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Volume Shrinkage and Rheological Studies of Epoxidised and Unepoxidised Poly (Styrene-block-butadiene-block-Styrene) Triblock Copolymer Modified Epoxy resin/Diamino Diphenyl Methane Nanostructured Blend System

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Abstract

Styrene-block-butadiene-block-styrene (SBS) copolymers epoxidised at different epoxidation degrees were used as modifiers for diglycidyl ether of bisphenol A/diamino diphenyl methane (DGEBA/DDM) system. Epoxy systems containing modified epoxidised styrene-block-butadiene-block-styrene (eSBS) triblock copolymer with compositions ranging from 0 to 30 wt% were prepared and cure reaction was monitored *in-situ* using rheometry and pressure-volume-temperature (PVT) analysis. By controlling the mole percent of epoxidation, we could generate vesicles, worm-like micelles and core shell nanodomains. At the highest mole percent of epoxidation, the fraction of the epoxy miscible component in the triblock copolymer (epoxidised polybutadiene (PB)) was maximum. This gave rise to core shell nanodomains having 10-15 nm size, in which the incompatible polystyrene (PS) becomes the core, the unepoxidised PB becomes the shell and the epoxidised PB interpenetrates with the epoxy phase. On the other hand, the low level of epoxidation gave rise to bigger domains having ~ 1 μm size and the intermediate epoxidation level resulted in worm-like structure. This investigation specifically focused on the importance of cure rheology on nanostructure formation, using rheometry. The reaction induced phase separation of PS phase in the epoxy matrix was carefully explored through rheological measurements. PVT measurements during curing were carried out to understand the volume shrinkage of the blend matrix, confirmimg that shrinkage behaviour is related to the block copolymer phase separation process during cure. The volume shrinkage was found to be maximum in the case of blends with unmodified SBS where a heterogeneous morphology was observed, while a decrease in the shrinkage was evidenced in the case of SBS epoxidation. It could be explained by two effects 1) solubility of the epoxidised block copolymer in the DGEBA leads to the formation of nanoscopic domains upon reaction induced phase separation and 2) the plasticisation effect of the epoxidised block copolymer in the epoxy resin.

Keywords: Epoxy resin; Triblock copolymer; PVT; Volume shrinkage; Rheology; Isothermal curing.

Introduction

The epoxy resins are the most widely used thermosetting matrices in aerospace and automobile industries, because of their good mechanical and excellent adhesion to other substances, low shrinkage upon cure and good thermal and chemical resistance. During curing, the low molecular weight epoxy resin is converted to high molecular weight polymer. The ultimate properties of epoxy resins are achieved by the complete curing reaction. However, after cross linking reaction, unmodified epoxies resulted as brittle materials. In order to improve the toughness of epoxy system, the addition of thermoplastic polymeric materials, as an alternative to rubber toughening, has been widely recognized [1-5]. Recently, block copolymers have been used to toughen epoxy systems: nanostructured blends can be obtained in this case due to the self-assembling property of different blocks in the thermosetting matrix [6-20]. This approach is known as toughening by nanostructures. It is demonstrated that the cure kinetic study in epoxy/block copolymer systems shows an autocatalytic behavior due to the presence of hydroxyl groups generated during the epoxy amine reactions that are able to further catalyze the curing reaction [21-23]. It is widely demonstrated that the rheological measurements can be used as a tool to study the kinetics of epoxy curing reaction; specifically viscosity and gel point are the most important rheological parameters to be monitored during the cure reaction of epoxy systems and other network forming polymers. The rheological characterization is one of the most accurate and reliable methods to find out the gel point, generally defined as the point at which the cross linking starts or the point in which a transition from the liquid to solid is observed, i.e. when the first macromolecule at infinite dimension is formed.

In the case of network forming systems, at the gelation point, a change in viscosity is observed and the network formation occurred [24]. In the case of rheological measurements, the gel point can be determined by the extrapolation of steady state viscosity to infinite viscosity [25]. Moreover, vitrification [26] and /or phase separation [27] are the other phenomena which are able to modify the viscosity profile.

