness of thermoplastic-modified BMI resins without compromising its stiffness [27]. In another study, Wei *et al.* investigated the toughening and strengthening of polypropylene using the rigid-rigid polymer toughening concept. In this method, it is possible to improve both modulus and toughness of isotactic

polypropylene (iPP) by incorporating a rigid engineering polymer, such as polycarbonate, polyethylene terephthalate, and PPO. It was found that the fracture toughness of iPP can be significantly improved by adding rigid NORYL (a mixture of PPO and high impact polystyrene) without causing any reduction in modulus because NORYL particles can act as stress concentrators to set off cavitation mechanisms, like interfacial debonding and crazing, and to relieve the crack tip triaxial stress constraint, causing large shear bands in the iPP matrix [28]. Another approach, Sue *et al.* indicating that the backbone rigidity of the epoxy network will effect T_g and modulus of epoxy resins, just like the crosslink density does. During toughening with rubber, it was found that backbone rigidity and the crosslink density played the most important role in the toughness of the epoxy [27].

Rubber modification as a major toughening approach plays a big role because this technique can overcome the inherent brittleness of epoxy polymers. [29]. There are several toughening mechanisms for epoxy resins toughened with rubbers. Primary mechanisms are rubber cavitation and dilatational void growth during shear deformation. There are also secondary mechanisms increasing toughness, for example rubber particles bridging crack deflection, as well as crack pinning. Yahyaie *et al.* investigated the toughening mechanisms of thin film epoxy resins modified with rubbers. They synthesized an epoxy terminated polybutadiene (ETPB) to enhance the toughness of epoxy system in bulk and coating [30]. The results showed that, plastic void growth, cavitation and shear yielding mechanisms were the main toughening mechanisms of the bulk epoxy systems and the mechanical properties of the ETPB modified epoxy resins were improved considerably.

Hsieh *et al.* investigated the mechanisms and mechanics of the toughening of epoxy polymers with modified silica nanoparticles [31]. In their study, the mechanical and fracture properties of four different epoxy polymers containing 0, 10 and 20 wt.% of well-dispersed silica nanoparticles were evaluated. These polymers are: 1) Anhydride-cured DGEBA (diglycidyl ether of bis-phenol A) epoxy polymer, 2) polyether-amine cured DGEBA/F epoxy polymer (this epoxy was a blend of DGEBA and diglycidyl ether of bisphenol F (DGEBF) resins), 3) polyether-amine cured DGEBA epoxy polymer, and 4) The amine-cured TGMDA (tetra-glycidylmethylenedianiline) epoxy polymer.

As shown in Figure 1.11., considering the Young's modulus of these materials, Young's modulus of the epoxy polymers was increased with the increase of the volume fraction of the silica nanoparticles and silica nanoparticles always led to an increase in the toughness of the epoxy polymer up to a certain volume fraction [31].

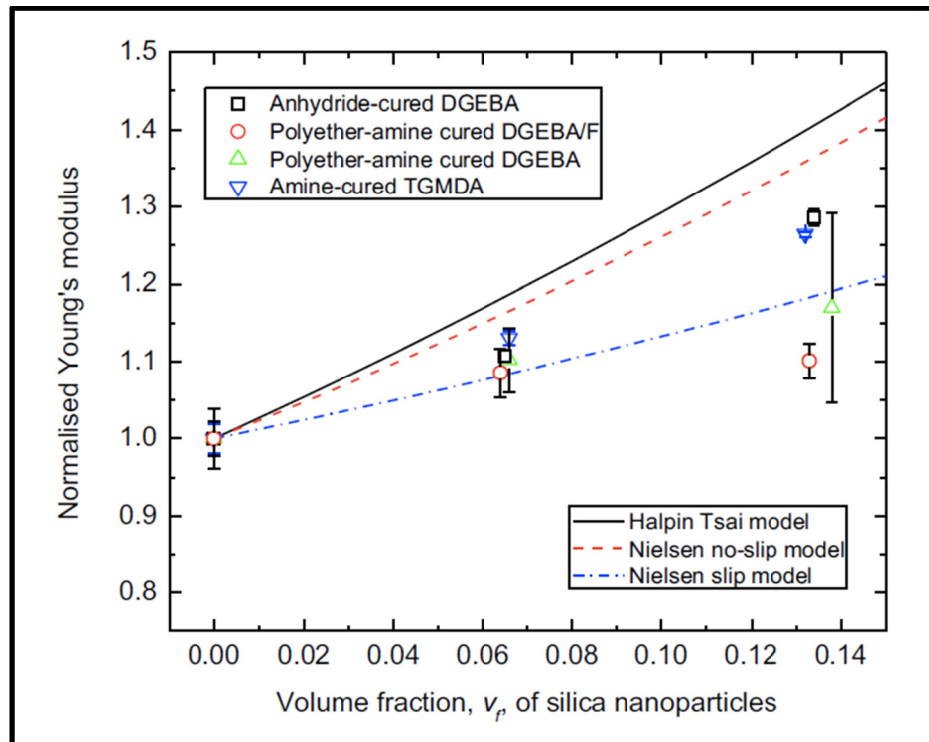


Figure 1.11. The normalized Young's modulus versus volume fraction, V_f , of silica nanoparticles for the different epoxy polymers. [31]

Although there are various toughening mechanisms that have been acknowledged by different scientists, it seems that a single theory is not adequate for understanding all the aspects of toughening mechanisms. Initial properties of the backbone polymers are very different from each other and this phenomenon makes it difficult to understand the toughening mechanisms of polymers. Consequently according to the literature, multiple crazing, shear-yielding and formation of dilatational bands following rubber cavitation or debonding from the matrix are the major toughening mechanisms of the polymer blends [32].

2. AIM OF THE STUDY

In recent years, usage of rigid polymers in our daily life has increased vastly due to their low cost in mass production, ease of recycling and wide variety of physical properties which can be further tailored for specific uses. Rigid polymers are among the most common of these commodity polymers. With the advances in nanoparticle technology, increasing the durability of polymers economically in mass production became viable through nanocomposites. In this sense, using a widely available commodity polymer like polystyrene with a highly effective nanoparticle is desirable. Since these nanoparticles are most effective when used in minor amounts, a very good dispersion of these nanoparticles throughout the matrix is required.

The ultimate aim of this research is to obtain increased mechanical properties and thermal stability by obtaining optimal dispersion through constructing 3-in-1 type co-core-shell structured reinforcer-toughener-compatibilizer for rigid polymer matrices with low cost. The crystalline PEO blocks were synthetically grafted onto maleic anhydride grafted polystyrene-*b*-poly(ethylene/butylene)-*b*-polystyrene (SEBS-*g*-MA). The grafting efficiency was followed by ^1H NMR, FTIR spectroscopic as well as gravimetric techniques. In the observation of their phase behaviors and thermal stabilities, DSC and TGA were intensively used. The graft copolymer having suitable polar sites were then reinforced with minor amount of P(AN-co-VAc) nanospheres by using high shear mixing technique in solution. Special attention were paid to emphasize the differentiative effect of expanded P(AN-co-VAc) against original one on morphology, mechanical and impact strength as well as thermal properties of the resultant structures. It is believed that nanosphere based zones will be surrounded by polyethyleneoxide chains attached to continuous nonpolar SEBS matrix by creating a reinforcer/toughener/compatilizer activity for the classic nonpolar rigid engineering polymers.

3. EXPERIMENTAL

3.1. Materials

Both SEBS-g-MA with 1.8% maleic anhydride, 30% styrene content by weight (Kraton Corporation -Houston, Texas, USA) and P(AN-co-VAc) were kindly supplied by EN-PLAST -Turkey and a research laboratory, respectively and used without further purification. THF, methanol and toluene were purchased from Merck Millipore Corporation (Darmstadt, Germany). Monomethyl ether -PEO ($M_n=2000$) was purchased from Fluka Chemical Corporation (Ronkonkoma, New York, USA)

3.2. Synthesis of PEO grafted SEBS-g-MA

PEO grafted SEBS-g-MA was synthesized with 1:2 MA:PEO mole ratios by using Dean-Stark Apparatus where water continuously removed from solution. The solutions of 20.04g of SEBS-g-MA having 1.8% MA by weight in 200 ml toluene and 14.59 g of PEO in 150 ml toluene were mixed and few drops of concentrated H_2SO_4 were added to react in Dean-Stark Apparatus at 110 °C for 12 hours (Figure 3.1.a). The mixture was precipitated in tenfold excess of methanol (Figure 3.1.b). Polymer was then repeatedly washed with methanol to get rid of excess PEO (Figure 3.1.c).



Figure 3.1. a) Synthesis, b) Precipitation and c) Washing of SEBS-g-PEO.

3.3. Expansion of Nanospheres

P(AN-co-VAc) nanospheres were cryoexpanded by first dispersing in water, freezing, and subsequent lyophilization techniques [33]. The typical procedure is described below. P(AN-co-VAc) (1 g) was well dispersed in 20 mL water at 50°C for 2 h, and then the solution was cooled to -22°C overnight in a freezer and dried via lyophilization at -45°C.

3.4. Preparation of SEBS-g-MA and SEBS-g-PEO Nanocomposites

SEBS-g-MA or SEBS-g-PEO was dissolved in THF with an elastomer to solvent ratio of 1:8 and solution was added to the dispersion having % 1 nanoparticle in THF. Initially by magnetic stirrer with 700 rpm for 2 hours then by High Shear Mixer (Figure 3.2) with 1500 rpm 3 times for 2 minutes. Prepared composites were then solvent casted in 5x5x1 cm Teflon molds at room temperature for 2 days and dried under vacuum to remove last traces of solvent.



Figure 3.2. High shear mixer.

3.5. In-situ Synthesis of Polystyrene / SEBS-g-MA and SEBS-g-PEO Nanocomposites

Styrene was first vacuum distilled over calcium hydride under inert nitrogen atmosphere. Five different compositions given in Table 3.1 having 80/20 Polystyrene/ PEO grafted SEBS-g-MA shelled P(AN-co-VAc) nanospheres were prepared by in-situ polymerization of styrene monomer.

Table 3.1. Compositions of co-coreshell nanocomposites.

Nomenclature	Composition
Neat PS	100% Polystyrene
PS/ SEBS-g-MA 1% P(AN-co-VAc)	80% Polystyrene, 20% SEBS-g-MA including 1% P(AN-co-VAc)
PS/ SEBS-g-PEO 1% P(AN-co-VAc)	80% Polystyrene, 20% SEBS-g-PEO including 1% P(AN-co-VAc)
PS/ SEBS-g-MA 1% XP(AN-co-VAc)	80% Polystyrene, 20% SEBS-g-MA including 1% XP(AN-co-VAc)*
PS/ SEBS-g-PEO 1% XP(AN-co-VAc)	80% Polystyrene, 20% SEBS-g-PEO including 1% XP(AN-co-VAc)

* X refers to expanded nanospheres,

20% by weight PEO Grafted SEBS-g-MA shelled nanocomposites having 1 % nanoparticles was first dispersed in styrene monomer (80% by weight) overnight , then AIBN (1% by weight of styrene monomer was added to mixture above and in-situ polymerization was conducted at 65°C under inert nitrogen atmosphere for 24 hours. Resultant nanocomposites were vacuum dried.

Prepared nanocomposites were then compression molded in steel molds with 1x4 cm dimensions and 1mm thickness by using a hot press (Figure 3.3.) operating at 200°C with 6 minutes heating followed by 2 minutes cooling cycle under 120 bar pressure .



Figure 3.3. Hot press and molds used for compression molding.

3.6. Characterizations

3.6.1. Structural Characterization (^1H NMR and FTIR)

Proton Nuclear Magnetic Resonance (^1H -NMR) measurements were conducted with Varian Gemini 400 MHz spectrometer using d-THF at room temperature. Thermo Scientific Nicolet 380 FTIR Spectrometer equipped with a diamond ATR accessory was used for qualitative grafting efficiency evaluations by using Essential FTIR[®] Spectroscopy Toolbox.

3.6.2. Thermal Characterization (TGA and DSC)

Thermogravimetric Analysis (TGA) of samples are done by TGA-Q50 TA Instruments (TA Instruments, New Castle, DE, USA) under inert nitrogen atmosphere flow from the room temperature to 600°C at a rate of 10°C/min.