Several techniques such as neutron scattering, light scattering, transmission electron microscopy, scanning electron microscopy and optical microscopy can be used to study the phase separation during curing. Rheometry represents an alternative method to find out the phase separation processes in epoxy systems toughened by rubber and thermoplastics, but, due to the complexity of the systems, the mechanism is not well understood. Therefore, studies on the monitoring of simultaneous curing and phase separation have been a topic of interest for many years [28]. Bonnet et al. [29] studied the phase separation of polyetherimide (PEI) containing epoxy/amine system by analyzing the viscosity traces of the blends and particular transitions were observed at the starting point of phase separation as a function of the thermoplastic content. The phase separation of the epoxy system containing reactive copolyethersulphone has been studied by Blanco et al. [30] and they found that the viscosity transitions shifted to lower times with increase of the curing temperatures. Tribut et al. [31] have studied and modeled the evolution of the viscoelastic properties of thermoset precursors blended with atactic PS blends during isothermal curing. Indeed, the rheological properties of thermosetting system modified with block copolymers are particularly important. Block copolymers are designed in a way that one of the blocks is miscible with epoxy resin and the immiscible block gets phase separated into different nanoscale morphologies. They have the ability to self-assemble in ordered and disordered morphologies when they are mixed with thermoset precursors such as epoxy resin [32-34]. The role of curing of epoxy resin is to lock the morphology that it is initially present or to keep the structure formed in the earlier stages of reaction. Finally, after the reaction, spherical micelles, wormlike micelles or vesicles are formed by the self-association of block copolymers in epoxy resin [35-39]. In order to prevent the macroscopic phase separation during the reaction, one of the block should be miscible with epoxy resin, as in the case of poly(methyl methacrylate), PMMA [35] or poly(ethylene oxide), PEO [39] in epoxy systems. In the paper published by Serrano et al. [15], an attempt was done to monitor the molecular dynamics and microphase separation of epoxy resin modified with an epoxidized poly(styrene-b-butadiene) (SepB) linear block copolymer during cure process, by using dielectric relaxation spectroscopy. The result was in agreement with the data obtained from rheological studies. The same approach was considered in the present study, where the volume shrinkage and rheology of epoxy/DDM system modified with epoxidised SBS at 47 mol% of epoxidation were analysed and correlated with the reaction induced phase separation of PS and unepoxidised PB block of epoxidised SBS (eSBS). In the present work we make an effort to illustrate the *in-situ* volume shrinkage behaviour of epoxy resin (DGEBA)/DDM modified with block copolymer (eSBS) by PVT analysis. The kinetics and detailed morphological studies of epoxidised SBS modified DGEBA was already considered in our previous publications [40,41] and the results showed that initially homogeneous eSBS modified epoxy resin/DDM blends go through the reaction induced phase separation during the curing process; leading to nanostructured morphology. We observed a delay in the rate of reaction, occurred by the addition of the epoxidised SBS as a result of the hydrogen bonding interactions of epoxidised butadiene block with the epoxy resin. The isothermal curing of the blends is followed by the polymerisation shrinkage and the increase in viscosity during the vitrification process. One of the major drawbacks of epoxy resins including other thermosetting polymer is the high volume shrinkage upon curing. The desired properties of themselves are adversely affected by the volume shrinkage. PVT analysis is one of the best techniques to follow the cure shrinkage properties. It is very important to indicate that there are only very few studies in the literature concerning the volume shrinkage during curing [42-45] of thermosetting-thermoplastic blends. Although, several papers have appeared in the literature on the microphase separation and morphology of epoxy resin/block copolymers till date no investigation has been done to follow the cure shrinkage of those systems and to correlate the shrinkage to the morphology and rheology. For many thermoset blend systems, it has been observed that volume shrinkage coincides with fractional conversion. Very recently, the volume shrinkage studies of styrene-*co*-acrylonitrile (SAN) and poly(acrylonitrile-butadiene-styrene) (ABS) modified epoxy blends have been reported from our group [44, 45]. In the present communication, rheological studies were carried on, by performing isothermal experiments at different heating rates by varying the epoxidation degree. During the isothermal curing of block copolymer toughened epoxy systems, it was observed that the viscosity profile of the medium increased from initially low viscosity to very high viscosity, but before the abrupt viscosity increase, a fluctuation in viscosity was also observed, due to the phase separation of epoxidised SBS. It is also important to mention that in the previous published works, little attention was given to the viscosity evolution during cure and to the effects of different amounts of block copolymer on the curing of epoxy. It should be also pointed out that, to the best of our knowledge, no studies have been reported in the literature where PVT analysis of thermoset/block copolymer blend systems was correlated with phase separation process. In the present paper, we have carefully analysed the rheological behaviour and volume shrinkage of epoxy resin/epoxidised SBS triblock copolymer blend system. The volume shrinkage has been for the first time correlated with the rheology and morphology of the system.

Experimental Section

Materials

The thermoset precursor used in the experiment consists of diglycidyl ether of bisphenol A (DGEBA) (Araldite LY556, Huntsman). The epoxide equivalent weight of LY556 was 186 g/mol. Diamine 4,4'-diaminodiphenylmethane (DDM), supplied by Aldrich, was used as curing agent. The selected triblock copolymer styrene-block-butadiene-block-styrene (SBS) (KRATON D 1101) has a molecular weight of 162,000 g/mol (analysed by GPC) and styrene weight percentage of 31. Tetrahydrofuran (THF) supplied by Sigma Aldrich was used as solvent used for blend preparation.

Sample Preparation

The epoxidation of SBS was done at three different epoxidation degrees (26 mol%, 39 mol%, and 47 mol%, respectively indicated as eSBS(26), eSBS(39) and eSBS(47)) by using hydrogen peroxide in the presence of an *in-situ* prepared catalyst system (methyl trioctylammonium tetrakis diperoxotungstate phosphate), the details of the reaction and the characterization methods are given in our previous publication [41]. Blends of epoxy/eSBS containing 5, 10, 15, 20 and 30 wt% of eSBS(47) were prepared by solvent casting method and in the case of eSBS(26) and eSBS(39) systems only 10 wt% of eSBS were used. The eSBS (or unmodified SBS) were dissolved in THF and then mixed with the epoxy resin. The solvent was then removed by heating at 80 ^{o}C in an oil bath. The curing agent DDM was added in stoichiometric amount at 90 ^{o}C and stirred well for about 5-10 min. The freshly prepared mixtures were directly cured (at temperatures 50 °C for 2 h, 80 °C for 3 h, and 140 °C for 3 h in an oven and then allowed to cool the samples slowly to room temperature) or used for analysis, or stored in a freezer at -20 °C before using.

Experimental Techniques

Optical microscopy

The optical microscopic analysis of the eSBS modified epoxy/DDM blends at different epoxidation degrees was performed by using a Hund mode H600 optical microscope. The samples were prepared *in-situ* and placed in the heating cell of the microscope. The Linkam cell was used for heating and the heating was carried out from 30 ^{o}C to 180 ^{o}C. The images of the morphological changes occurred during curing were taken by the in built CCD camera mounted on the microscope.

High Resolution Transmission Electron Microscopy

High resolution transmission electron microscopy (HR-TEM) was used to analyze the morphology at higher magnifications. HR-TEM images were obtained with a JEOL JEM −2100 microscope applying an acceleration voltage of 100 kV in bright field and dark field mode. The LEICA Ultracut ultramicrotome was used for preparing the specimens. Thin sections of about 70 nm were obtained with a diamond knife at room temperature. A 0.5 wt% aqueous solution of ruthenium tetroxide (RuO_4) was used to stain and to make contrast between PS, PB and epoxy phases, for 4-10 min. RuO_4 preferentially stains PS microdomains for the system examined (appearing black in the micrographs). The staining time of samples was carefully chosen to keep away from the possibility of staining all the phases in the investigated systems and deposited on copper grids.

Rheological analysis

A parallel plate rheometer with a diameter of 12.5 mm (ARES Rheometric Scientific model) was used for the analysis. The non-isothermal analysis of the freshly prepared samples (about 5-10 mg) was done starting from room temperature up to the temperature at which the vitrification is completed and at a frequency of 1 Hz and 0.5 % strain. The isothermal tests were carried out at three different temperatures 90, 110 and 130 ^{o}C for the epoxy/eSBS(47)/DDM blend systems.

Pressure-volume-temperature analysis

GNOMIX high pressure mercury dilatometer, capable of measuring volume changes as small as 0.0002 cm^{3}/g within an accuracy limit of 0.002 cm^{3}/g (below 200 ^{o}C), was used for the specific volume change (V_{sp}) analysis. The apparatus was pressurised to 10 MPa, heated to the desired temperature, and then the changes in specific volume of the sample were recorded over time. The data acquisition mode (DAQ) was used for the characterization of cross linking reaction.

Table 1. Experimental specific volume values of epoxy/block copolymer systems at 110 ^{o}C.

eSBS (wt%)	**Specific volume (experimental)/cm^{3}g^{-1} (V_{E0})**
0 (neat epoxy)	0.8908
10 SBS	0.9168
10 eSBS(47)	0.9002

Results and Discussion

Phase Separation by Microscopic Analysis

Optical Analysis

The optical microscopic measurements of freshly prepared blends were analysed during curing. Blends of 10 wt% epoxy/eSBS/DDM were prepared with different epoxidation degrees (26, 39 and 47 mol%) and the evolution of phase separation during curing has been studied. The mixtures were placed in the optical microscope at room temperature and the heating was done from room temperature up to 180 ^{o}C at a heating rate of 5 ^{o}C/min. The microscopic images were recorded at 30, 60, 90, 120, 150 and 180 ^{o}C. The results are shown in Figures 1a, b and c. In the case with unmodified SBS blends the optical images shows the heterogeneous phase separation at the starting temperature itself. Hence an obvious change could not be observed during the curing (not shown in the manuscript). A continuous structure of epoxy rich phase is observed for all the epoxidised SBS blends at low temperatures. In the case of the blend containing eSBS(26), the heterogeneous phase separation is detectable after 120 ^{o}C (Figure 1a), while a homogeneous system is visible at lower temperatures. Figure 1a shows a typical evolution process of the polymerization induced viscoelastic phase separation in epoxy/eSBS(26) system. The epoxidised PB blocks are miscible in epoxy rich phase and transparent to light. The phase separated PS and unepoxidised PB domains are immiscible in epoxy and opaque to light. Therefore, dark regions correspond to the phase separated PS and unepoxidised PB-rich phase, while the bright regions to the epoxy-rich phase. Thus, a micro-bicontinuous phase structure is observed after 150 ^{o}C. A micro-phase separated structure with much smaller characteristic length scale is obtained at the end of phase separation.

However, when the degree of epoxidation reaches 39 mol% (eSBS(39)), the miscibility of the system is increased. Initially, a homogeneous system is visible, while the phase separation occurs in the nanometre level, with presence of very small spherical particles that are gathered together at the end (Figure 1b). Since a clear picture is not visible in the case of optical microscopy investigation, the studies of evolution of phase transitions, during the curing of eSBS modified epoxy by DDM, by means of optical analysis cannot be considered as an efficient method. The same situation was also observed in the presence of 10 wt% of eSBS(47). Here, the matrix is epoxy-rich phase from the beginning to the end of the process, containing spherical particles of block copolymer phase and which would remain at the end of curing (Figure 1c).

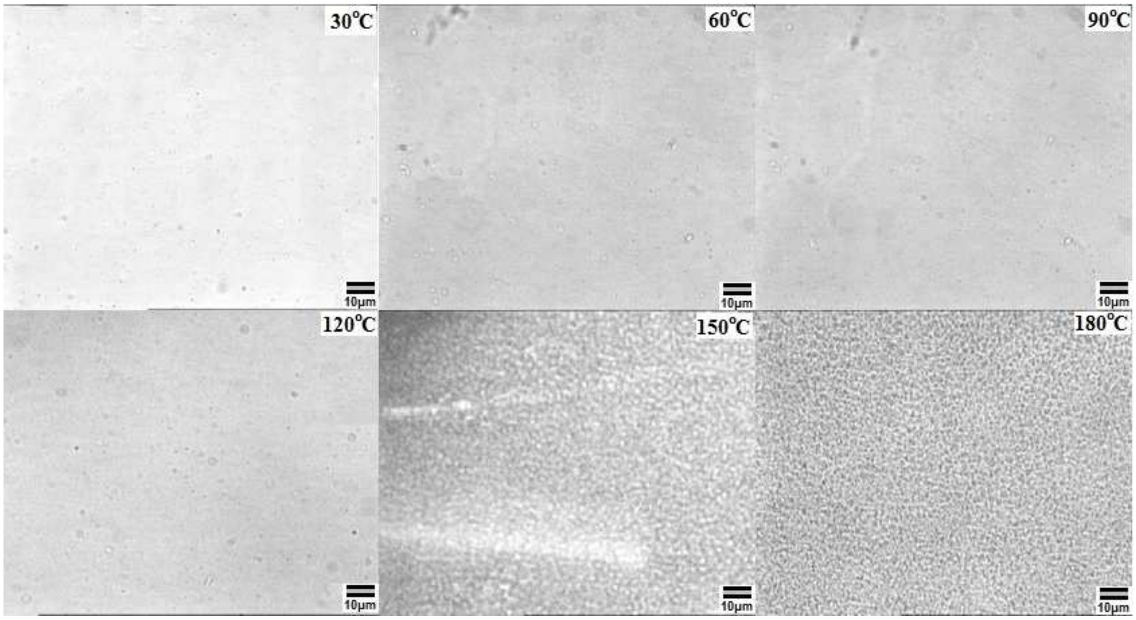


Figure 1a. Optical Micrographs of epoxy/10wt% eSBS(26)/DDM blend at 30, 60, 90, 120, 150 and 180 ^{0}C during curing.