Differential Scanning Calorimeter (DSC) (TA Instruments, New Castle, DE, USA) was also used to investigate the phase transitions of samples between -90°C and 200°C temperature ranges with a heating rate of 10 °C/min under inert nitrogen flow.

3.6.3. Dynamic Mechanical Characterization (DMA)

The Dynamic mechanical analyses (DMA) of nanocomposites are done by using the DMA-Q8000 TA instrument (TA Instruments, New Castle, DE, USA) in single-cantilever mode with a 1Hz frequency and 5°C/min heating over a temperature range -90°C to 130°C.

3.6.5. Static Mechanical Characterization (Universal Tensile Testing)

Static mechanical tests were performed by using a Zwick / Roell Z1.0 Universal Testing Instrument (Zwick GmbH & Co.KG, Germany). Test specimens were prepared in the dimensions (t x w x l) 0.1 x 1 x 4 cm and drawn with a drawing rate of 5mm/min. Tensile strength, Elongation at break value, Elastic modulus and Work up to break (Toughness) values were determined by using Zwick/Roell testXpert II software.

3.6.6. Morphological Characterisation (SEM and STEM)

Morphological characterization of nanocomposites in terms of both fracture and normal surfaces are done by the instrument ESEM-FEG/EDAX Philips XL-30 (Philips, Eindhoven, The Netherlands) with an accelerated voltage 5,00, 7,00 and 10,00 kW.

Co-coreshell nanocomposite films were also sectioned by ultra-microtome and analyzed by using the same instrument with a STEM detector.

4. RESULTS AND DISCUSSION

4.1. Synthesis and Characterisation of PEO grafted SEBS-g-MA

PEO was grafted onto SEBS-g-MA backbone via hydrolysis reaction given in Scheme 4.1.

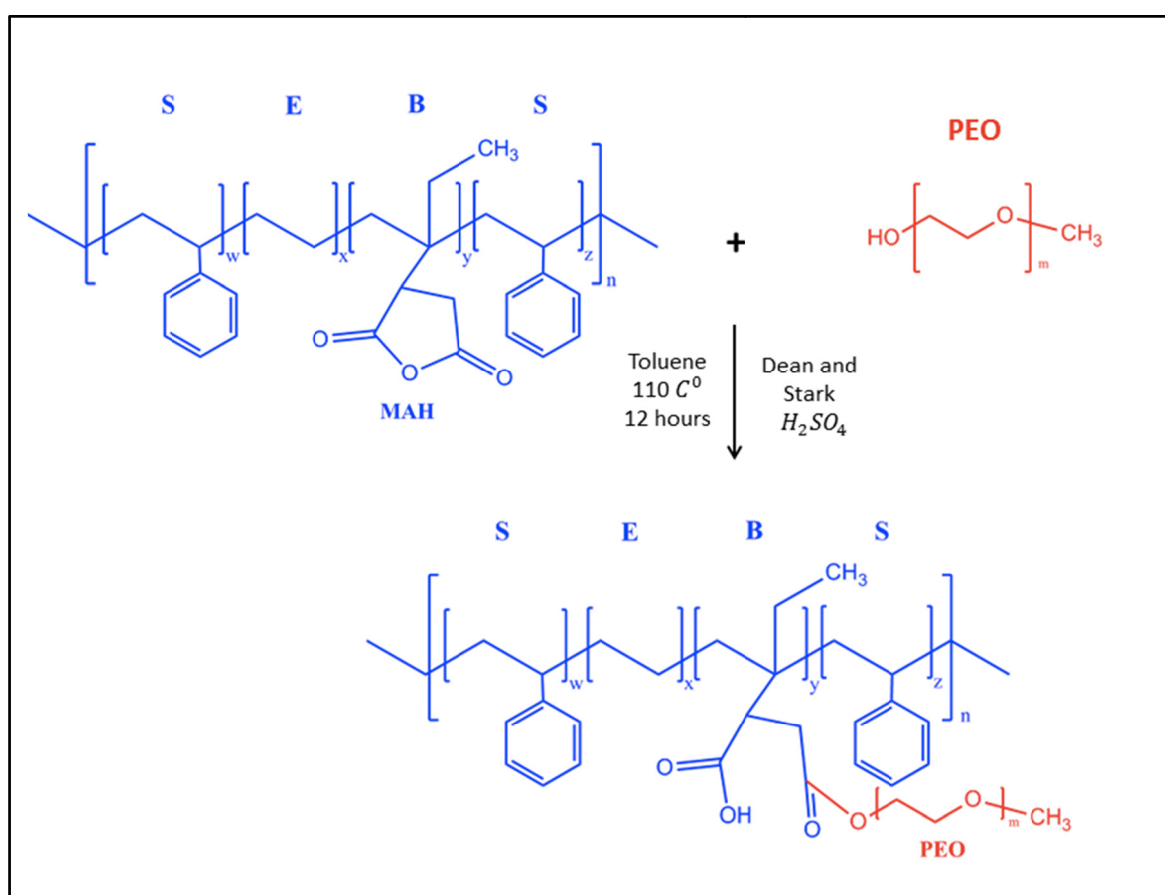


Figure 4.1. Grafting reaction of SEBS-g-MA with PEO.

Grafting was characterized by following the carboxylic acid and ester groups forming as a result of hydrolysis and maleic anhydride ring opening reactions in the presence of PEO and with FTIR spectra of both SEBS-g-MA and SEBS-g-PEO are given in Figure 4.2. Appearance of carboxylic acid peak at 1350 cm^{-1} after grafting reaction can be accepted as another confirmation of the ring opening reaction and formation of acid groups [34].

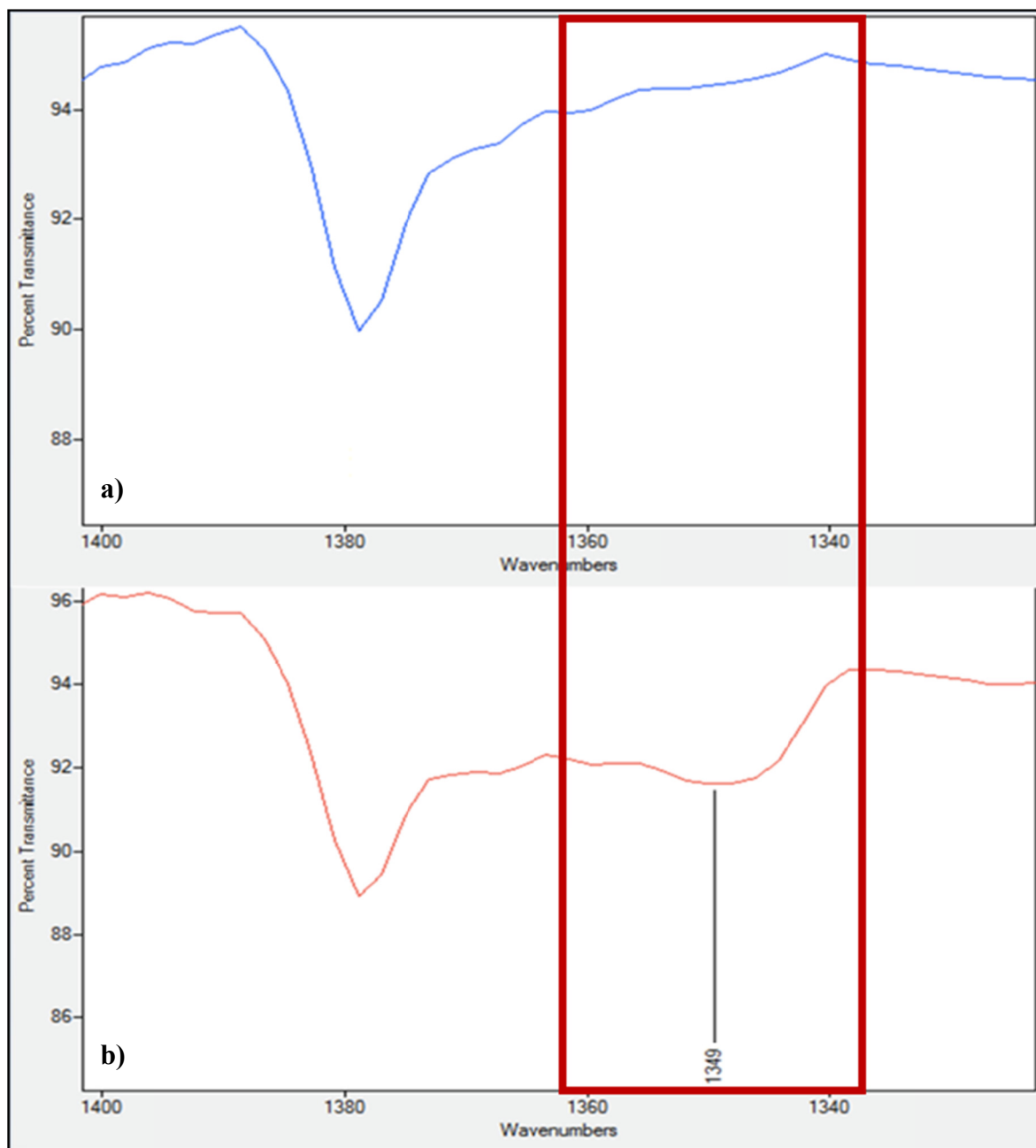


Figure 4.2. FTIR spectra of a) SEBS-g-MA, b) SEBS-g-PEO between wavenumbers of 1320- 1400 cm^{-1} .

Moreover, Figure 4.3. shows that the presence of 1738 -1741 cm^{-1} ester peaks in the spectrum of SEBS-g-PEO confirms the existence of PEO grafting in the structure. [35].

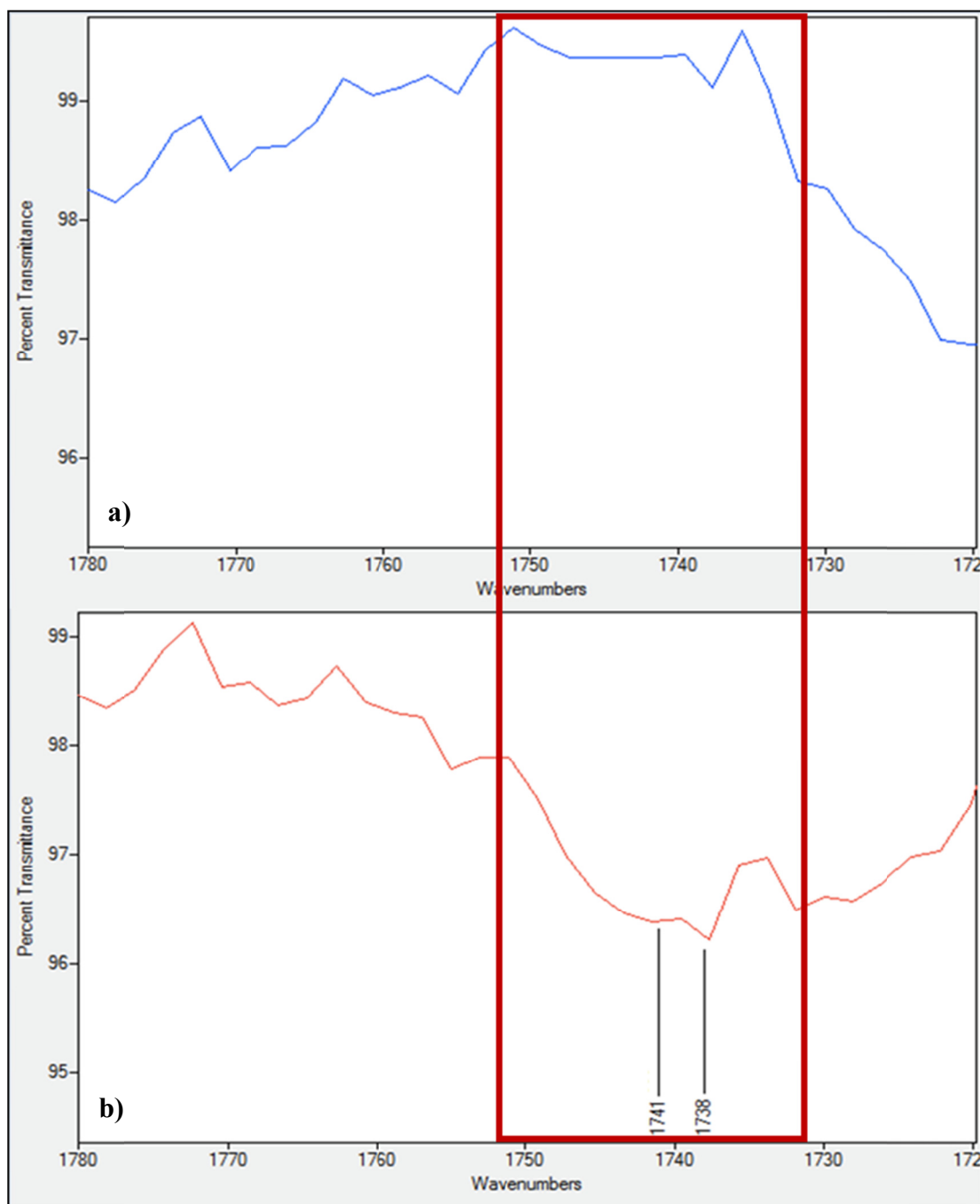


Figure 4.3. FTIR spectrums of a) SEBS-g-MA, b) SEBS-g-PEO between wavenumbers of 1720- 1780 cm^{-1} .