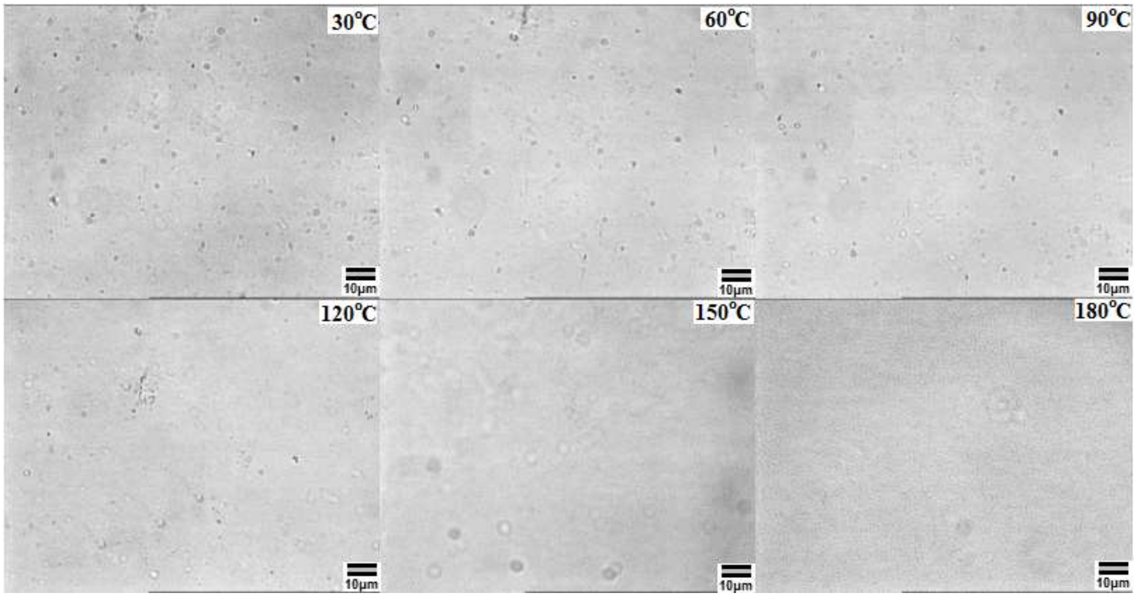


Figure 1b. Optical Micrographs of epoxy/10wt% eSBS(39)/DDM blend at 30, 60, 90, 120, 150 and 180 ^{0}C during curing.

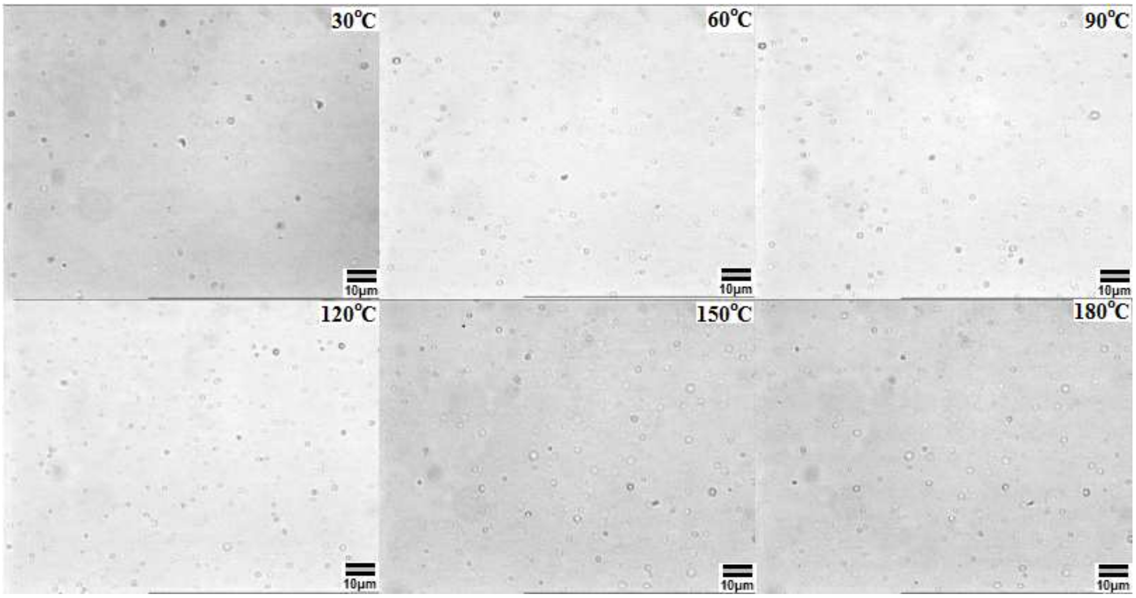


Figure 1c. Optical Micrographs of epoxy/10wt% eSBS(47)/DDM blend at 30, 60, 90, 120, 150 and 180 ^{0}C during curing.

HR-TEM Analysis

The structure at the nanolevel was confirmed by the HR-TEM images of the 10 wt% of eSBS (26, 39 and 47) system in epoxy/DDM blends at different epoxidation degrees, visible in Figure 2 (a-c). A transition of phase morphology from macroscopic to nanoscopic length scale was observed. The TEM micrograph of eSBS(26) modified epoxy system (Figure 2a) shows an interesting morphology constituted by both micro and nano domains. Since the specimen is epoxidised at lower degree, unepoxidised SBS microdomains are present. The microdomains having the size ~ 1μm were observed. The unepoxidised block copolymer is able to form disordered lamellar structures and are held together to form microdomains. The eSBS chains come out of the unepoxidised SBS domains forms nano domains, vesicles in the epoxy matrix. For the blends with eSBS(39) most of the PB chains are epoxidised, hence form interconnected tiny and elongated vesicles, and these elongated vesicles form worm like micelles in nano dimensions (Figure 2b). Finally, for eSBS(47), modified epoxy blends nano core shell domains (Figure 2c) were observed. The size of these particles is between 10-15 nm. The inset of Figure 2a, 2b and 2c shows the schematic representation of vesicle, wormlike and spherical micelles. As previously commented, a reaction induced phase separation was observed in the blends.

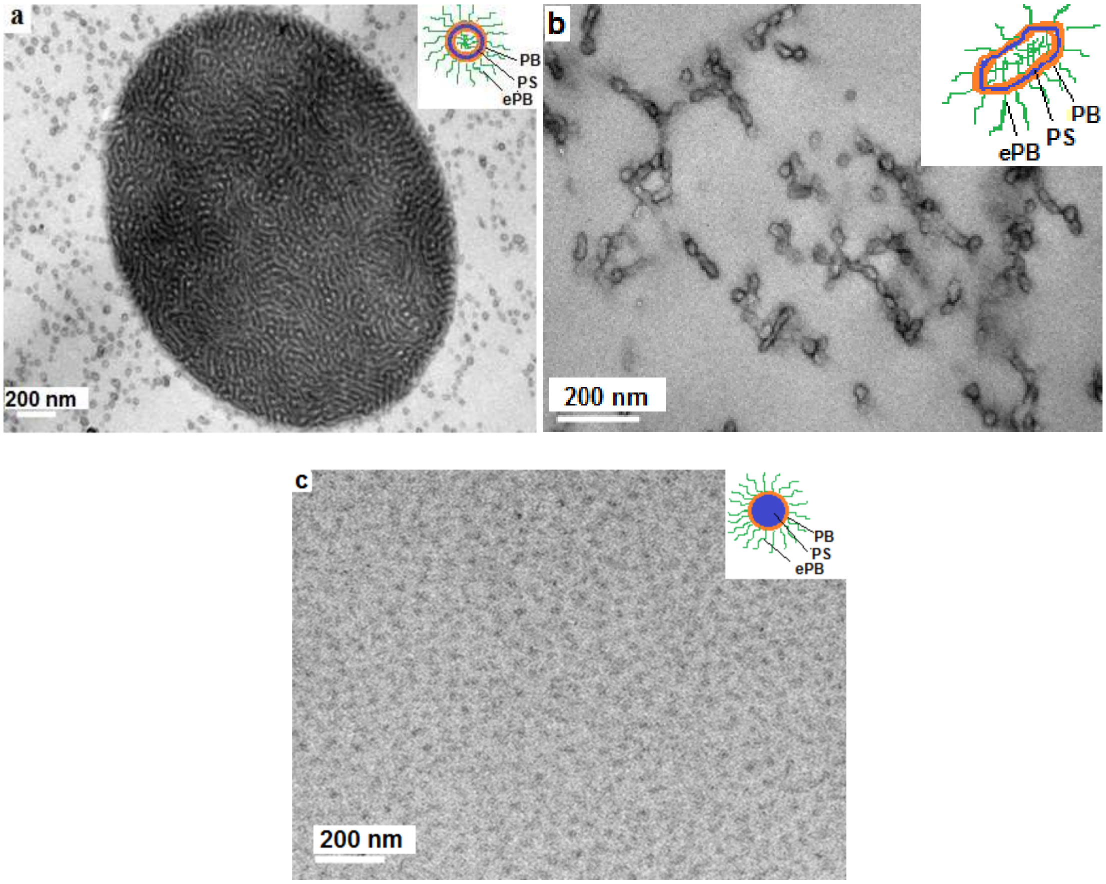
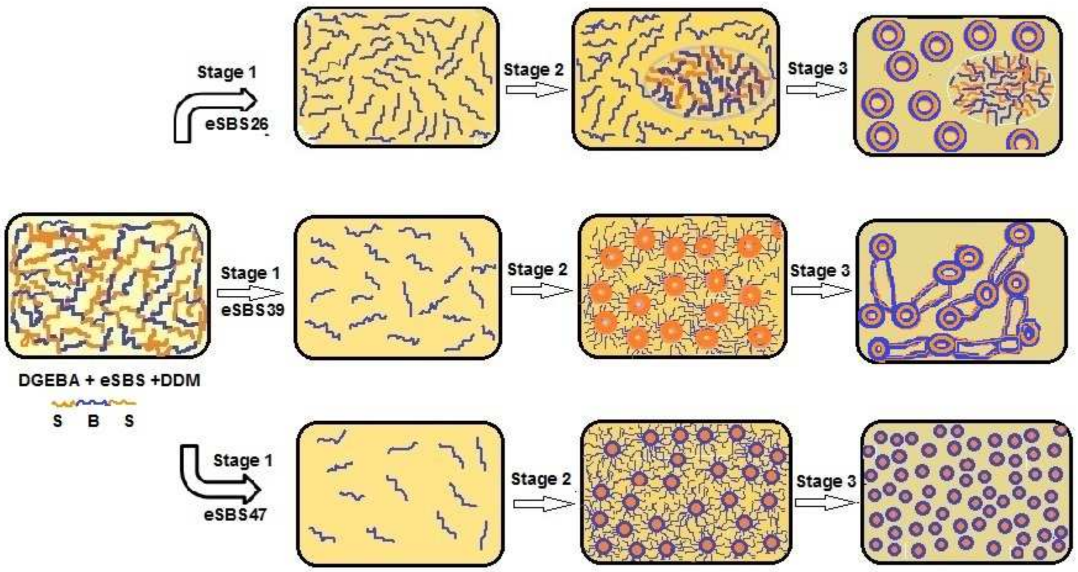


Figure 2. HR-TEM images of DGEBA/DDM blends modified with 10 wt% of (a) eSBS(26), (b) eSBS(39), and (c) eSBS(47).

The epoxidised triblock copolymer contains PS, PB and epoxidised PB blocks, in which PS block is capable of experiencing reaction induced phase separation in epoxy, one of the block (epoxidised PB) is miscible with epoxy before and after the curing reaction, and the other block PB remain immiscible with epoxy. The formation of nanostructures in epoxy matrix is indeed complicated by the addition of epoxidised triblock copolymer.

The evolution of nanophase morphology is schematically represented in three different stages of curing. The immiscible PB phase is shown in stage 1 of Scheme 1. As the degree of epoxidation increases the number of immiscible PB or unepoxidised PB phase decreases which means the increase in the number of epoxidised PB phase. In stage 2, the reaction induced phase separation of PS phase occurs by nucleation and growth mechanism (NG), when eSBS(26) is used as a modifier results in the formation of microdomains having PS and PB phases. In the case of eSBS(39) the PS rings forms, followed by PB phase that self-assembled on the surface of PS rings. When the degree of epoxidation reaches 47, the spherical PS domains form and self-assembling of PB phase occurs on the surface. In the stage 3 of curing, the vesicle formation is observed, along with the micro domains present in eSBS(26) modified system. The interconnected and elongated vesicles or wormlike micelles are formed in eSBS(39) system, consisting of PS phase in between two PB phases. The eSBS(47) modification shows a core shell domain structure with PS core and PB shell. In all the systems the epoxidised PB phases are miscible with the epoxy matrix by hydrogen bonding interactions [41].



Scheme 1: Schematic representation of spherical, wormlike and micro domains like morphologies in epoxy/eSBS/DDM blends with epoxidation degrees of 47, 39 and 26 mol% in eSBS, respectively.