^1H NMR spectra of both SEBS-g-MA and SEBS-g-PEO are given in Figure 4.4 (a and b), respectively. In Figure 4.4 b, a new peak appearing at 3.5 ppm belongs to PEO protons [36] and at the same time confirms the successful grafting of PEO on to SEBS-g-MA chains. The grafting efficiency of PEO chains onto SEBS-g-MA was also calculated as 22.37% by using ^1H NMR peaks integration method [37-39]. Integral areas of PEO protons and benzylic protons of polystyrene were compared and grafting efficiency was calculated by using following formula;

X : Peak Intensity Y: Proton Number Z: Weight Percent M: Molecular Weight

$$\% \text{ Grafting Efficiency} = \frac{X_{\text{PEO}} \times Z_{\text{PS}} \times Y_{\text{PS}} \times M_{\text{MA}} \times 100}{Y_{\text{PEO}} \times Z_{\text{MA}} \times M_{\text{S}} \times \text{DPn}_{\text{PEO}} \times X_{\text{PS}}}$$

Weight percent of MA in SEBS-g-MA = 1.8

Weight percent of PS in SEBS-g-MA = 30

$M_{\text{EO}} = 44 \text{ g/mol}$ $M_{\text{S}} = 104 \text{ g/mol}$ $M_{\text{MA}} = 99 \text{ g/mol}$ $M_{\text{PEO}} = 2000$

$\text{DPn}_{\text{PEO}} = 2000 / 44 = 45.45$

$$\text{Grafting Efficiency} = \frac{243,98 \times 30 \times 5 \times 99 \times 100}{4 \times 1.8 \times 99 \times 45.45 \times 500}$$

$$\text{Grafting Efficiency} = 22.37 \%$$

It can be stated that almost 23 % of MA groups in SEBS-g-MA chains were grafted with PEO.

Thermal transitions of SEBS-g-MA and SEBS-g-PEO were followed by DSC technique (Figure 4.5). Two endotherms at temperatures of 13.61°C and 38.28°C belonging to ethylene butylene crystalline regions [9] broadens in SEBS-g-PEO polymer which is most probably due to disturbance of the crystallinity via PEO grafting [40]. Tg of PS block was found be much lower than that of PS homopolymer (around 100 °C) due to the plastifying effect of flexible polyethylene-polybutylene units [41] , as well as low PS content (30 %) in SEBS-g-MA.

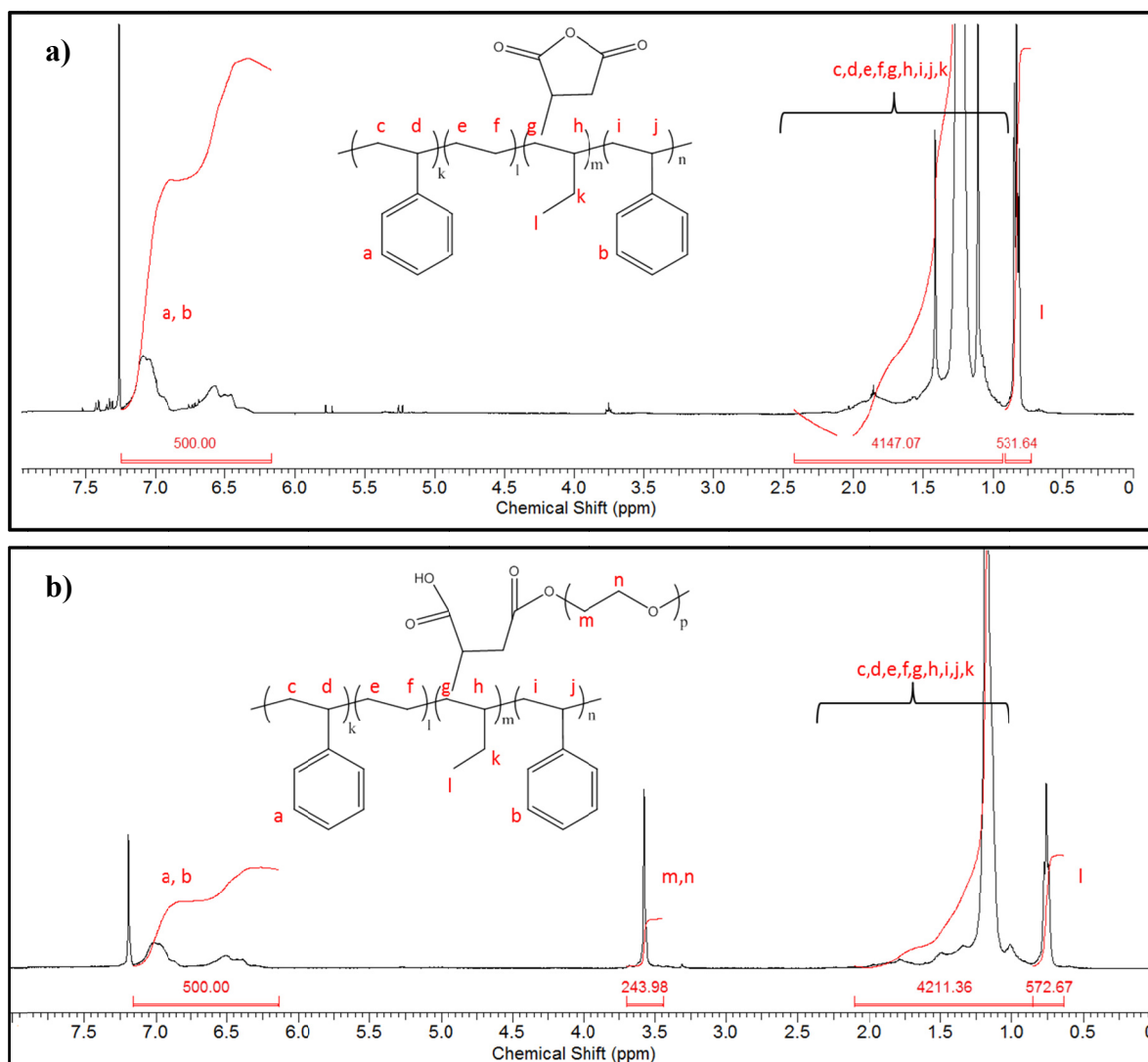


Figure 4.4. ¹H NMR Spectrums of a) SEBS-g-MA, b) SEBS-g-PEO

On the other hand, T_g value of ethylene-butylene unit in SEBS-g-MA (-52.3 °C) shifted to -50 °C in SEBS-g-PEO due to possible H-bonding between carboxylic acid groups and PEO units of polymer molecules restricting chain mobility. Also melting peak temperature of PEO polymer appears at 48 °C in the SEBS structure as a confirmation of PEO grafting. It was lower than that of PEO homopolymer (around 55 °C) which may be ascribed to disturbance of PEO crystallinity by the existence of other comonomers [42].

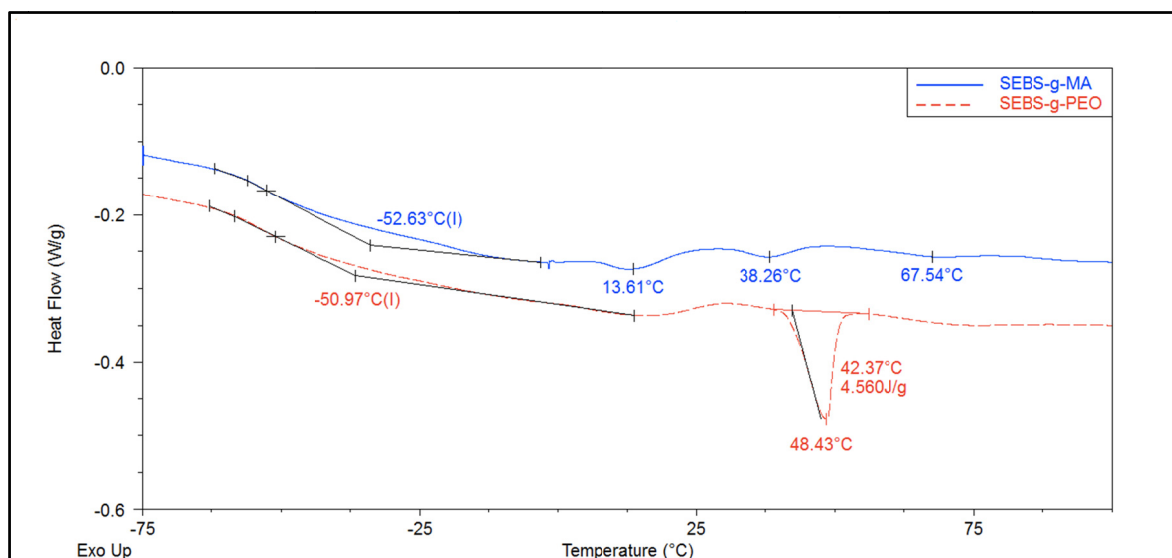


Figure 4.5. DSC Thermograms of SEBS-g-MA and SEBS-g-PEO.

4.2. Preparation and Characterization of SEBS-g-MA and SEBS-g-PEO Nanocomposites

Agglomeration of nanoparticles in the matrix is the main reason that causes phase separation and decreased mechanical properties. Both rupture and erosion on large agglomerates can be observed using traditional mixing methods, but sub-micron aggregates cannot be broken into single nano-particles even at the highest energy input and at the highest repulsive interparticle forces, using traditional mixing methods. High shear mixing is a recent method to disturb sub-micron agglomerates into individual nanoparticles by both high shear rate and two dimensional rotations (Section 3.4.) [43]. In this study, high shear mixer was used to provide homogenous dispersion of nanoparticles in the structure.

PEO grafts are randomly distributed on SEBS-g-MA backbone with 22% grafting efficiency as discussed in Section 4.1. These grafted chains has polar “-CH₂CH₂O-” groups in their structure and P(AN-co-VAc) is also a highly polar material due to CN groups in its structure as discussed in Section 1.3.2. It is believed that formation of carboxylic acid on SEBS-g-PEO resulted from the grafting reaction is another advantage in terms of extra interactions sites for nanospheres. Due to those specific interactions given in the Figure 4.6., PEO chains are expected to surround both P(AN-co-VAc) and XP(AN-co-VAc)

nanospheres by dipole-dipole interactions and hydrogen bonding between PEO chains and nanospheres as well as between carboxylic groups and nanospheres.