Rheological Properties

Uncured samples were used for dynamic and isothermal rheological measurements. The dynamic curing experiments were performed at a heating rate of 10 ^{o}C/min for epoxy/DDM blends modified with 10 wt% of eSBS at different epoxidation degrees (0, 26, 39 and 47 mol%). The dynamic scans were performed cooling the plates to 20 ^{o}C. Once the material to be cured had been inserted, the plates were closed to 0.6 mm and newly cooled to 20 ^{o}C. The scan interval was set from 20 ^{o}C to 200 ^{o}C (but the tests were stopped before reaching the upper temperature limit, i.e. just after that an evident gelation of the system was detected). Dynamic tests performed in the case of DGEBA blends with 10 wt% of eSBS epoxidised at different epoxidation degrees are reported in Figure 3. The figure illustrate the evolution of the complex viscosity *(η*)* as a function of the temperature. It was observed that in the beginning of the test, the viscosity is found to increase with the increase in epoxidation degree. This is mainly due to the increase in compatibility of high molecular weight epoxidised SBS in epoxy resin or due to some specific type of interaction (hydrogen bonding) between the epoxidised SBS and the epoxy resin [41]. When the temperature reaches 160 °C, a sudden increase in viscosity occurred due to the gelation. A fluctuation or a small hump in viscosity, in addition to the sharp increase, can be observed at 150-170 °C temperature range for the blends of eSBS having 39 and 47 mol% epoxidation, and this behavior can be related to the generation of nanophase separation in the epoxy network, concurring with the physical gelation just before the chemical gelation point [46]. This network formation could be due to some anomalous reaction induced phase separation of epoxy in block copolymer or vice versa. The same trend can also be observed in DGEBA/DDM modified with 20 and 30 wt% of eSBS(47) (Figure 4). As the weight percentage of eSBS(47) increases from 10 to 30 %, the initial viscosity also increases and a hump in viscosity plot can be clearly seen at 160 °C. The hump in the cure has been shown with the corresponding change in the morphology.

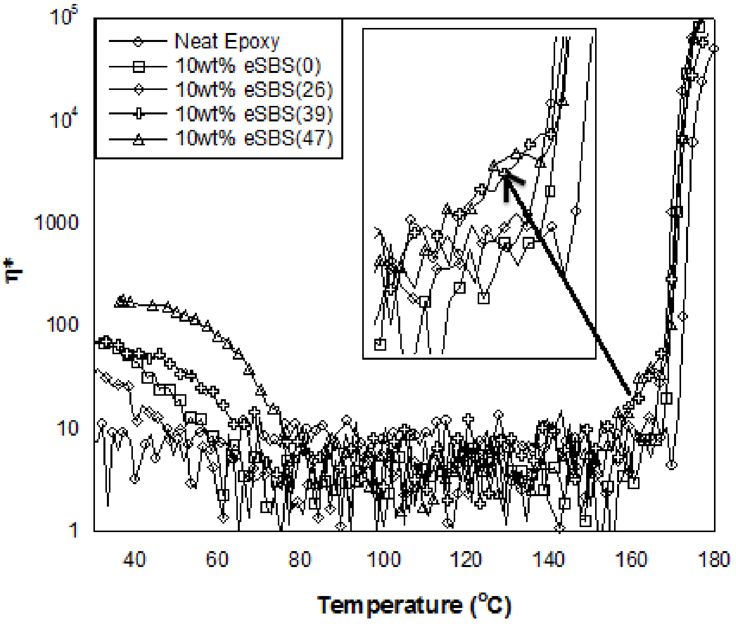


Figure 3. Dynamic tests for 10 wt% eSBS (0, 26, 39 and 47 mol%) in DGEBA/DDM blend

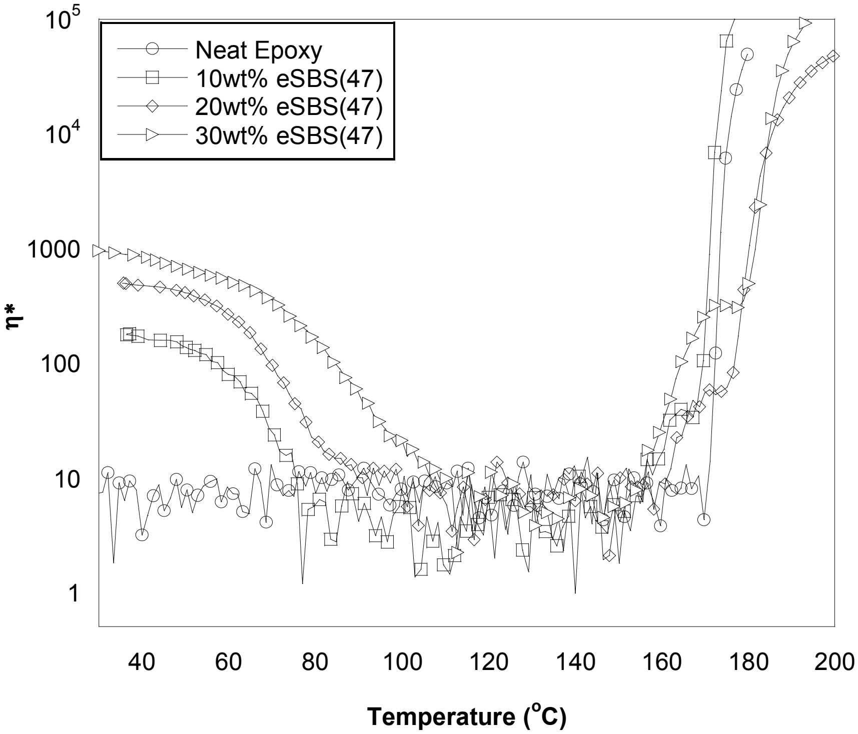


Figure 4. Dynamic tests for 0, 10, 20 and 30 wt% eSBS(47) in DGEBA/DDM blend.

To further understand the phase separation process, isothermal rheological measurements were performed. Isothermal rheological measurement can be considered as a widely accepted method to understand the structure development in epoxy blends during curing. Isothermal experiments were performed under three different temperatures 90, 110 and 130 °C. The test fixture was preheated to the isothermal cure temperature and the plate spacing was zeroed. The chamber was then opened, the plates separated, and the resin sample rapidly inserted. The plates were then quickly brought back to a gap of approximately 0.6 mm. The chamber surrounding the plates was closed and the experiment initiated. The viscoelastic properties of the sample during cure, including the complex dynamic viscosity (η*), shear storage modulus

(G'), and shear loss modulus (G"), were monitored. However, the changes in complex viscosity with respect to cure and phase separation are only highlighted in the manuscript.

Figure 5 reveals the complex viscosity profile of neat epoxy system during the isothermal cure at different temperatures. At the beginning of the test, the complex viscosity slowly increases with cure time and then, at a certain point, a very rapid increase is observed, this point is considered as the chemical gelation point. It is important to mention that the chemical gelation point is shifted to shorter times with increase in temperature; this is because at higher temperature the extent of epoxy amine reaction is faster. The reaction between epoxy and amine proceeds until vitrification or the samples become glassy.