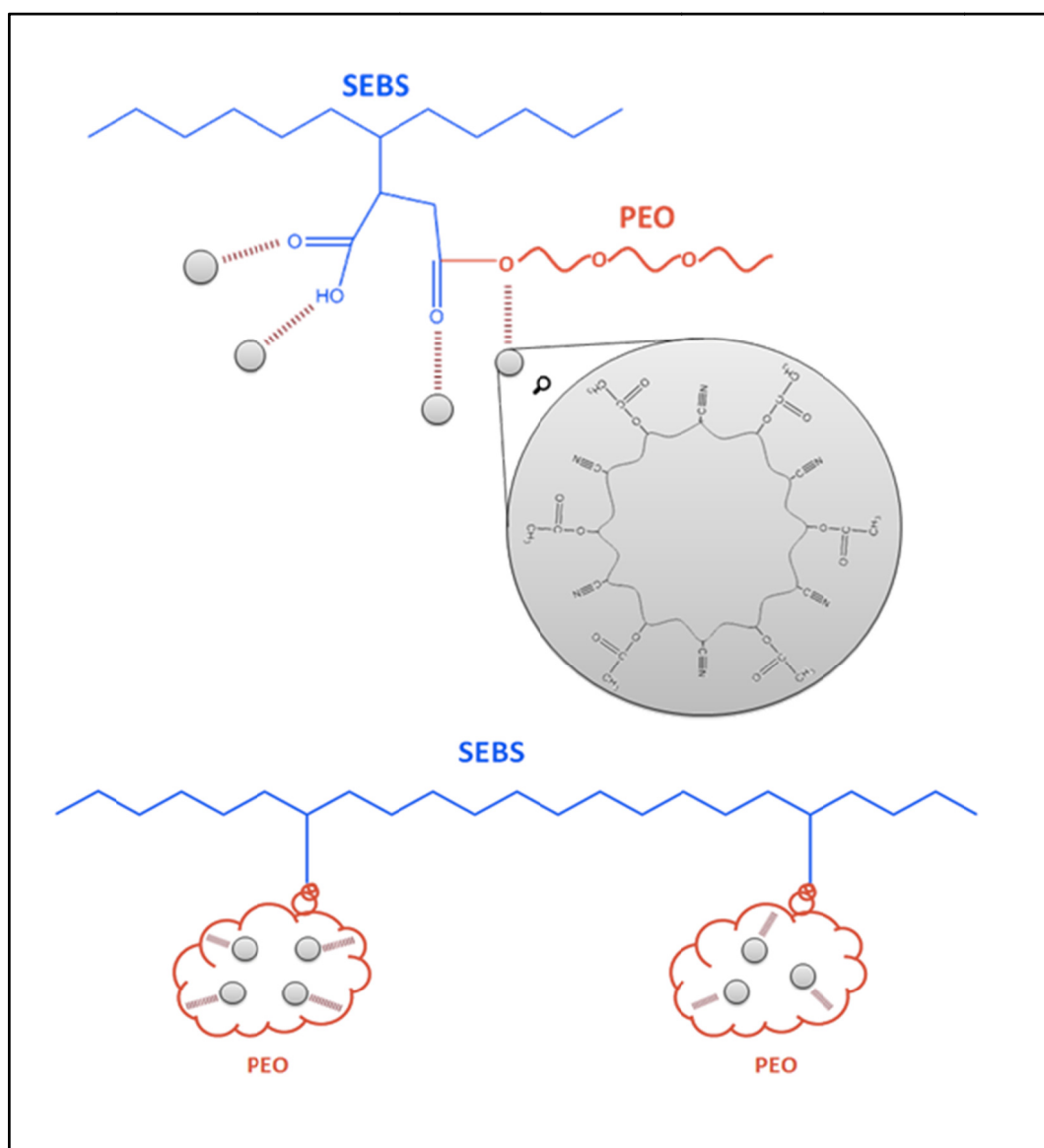


Figure 4.6. Representative schemes of interactions between PEO chains and nanospheres and resultant morphology.

Both schematic representations of predicted structures as well as surface morphologies of solvent casted films of SEBS-g-PEO with 1% P(AN-co-VAc) and 1% XP(AN-co-VAc) are given in Figure 4.7 where blue matrix refers to SEBS, red chains refer to the PEO chains and spheres are the P(AN-co-VAc) in both non-expanded (Figure 4.7.a) and expanded (Figure 4.7.c) forms. SEM images taken from the surface of the solvent casted films of the resultant structures are given in Figure 4.7.b and d.

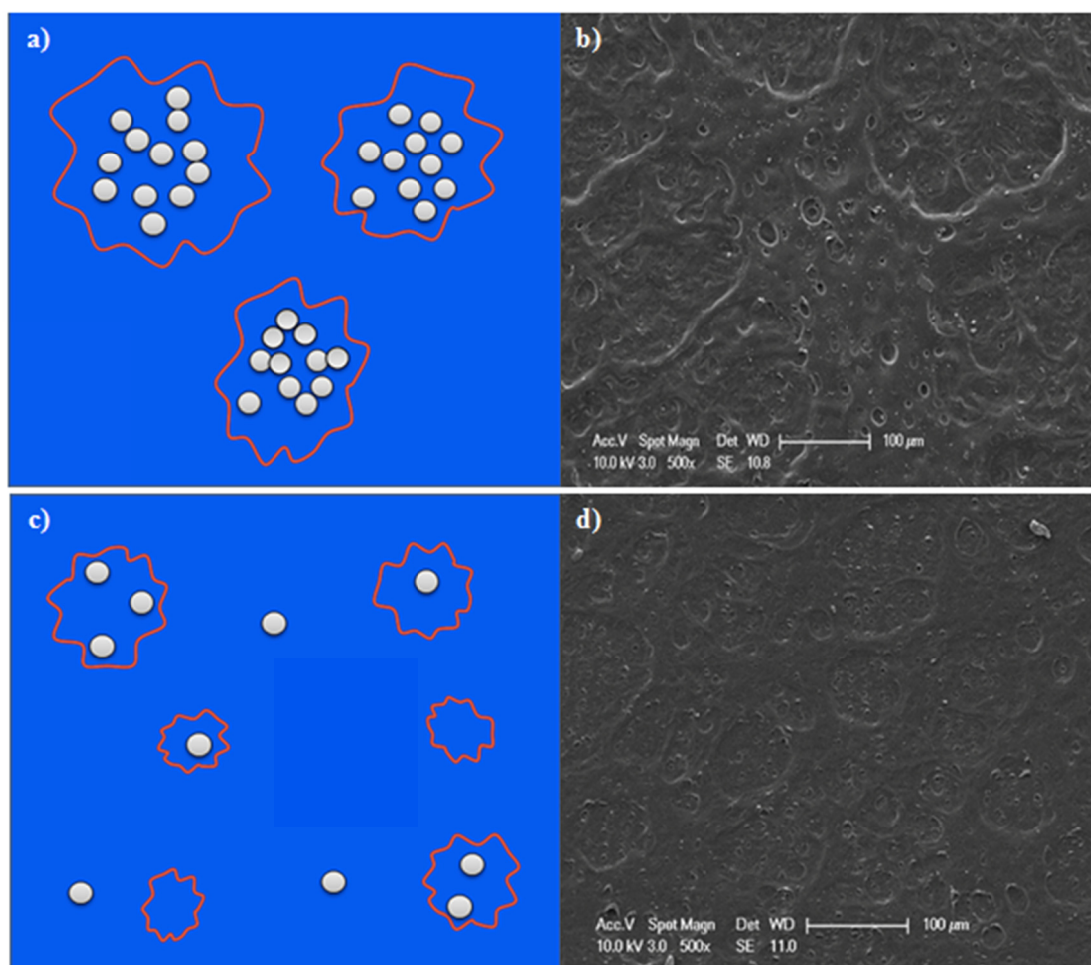


Figure 4.7. Predicted and surface structures of a) SEBS-g-PEO with 1% P(AN-co-VAc), c) SEBS-g-PEO with 1% XP(AN-co-VAc) and SEM images of b) SEBS-g-PEO with 1% P(AN-co-VAc), d) SEBS-g-PEO with 1% XP(AN-co-VAc), respectively.

The formation of co-coreshell domains in SEBS matrix can be clearly seen in the images confirming the suitability of the assumptions in the predicted schemes. Moreover, there is a noticeable difference between co-coreshells prepared with non-expanded and expanded form of P(AN-co-VAc) nanospheres. 200-300 micron sized heterogeneously distributed cores including 10-20 micron co-coreshell structures in SEBS-g-PEO 1% P(AN-co-VAc) (Figure 4.7.b) turns into homogeneous dispersion of smaller co-coreshells (50-100 micron) in SEBS-g-PEO 1% X P(AN-co-VAc) (Figure 4.7.d). It can be safely stated that expansion of nanosphere aggregates into smaller individuals provides homogenous distribution of them in the matrix which then resulting in smaller co-coreshells in the structure. The expansion seems to be particularly effective in preventing

agglomeration of the spheres. This beneficial effect of cryoscopic expansion of nanotubes was first reported by our group [33]. It has been found that expansion of halloysite nanotubes resulted in their enhanced dispersion in hydrogel matrix without agglomeration. The process simply involves penetration of water molecules between polar P(AN-co-VAc) nanospheres and separates them by increasing the volume of water during freezing process.

Fracture surface morphology is accepted as another important indicator to prove the dispersion quality of nanospheres and to verify the co-coreshells structures in the matrix. The distribution of cavities that are formed due to nanosphere extraction from this area during fracture is an indication of size of domains, homogeneity in distribution and co-coreshell verification [44].

The cavity structures on the fractured surfaces of both SEBS-g-MA and SEBS-g-PEO were examined by SEM analyses and resultant images are given in Figure 4.8 and 4.9, respectively, to determine the effect of both PEO grafting and expansion process of P(AN-co-VAc) nanospheres.

Better, more homogeneous nanoparticle dispersion with smaller domains in SEBS-g-MA was observed with expanded P(AN-co-VAc) nanospheres, leading to flexible PEO surrounded nanoparticle oriented fibrous fracture as it is seen in the SEM images of the fracture surfaces (Figure 4.8.).

In the Figure 4.9 a, b and c, PEO surrounded P(AN-co-VAc) aggregates seems to leave behind 6-10 micron sized large holes after fracture. However, those holes were found to be much smaller and better dispersed in XP(AN-co-VAc) due to homogeneous distribution of XP(AN-co-VAc) surrounded PEO as it is shown in Figure 4.9.d, e and f.

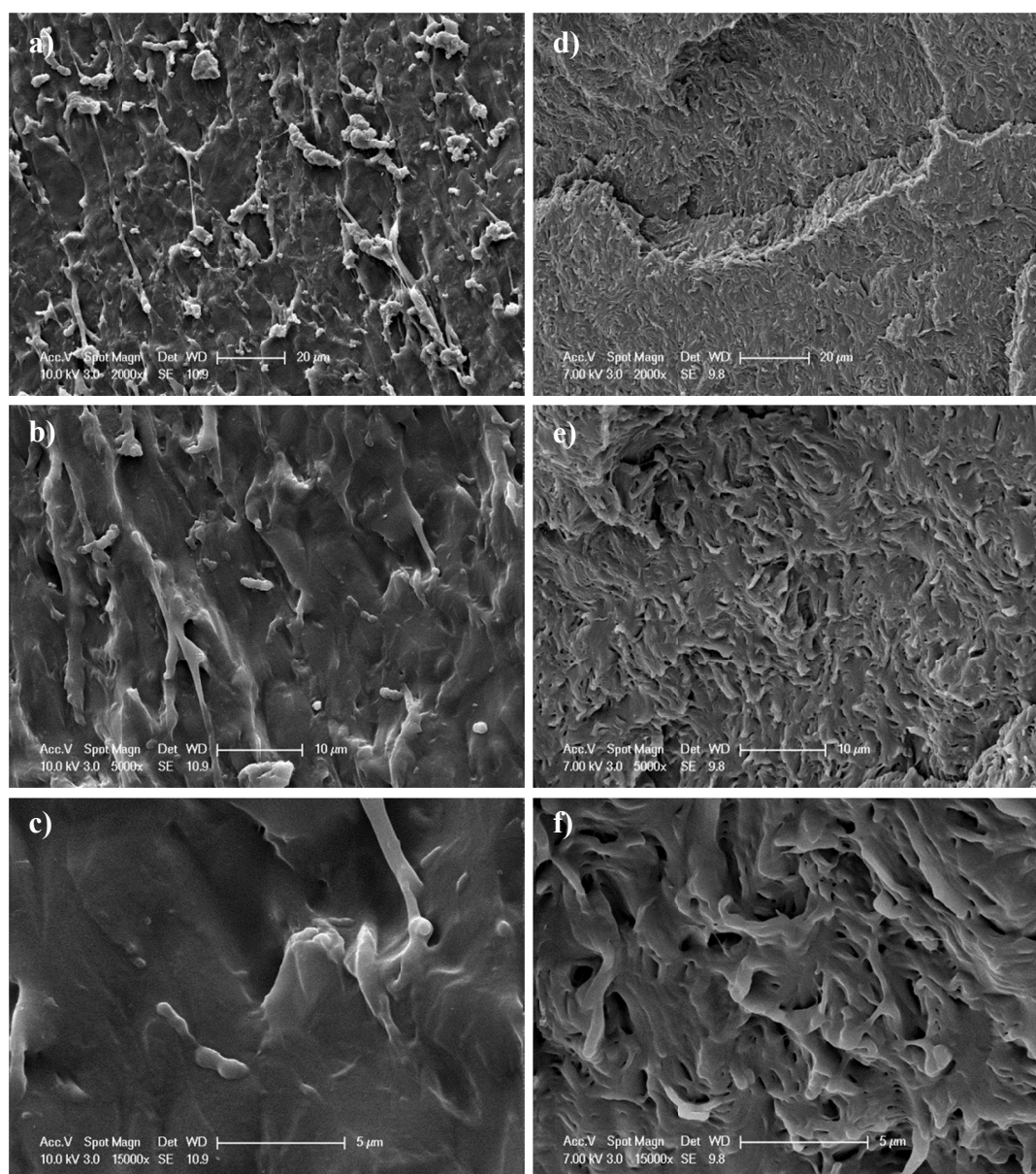


Figure 4.8. Fracture surface SEM images of a) b) c) SEBS-g-MA with 1% P(AN-co-VAc), d) e) f) SEBS-g-MA with 1% XP(AN-co-VAc) with x2000, x5000, x15000 magnifications respectively.