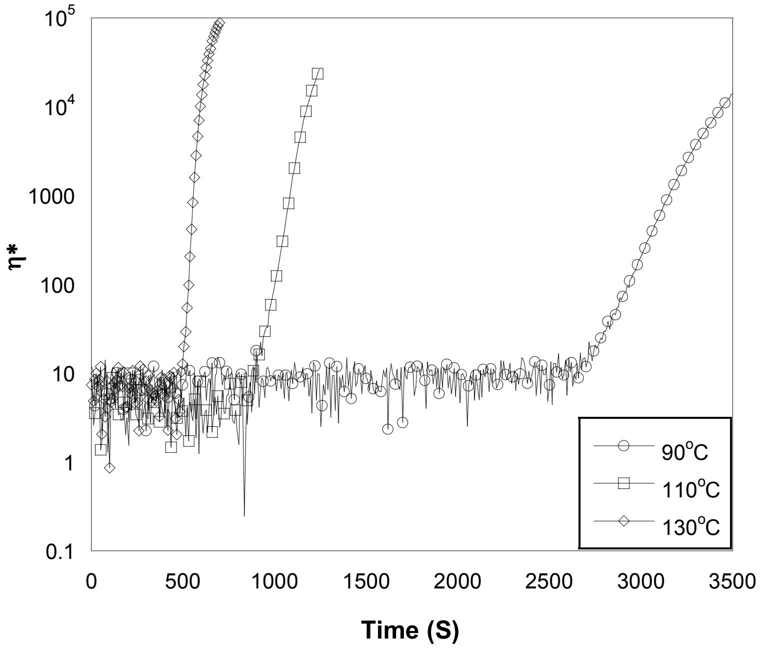


Figure 5. Isothermal tests for neat epoxy system at 90, 110 and 130 °C.

Figure 6 reveals the complex viscosity profile of DGEBA/10wt% eSBS(47)/DDM blend system during the isothermal cure at different temperatures. For the blends with eSBS, as observed for neat epoxy system at the beginning of the test, the complex viscosity slowly increases with cure time and then, at a certain point, a very rapid increase is observed, but this rapid increase in complex viscosity is much before the chemical gelation in the case of DGEBA/eSBS(47)/DDM system. The reason is related to the nanophase separation of PS and nonepoxidised PB domains in the continuous epoxy rich phase and is termed as physical gelation. Thus physical gelation is due to the reaction induced phase separation of nanostructures in growing epoxy networks.

A complete vitrification of the blend system will not occur during the physical gelation process, which has a relation on the viscosity and elasticity of the epoxy resin. After the physical gelation, the plateau region indicates the starting phase of preferential orientation of the separated blocks in the epoxy matrix and finally, the fixation of the nanophase morphology occurs with the increase of time and complete vitrification of the system happens. The phenomena which are occurred during the vitrification are the chemical gelation process which can be observed as an increase in modulus and viscosity. These results validate the dynamic rheological measurements, where a hump in viscosity can be seen after 160 ^{o}C. The schematic representations of the morphologies during various stages of curing are represented in the insets of the Figure 6. The processes which are occurred at different stages of curing, during the physical gelation, chemical gelation and in the fully cured systems are represented schematically (Scheme 2).

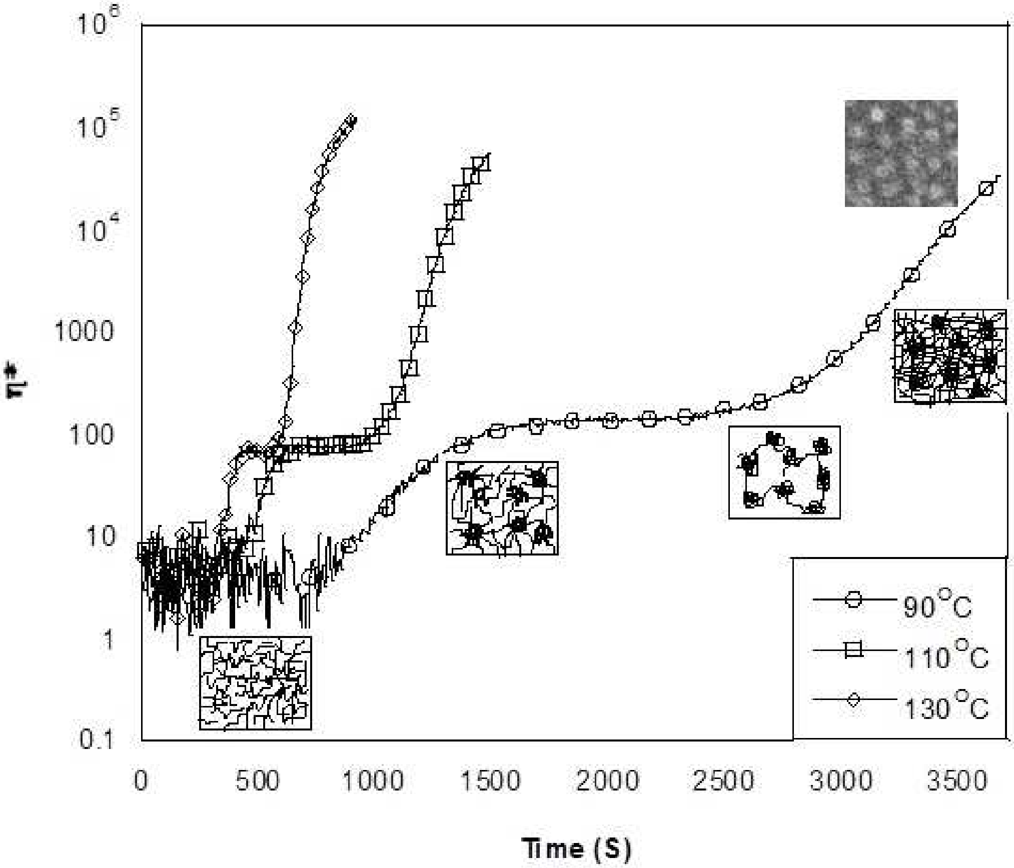
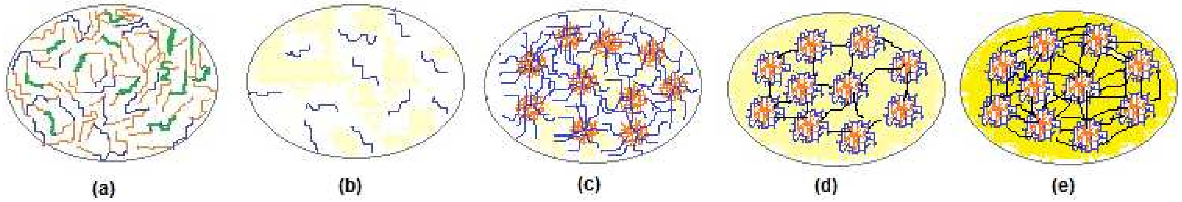


Figure 6. Isothermal tests carried out for 10 wt% eSBS(47) in DGEBA/DDM blend at 90, 110 and 130 °C.