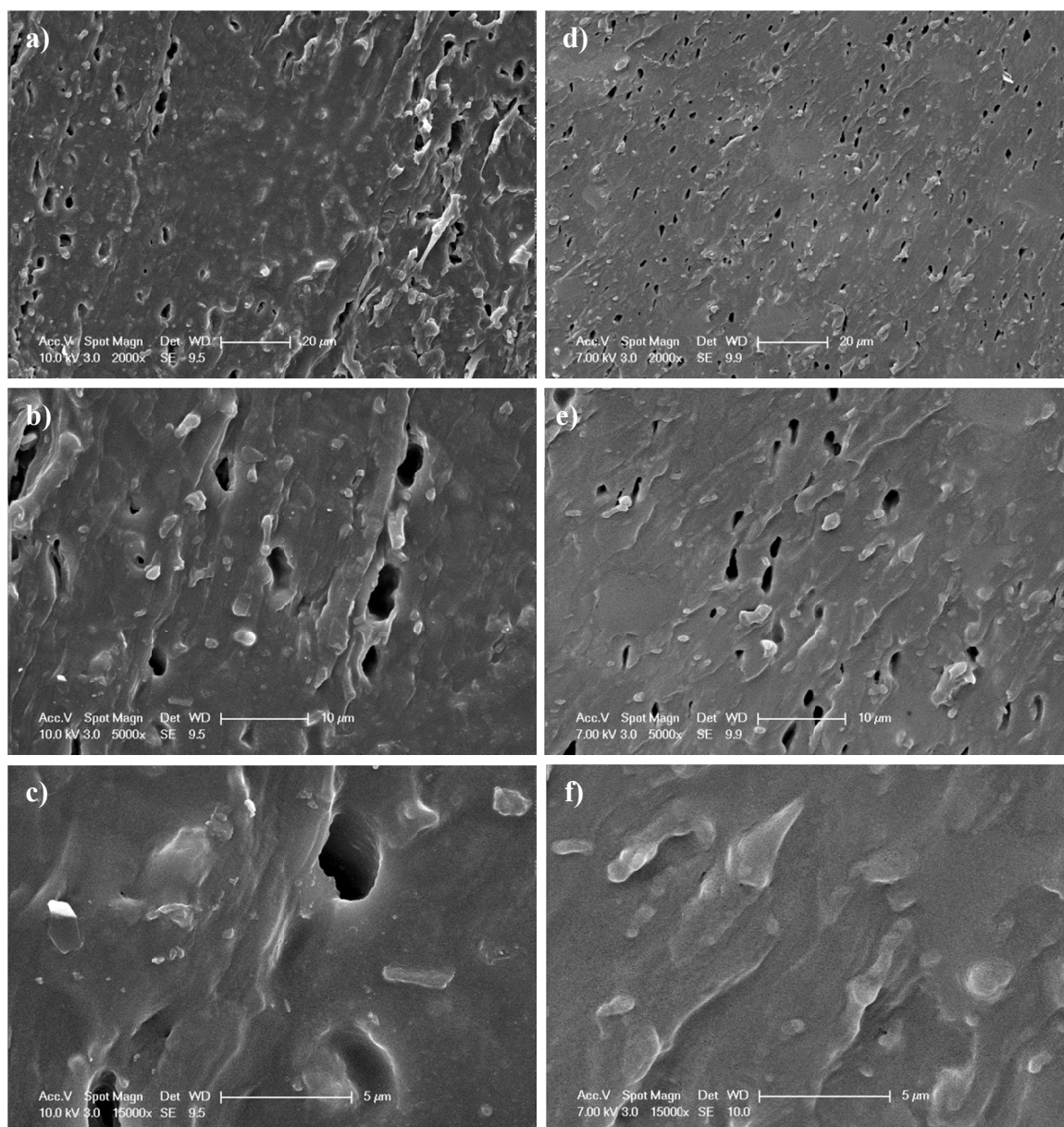


Figure 4.9. Fracture surface SEM images of a) b) c) SEBS-g-PEO with 1% P(AN-co-VAc), d) e) f) SEBS-g-PEO with 1% XP(AN-co-VAc) with x2000, x5000, x15000 magnifications respectively.

In order to determine both thermal stability and flame retardancy properties of the P(AN-co-VAc) and XP(AN-co-VAc) nanosphere containing SEBS-g-MA and SEBS-g-PEO elastomers thermogravimetric analyses were conducted. The degradation onset temperature of the materials gives an idea about their thermal stabilities. Also the residue of materials is an indicator for their flame retardancy properties [45].

TGA data; onset degradation temperature, residue percent and degradation rate values are all given in Table 4.1. The TGA thermograms are presented in Figure 4.10. and Figure 4.11.

Table 4.1. TGA results in terms of onset temperature, T_{10} , residue and degradation rate.

Sample	T_{onset} ($^{\circ}\text{C}$)	T_{10} ($^{\circ}\text{C}$)	Residue (%)	Degradation Rate (%.min/$^{\circ}\text{C}$)
PEO	402,14	371,16	1,03	9,75
SEBS-g-MA	419,14	409,84	0,72	9,82
SEBS-g-PEO	414,40	383,13	0,45	9,46
SEBS-g-MA 1% P(AN-co-VAc)	417,53	406,19	1,01	9,37
SEBS-g-PEO 1% P(AN-co-VAc)	421,96	413,51	0,66	9,50
SEBS-g-MA 1% XP(AN-co-VAc)	427,00	421,78	0,81	9,54
SEBS-g-PEO 1% XP(AN-co-VAc)	416,59	399,59	1,35	9,22

From the TGA results given in Table 4.1 and., it can be seen that although P(AN-co-VAc) nanosphere addition to SEBS-g-MA causes negligible decrease in onset T , and T_{10} , the addition of XP(AN-co-VAc) (Figure 4.10.) significantly increases onset T , T_{10} most probably due to the enhanced polar interactions in latter structure [46] . Decrease in degradation rate as well as increase in residue with abovementioned addition may be attributed to both inherent high stability of PAN based materials and tortuous paths in the structures inhibiting diffusion of the degradation products from the system [46].

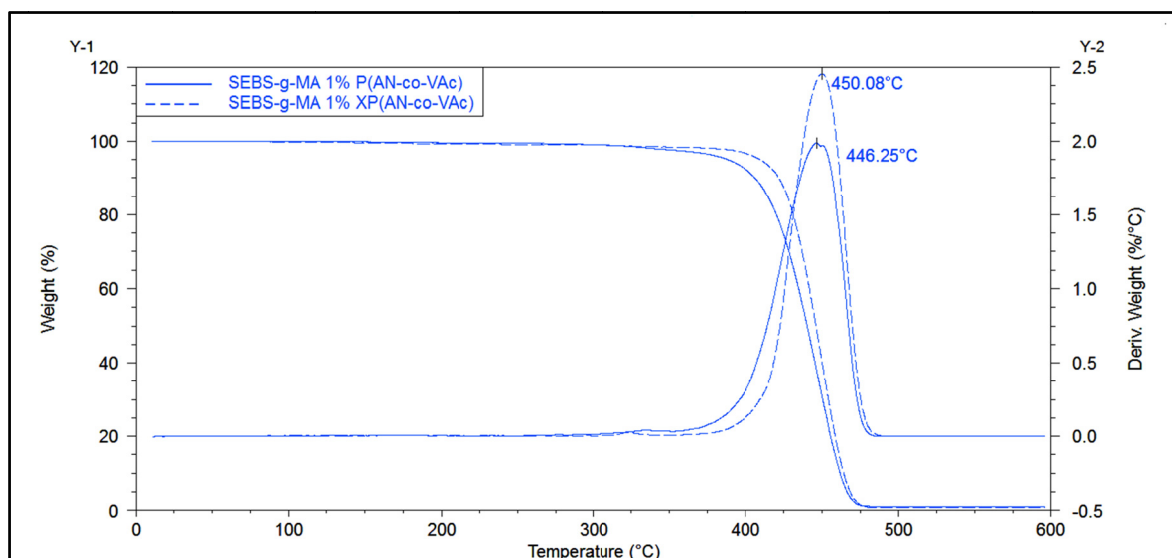


Figure 4.10. TGA Thermograms of SEBS-g-MA 1% P(AN-co-VAc) and SEBS-g-MA 1% XP(AN-co-VAc).

On the other hand, nanosphere addition to SEBS-g-PEO in each cases (expanded or non-expanded forms) (Figure 4.11) cause an increase in the thermal stability in terms of both onset degradation temperature and degradation rate as compared to virgin PEO grafted copolymer.

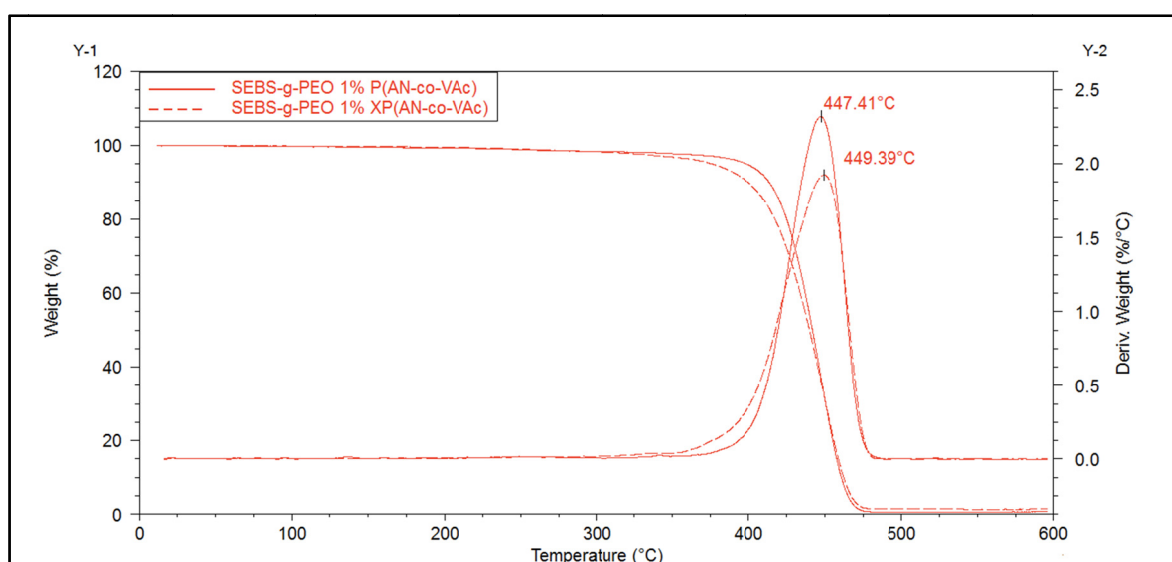


Figure 4.11. TGA Thermograms of SEBS-g-PEO 1% P(AN-co-VAc) and SEBS-g-PEO 1% XP(AN-co-VAc).

Moreover, in the presence of XP(AN-co-VAc) nanospheres this copolymer exhibits the highest residue at 600 °C because of the most tortuous pathway containing special morphology . It seems that the usage of expanded nanoparticles can be accepted as a highly effective way increasing flame retardancy of SEBS-g-PEO graft copolymer.

DSC analysis is known to be an effective method to determine the change in thermal transitions in material due to the change in structure. Glass transition temperature, crystalline melting temperature and crystallinity related peak endotherms for SEBS-g-MA and SEBS-g-PEO matrices with P(AN-co-VAc) or XP(AN-co-VAc) nanospheres are all given in Table 4.2. and Figures 4.12. and 4.13.

Table 4.2. DSC results in terms of T_g, T_g Range, T_m, peak endotherm.

Sample	T_g (°C)	T_g Range (ΔT_g) (°C)	T_m (°C)	Peak Endotherm (ΔH) (J/g)
SEBS-g-MA	-52,63	22,11	-	-
SEBS-g-PEO	-50,97	21,88	48,43	4,56
SEBS-g-MA 1% P(AN-co-VAc)	-46,74	26,28	-	-
SEBS-g-PEO 1% P(AN-co-VAc)	-48,32	24,93	46,34	3,18
SEBS-g-MA 1% XP(AN-co-VAc)	-48,15	21,49	-	-
SEBS-g-PEO 1% XP(AN-co-VAc)	-48,22	28,70	50,79	7,95

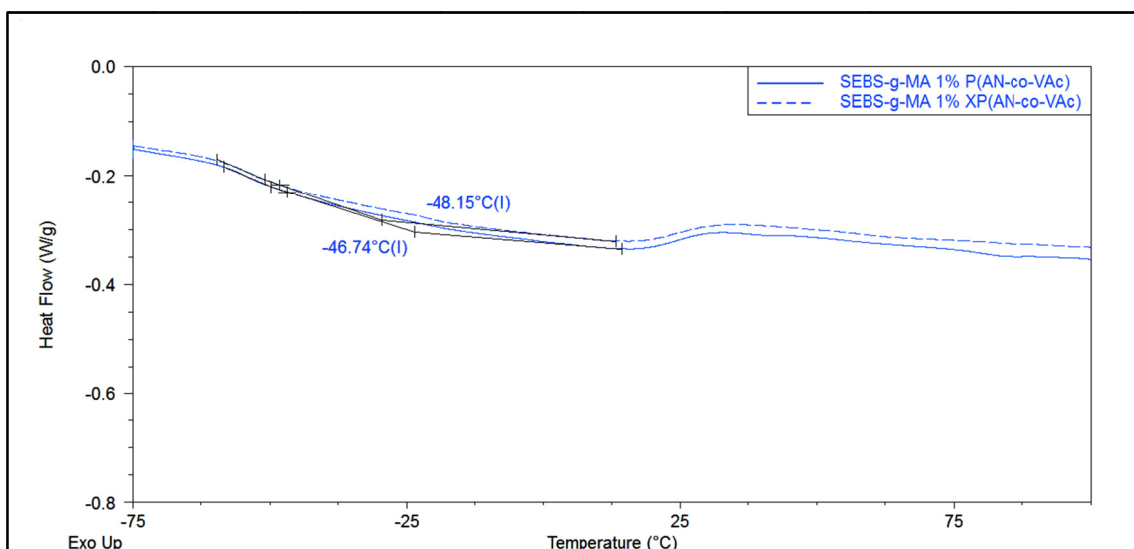


Figure 4.12. DSC Thermograms of SEBS-g-MA 1% P(AN-co-VAc) and SEBS-g-MA 1% XP(AN-co-VAc).

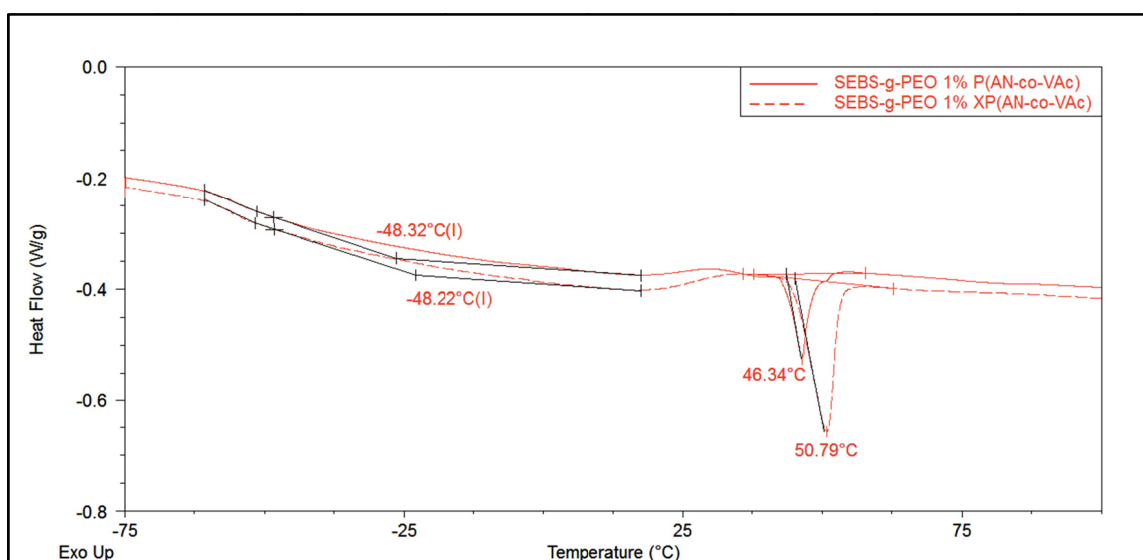


Figure 4.13. DSC Thermograms of SEBS-g-PEO 1% P(AN-co-VAc) and SEBS-g-PEO 1% XP(AN-co-VAc).

As it can be seen from the Table 4.2 and the Figures 4.12 and 4.13, nanosphere addition to the both SEBS-g-MA and SEBS-g-PEO matrices increases the glass transition temperature range of SEBS-g-PEO due to extra and extensive interchain interactions coming with PAN based spheres which then leading to multiple relaxation zones. Those then provide a longer phase transition temperature range to the matrices. The longest glass transition temperature range which can be addressed to abovementioned multiple relaxing

zones was obtained by using XP(AN-co-VAc) in SEBS-g-PEO matrix as it is shown in Table 4.2. This characteristics of latter structure can be accepted as a credit since it is well known that polymers exhibit their maximum performances around their glass transition temperatures so larger the transition range better the performance [47].

Moreover, when peak endotherms of SEBS-g-PEO matrix are compared, a 30% decrease was observed in presence of P(AN-co-VAc). However, a 74% increase was observed in the presence of XP(AN-co-VAc) in the matrix. Although addition of P(AN-co-VAc) causes a decrease in crystalline melting peak area due to disturbance in the crystallinity of PEO [48], most interestingly, expanded P(AN-co-VAc) gives rise to an increase in the crystallinity, due to better dispersion oriented nucleation effect [49].

4.3 In-situ Synthesis and Characterization of Polystyrene / SEBS-g-MA and SEBS-g-PEO Nanocomposites

Co-coreshell based PS Nanocomposites are prepared throughout mainly four successive steps as represented in Figure 4.14.

It is known that multiple component blends form co-coreshell morphologies depending on the polarity gradient and specific interchain interactions connect the phases to each other. In our case, it is assumed that polar P(AN-co-VAc) nanospheres are the inner part of the co-coreshell structure, second layer of the co-coreshells is the PEO chains that surround nanospheres, third and outermost layer of the co-coreshell structure is the SEBS-g-MA backbone which surround grafted PEO chains with nanospheres in it. This co-coreshell structure is very well dispersed in nonpolar polystyrene matrix due to the common component polystyrene in both PS and SEBS-g-MA resulting in high compatibility. The idealized structure is given in Figure 4.15. The beauty of the system is coming from the existence of the covalently bonded bridges between each layers via grafting which inhibiting the extensive phase separation and forming smaller domains.

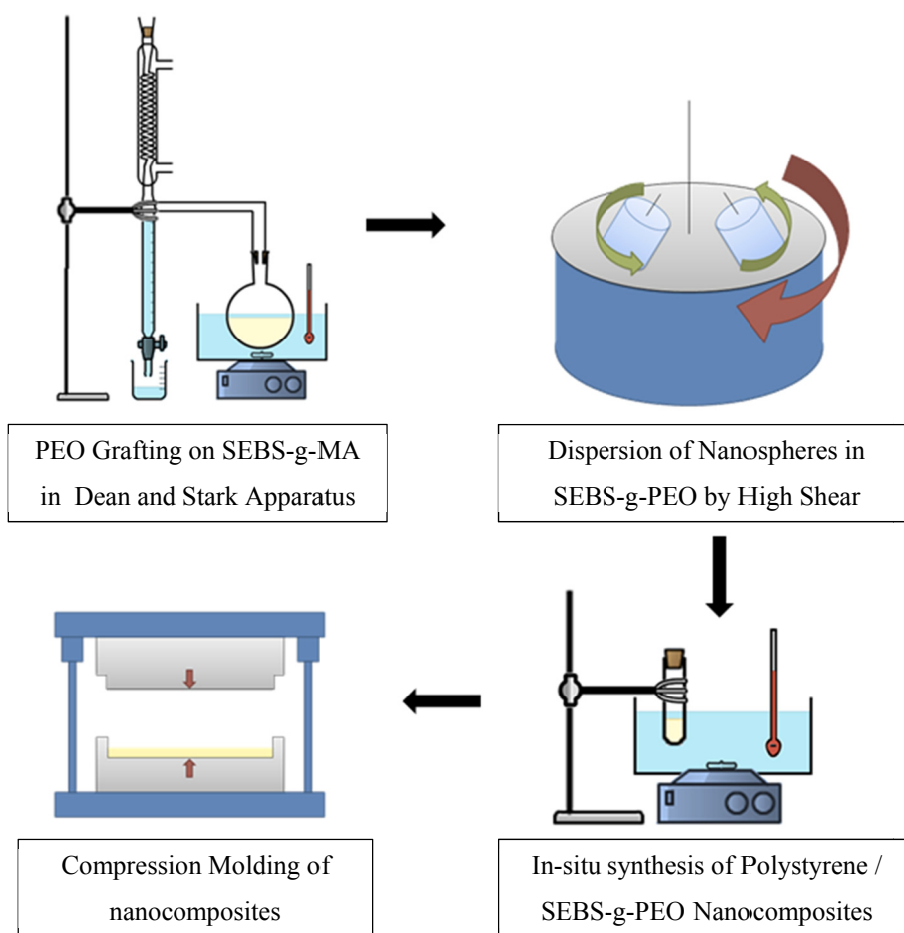


Figure 4.14. Schematic representation of the whole process.

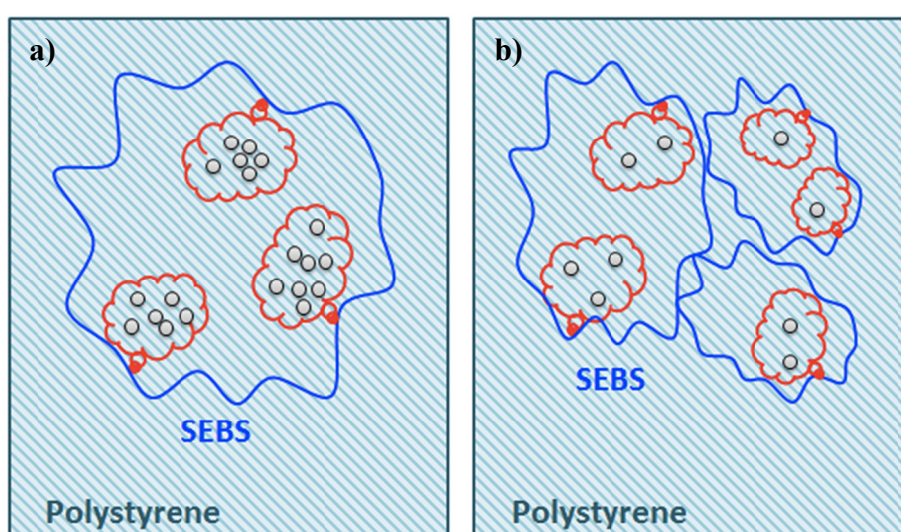


Figure 4.15. Idealized morphologies of co-coreshell structures in PS matrix with
a) P(AN-co-VAc) and b) XP(AN-co-VAc) nanospheres.

Selected neat PS, PS / SEBS-g-MA 1% XP(AN-co-VAc) and PS / SEBS-g-PEO 1% XP(AN-co-VAc) nanocomposites film surfaces were first analyzed by STEM to verify the co-coreshell formation (if any) in PS. Low and high magnification STEM images given in Figures 4.16 and 4.17, respectively show that ,although polystyrene is quite smooth (Figure 4.16 a), SEBS-g-MA based elastomeric nanocomposite phase (Figure 4.16 b) forms continuous elongated but interconnected sequences including some aggregates in 500 nm sizes (Figure 4.19 a) . But quite different – well dispersed almost 50-100 nm sized co-coreshell morphology in the case of expanded nanosphere (Figure 4.16.c and 4.17 b) is obvious. Compared to SEBS-g-MA, distribution of SEBS-g-PEO based co-coreshells seems more homogenous and smaller sized due to prevention of nanosphere agglomeration by PEO chains throughout extra strong interactions.

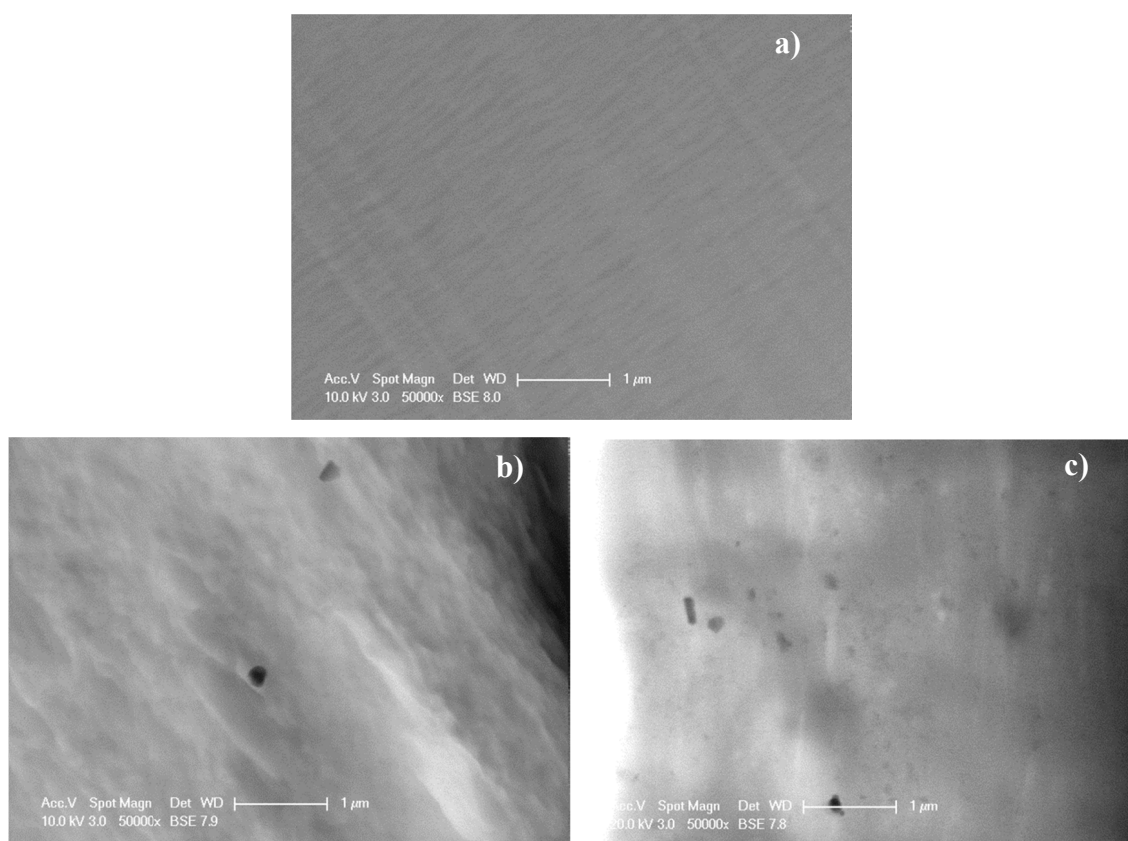


Figure 4.16. STEM images with x50000 magnification of a) Neat PS b) PS / SEBS-g-MA 1% XP(AN-co-VAc) c) PS / SEBS-g-PEO 1% XP(AN-co-VAc) (80/20% ratio by weight).

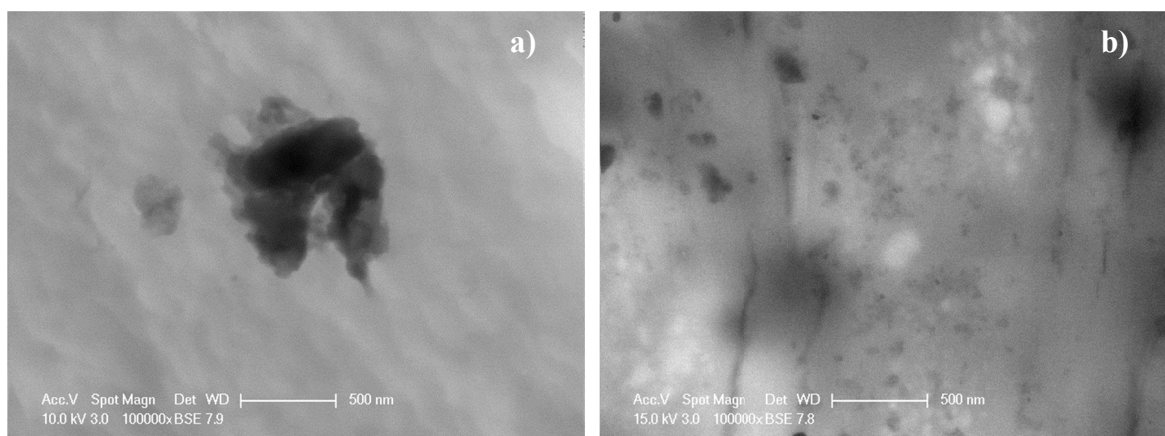


Figure 4.17. STEM images with x100000 magnification of a) PS / SEBS-g-MA 1% XP(AN-co-VAc) b) PS / SEBS-g-PEO 1% XP(AN-co-VAc).

Fracture surface images of the composites are also important to understand the nature of the fracture- ductile or brittle or shortly fracture mechanism. Fracture occurs under mechanical stress, through the separation of building blocks of a material. It starts with an initiated crack, and then this crack propagates and results in complete failure. The mechanism behind this is the breaking of bonds in an atomic level, under static loading conditions [50].

Breaking of atomic bonds is most effectively utilized and measured through the application of normal stresses. Figure 4.18. shows various failure modes, ranging from brittle to ductile. The failure mode determines the amount of energy consumed through plastic deformation. In brittle fracture, the failure occurs suddenly and without much deformation, therefore a low amount of energy is consumed through plastic deformation [50].

Gao *et al.* reported the study of fracture mechanisms of neat PS and butadiene grafted PS (PB-g-PS) /PS blends. Morphology of the fracture surfaces were inspected through SEM images. Voiding and ductile tearing were easily observable on the fracture surfaces of the PB-g-PS toughened PS blends. Therefore, it was concluded that plastic deformation implying the shear yielding of PS matrix took place [44].

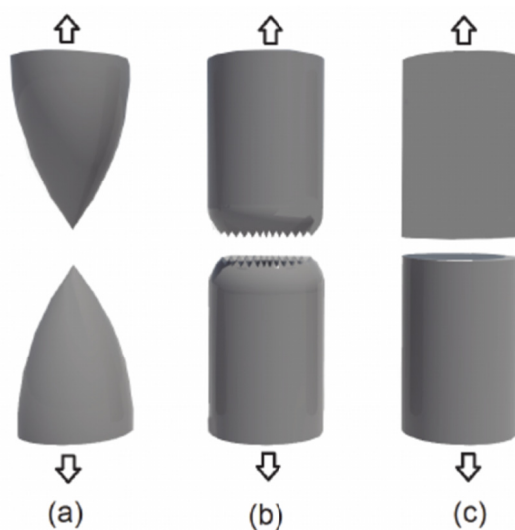


Figure 4.18. Brittle versus ductile fracture a) Very ductile fracture, b) Moderately ductile fracture, (c) Brittle fracture [46].

In our study, neat PS has a brittle fracture as seen in the Figure 4.19.a whereas PS / SEBS-g-MA 1% XP(AN-co-VAc) nanocomposite has a moderately ductile fracture as shown in Figure 4.19.b. On the other hand, PS / SEBS-g-PEO 1% XP(AN-co-VAc) exhibits very ductile fracture with easily observable fibrils and small voids on the fracture as an indication of plastic deformation history (Figure 4.19.c) [51].

As expecting completely different mechanical responses from above mentioned different morphologies, the mechanical characterization of neat PS and selected PS nanocomposites were conducted by using tensile testing method and the results were compared. Figure 4.20. shows that the stress-strain curves of neat PS, PS / SEBS-g-MA 1% XP(AN-co-VAc) and PS / SEBS-g-PEO 1% XP(AN-co-VAc) nanocomposites and their Young modulus, ultimate strength and work up to break values are given in Table 4.3. Work up to break is the integral area of stress-strain curve that correspond to the toughness value of the material.

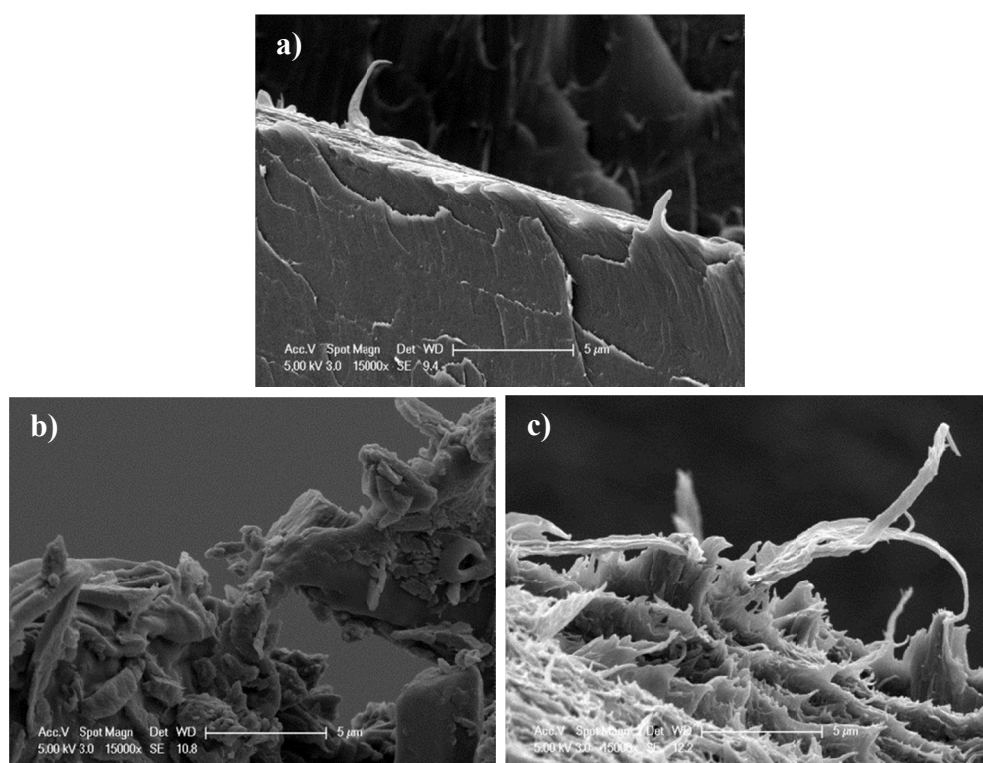


Figure 4.19. Fracture surface SEM images of a) Neat PS b) PS / SEBS-g-MA 1% XP(AN-co-VAc) c) PS / SEBS-g-PEO 1% XP(AN-co-VAc) (80/20% ratio by weight).

Table 4.3. E- modulus, ultimate strength and work up to break of neat PS and PS nanocomposites.

Sample	E-Modulus (MPa)	Ultimate Strength (MPa)	Work up to Break (N/mm)
PS	1250	17.7	66.35
PS / SEBS-g-MA 1% XP(AN-co-VAc)	285	8.35	210.57
PS / SEBS-g-PEO 1% XP(AN-co-VAc)	480	12.3	342.67

SEBS-g-MA is known to be a good elastomer to increase both compatibility of the matrices and impact strength of the blends [52]. It also take place in the lists of toughening agents for PS together with PVAc and some PAN copolymers [53]. Jose *et al.* [54] studied on the blends of SEBS and SEBS-g-MA with PA12 compounded in twin screw extruder. It was concluded that better dispersion of elastomeric phase using SEBS-g-MA, compared to SEBS can result in improved impact toughness and elongation.

Moreover, it is also known that SEBS-g-MA can be used as an impact modifier and compatibilizer for nanoparticles. A study carried out by Li *et al.* [55] presents the compatibilizing and toughening effect of SEBS-g-MA in PS matrix. It shows the improved dispersion of polyamide 1212 (PA 1212) within the PS matrix when SEBS-g-MA is used as compatibilizer. The microstructure of the blend was shown to be varying with increasing SEBS-g-MA content. Lower mix rates results in the formation of sheet structures while higher concentrations give rise to co-continuous phase with co-coreshell structure, but increasing the SEBS-g-MA content even further prevents the crystallization of PA1212. Overall, the highest improvement in the impact strength was observed in the co-continuous phase.

In our study, Table 4.3 and Figure 4.20 indicate that SEBS-g-MA 1% XP(AN-co-VAc) increases the toughness of neat PS by 217%. Most interestingly, SEBS-g-PEO 1% XP(AN-co-VAc) give rise to increase in toughness by 417% . In both cases, nanospheres are somehow surrounded by SEBS-g-MA and SEBS-g-PEO but the reason for the remarkable increase coming with latter is the prevented agglomeration of nanospheres and the creation of smaller co-coreshell structures in presence of polar PEO graft in PS matrix. It is worth to say that , those co-coreshell structures with SEBS-g-PEO seems to be promising for the preparation of 3-in 1 type novel structures having toughening, reinforcing and compatibilizing actions in them.

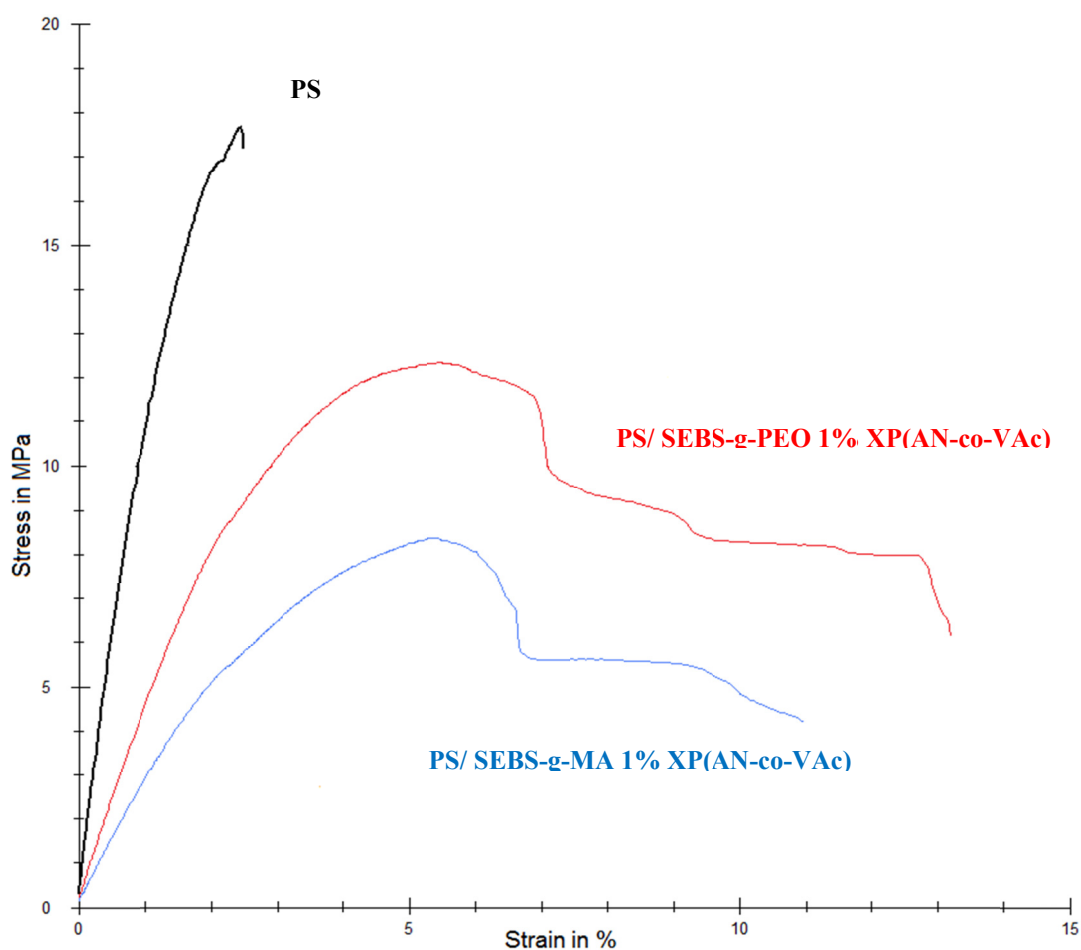


Figure 4.20. Stress & Strain curves of neat PS, PS / SEBS-g-MA 1% XP(AN-co-VAc) and PS / SEBS-g-PEO 1% XP(AN-co-VAc).

The thermal stability of the PS composites has been investigated by TGA analyses and the data such as onset degradation temperature, the temperature at which 10% weight loss occur (T_{10}) and the residue at 600°C were all tabulated in Table 4.4.

Table 4.4. Onset T, T_{10} , residue and degradation rate of neat PS and PS nanocomposites.

Polymer	Onset T (°C)	T_{10} (°C)	Residue (%)	Degradation Rate (%.min/°C)
PS	390,23	369,62	0,18	9,52
PS / SEBS-g-MA 1% XP(AN-co-VAc)	410,06	406,31	0,43	9,53
PS / SEBS-g-PEO 1% XP(AN-co-VAc)	405,74	397,62	0,87	9,41

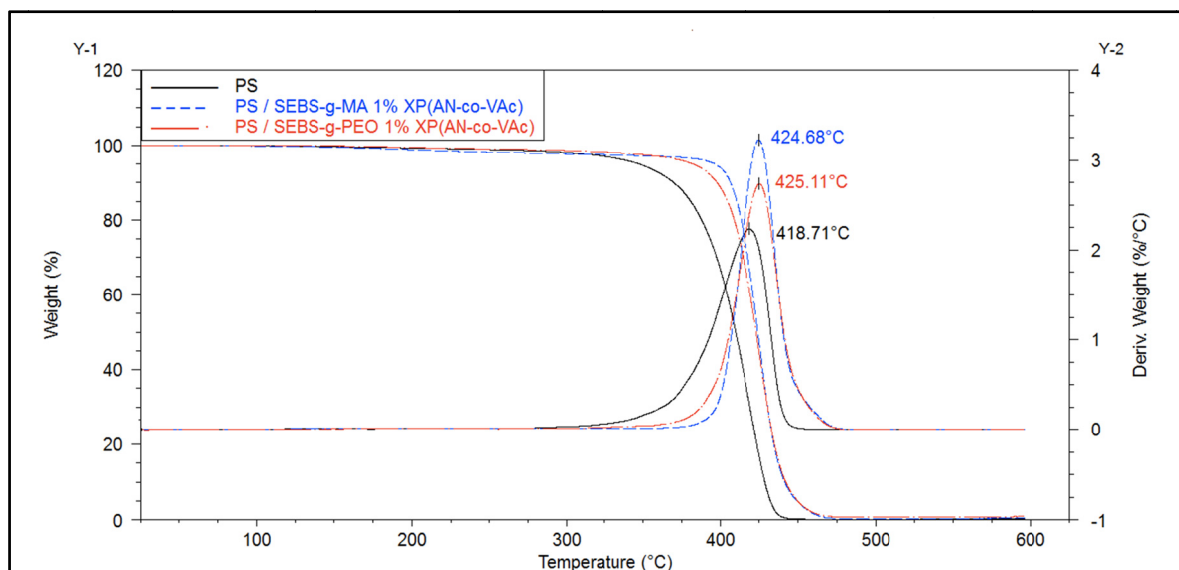


Figure 4.21. TGA and DTGA results of neat PS and PS nanocomposites.

As it can be seen from the Table 4.4. and the Figure 4.21, both PS composites show improved thermal stability compared to neat PS homopolymer. The onset degradation temperature and T_{10} are about 20 °C and 35 °C higher for PS / SEBS-g-MA 1% XP(AN-co-VAc) composite than neat PS. Although PEO containing nanocomposite revealed a little bit lower degradation temperature than PS / SEBS-g-MA 1% XP(AN-co-VAc), but still higher than PS, due to the presence of weak ethylene oxide units. Highest char/residue content for this nanocomposite can be attributed to encapsulation of nanoparticles via elastomer phase mainly with the help of PEO units and carboxylic acid groups compared to MA group. This co-core-shells structure may lead to more homogeneous dispersion of XP(AN-co-VAc) nanoparticles throughout the system providing better insulation between polymer matrix and heat flux as well as resulting in restricted diffusion for degraded products. On the other hand, from the derivative curves, the peak temperature at which the maximum degradation occurs was found to be shifted to a value of 424-425 °C for both composites, but among the composites the degradation rate was much lower for PS / SEBS-g-MA 1% XP(AN-co-VAc) composite which is also an indication of its high thermal stability.

5. CONCLUSION

In this thesis, polystyrene nanocomposites were successfully prepared using P(AN-co-VAc) nanospheres both in expanded or non-expanded forms as reinforcer and SEBS-g-MA or SEBS-g-PEO thermoplastic elastomers as toughener/compatibilizer. The effects of nanosphere and thermoplastic elastomer additions and their outcomes in terms of dispersion quality, morphological, thermal and static/dynamic mechanical properties were studied in detail.

In the first part of study, PEO chains were successfully grafted onto SEBS-g-MA backbone and the grafting was proved by the presence of carboxylic acid and ester peak formations in FTIR spectroscopy. 22% grafting efficiency was determined using the outcomes obtained from ^1H NMR spectroscopy. DSC data showed that both broadening of two endotherms belonging to ethylene butylene crystalline regions as well as decreased rigid PS phase relaxation in SEBS-g-PEO polymer verified the existence of PEO grafts.

In the second part of the study, co-core-shell structures using nanospheres within thermoplastic elastomers were prepared via high shear mixer to provide better dispersion by breaking sub-micron agglomerates into individual nanospheres. Morphological studies showed that PEO chains surround nanospheres due to hydrogen bonds and dipole-dipole interactions between each other; therefore SEBS-g-PEO with expanded nanospheres provided the best dispersion. It has been also found that SEBS-g-MA 1% XP(AN-co-VAc) exhibited the highest thermal stability in terms of degradation rate, while SEBS-g-PEO 1% XP(AN-co-VAc) showed the highest flame retardancy with a remarkable amount of increase in residue.

In the last part of our study, in-situ syntheses of special polystyrene nanocomposites were successfully performed in the presence of co-core shells obtained from the previous section of the study. Mechanical characterization showed that compared to neat PS, PS / SEBS-g-PEO 1% XP(AN-co-VAc) exhibited the highest toughness by a 4-fold increase. Fracture surface morphology verified this result by revealing the highest plastic deformation. Moreover, increased thermal stability for both PS / SEBS-g-MA 1%

XP(AN-co-VAc) and PS / SEBS-g-PEO 1% XP(AN-co-VAc) were detected . Compared to neat PS, highest residue with 483% increase indicating flame retardancy for PS / SEBS-g-PEO 1% XP(AN-co-VAc) was remarkable.

It is worth to say that, due to the existence of covalently bonded bridges between each layers via grafting inhibiting the extensive phase separation , these novel co-coreshell structures seem to be promising extra simultaneous benefits for reinforcing, toughening and compatibilizing issues of rigid polymers

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