Scheme 2. Schematic 2-D representation of nanostructure blend formation: a) eSBS block copolymer in epoxy; b) Miscible blocks below gel point; c) Nanostructure formation at physical gelation point; d) Incompletely crosslinked network at chemical gelation; e) Fully cured epoxy thermoset with nanostructures.

The results for gel times (chemical gelation) obtained from rheological tests for DGEBA/eSBS(47)/DDM blends are summarized in Table 2. The gel time values are found to increase with increase in concentration, but they decreased with increase in isothermal temperature. This result validates the calorimetric measurements, for which cure reaction is delayed by increase in block copolymer content [41]. It was also observed that the reaction rate decreases with decreasing cure temperature and increasing block copolymer content in the blends. Three aspects contribute to the behaviour. The first two aspects are the combined effect of the plasticization and dilution effect of the block copolymer in epoxy [41, 45, 46]. The third contribution comes from the partitioning of the epoxy resin in the epoxy and block copolymer rich phases. This is associated with the phase separation at the nano level. The dilution effect is mainly associated with the formation of nanostructures like vesicles, worm-like micelles and spherical micelles. The dilution effect is more evident when there is the formation of spherical micelles because miscibility is directly proportional to the epoxidation degrees. Hence, after the nanophase separation, the distribution of the epoxy/amine mixture would be disturbed. The molecular weight of the epoxy resin increases during the epoxy amine cure reaction, hence the initial blend system breaks up into two phases, an epoxy rich phase and an epoxidised SBS rich phase. The epoxy resin in block copolymer rich phase would be expected to be far less reactive than the epoxy resin in the epoxy rich phase; therefore, the rate of the reaction is expected to decrease with the increase in block copolymer. In block copolymer rich phase, there is a low probability of reaction for epoxy/amine, while in epoxy rich phase the reaction will be very fast leading to vitrification. When more block copolymers are present in the blend, they hinder the epoxy/amine reaction more effectively. The system containing block copolymers takes longer time for attaining complete conversion. Thus the delay in cure reaction rate can be linked very well with the morphology of the blends; when the epoxidation degree is 47 mol%, the spherical micelles are formed in the continuous epoxy, the miscibility of block copolymer increases and the content of epoxy resin in the block copolymer increased, hence the delay; with the decrease in the weight % (10 and 20 wt%) of eSBS, the number of spherical micelles decreases, the content of epoxy resin in the block copolymer slightly decreased correspondingly a decrease in the gel time.

Table 2. Gel time (in minutes) for DGEBA/eSBS/DDM blend at different compositions and temperatures from rheological analysis

Samples	**90 ^{o}C**	**110 ^{o}C**	**130 ^{o}C**
DGEBA/DDM	58.39	18.25	9.27
DGEBA/10wt% eSBS(47)/DDM	59.68	20.57	10.82
DGEBA/20wt% eSBS(47)/DDM	75.60	28.68	10.70
DGEBA/30wt% eSBS(47)/DDM	79.53	30.66	12.25

Pressure–Volume–Temperature (PVT) Studies

The PVT analysis is an effective tool for studying the volume shrinkage behaviour with respect to the cure time of epoxy systems. PVT is used for our system based on DGEBA cured with DDM and modified with 10 wt% unepoxidised and epoxidised SBS. The changes in specific volume (*Vsp*) with respect to cure time for different epoxy/eSBS/DDM blend systems are analysed and the results are shown in the Figure 7. The PVT analysis was carried out at a pressure of 10 MPa and a temperature of 110 ^{o}C for 10 hours. From the analysis it was observed that, as the epoxy-amine reaction proceeds, the *Vsp* is decreased. The *Vsp* increases with lower density eSBS content. *Vsp* is maximum for the unepoxidised system this is expected since it is unepoxidised. After heating the mixture for about two hours, the *Vsp* remains constant and the final levelled region indicates the vitrification process even though the curing process is gradually continues.

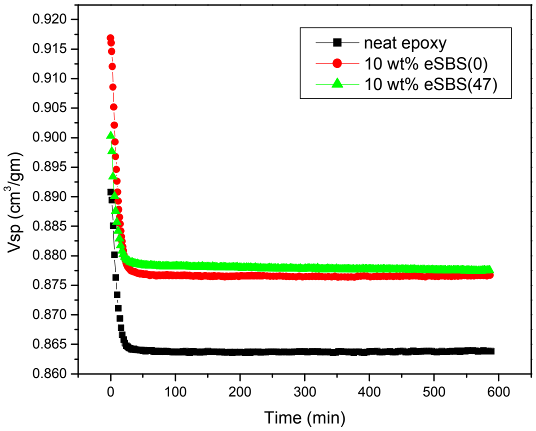


Figure 7. The variation of specific volume (*Vsp*) of epoxy/DDM blends during curing by the addition of 10 wt% eSBS(0) and eSBS(47).

The *Vsp* values can be used to calculate the percentage volume shrinkage of the eSBS modified epoxy blends at any time t, using the following equation 1.

$$\Delta V = ((V_{E0}-V_{E})/V_{E0})\ x\ 100 \text{ ------------------- } (1)$$

where V_{E0} and V_E are the experimental specific volumes of the blends at time t=0 and at any time *t*, respectively. Figure 8 reveals an interesting observation; it shows an increase in volume shrinkage with unepoxidised SBS and a decrease in volume shrinkage with epoxidised SBS. It is important to mention that, the time dependence of volume shrinkage for the epoxy/amine reaction is maximum for the 10 wt% eSBS(0) and is minimum for 10 wt% eSBS(47) from the initial to final stages of the reaction.

For the better understanding of the effect of epoxidised and unepoxidised SBS on the volume shrinkage, we have calculated the normalized shrinkage (ΔV_N) with respect to the epoxy volume content in the blend using the equation

$$(\Delta V_N) = (\Delta V / wt\ \%\ of\ epoxy\ phase) \times 100 \text{ ------------------- } (2)$$

Figure 9 reveals the volume shrinkage together with normalized values for the systems studied. The normalised volume shrinkage is highest for unepoxidised SBS and minimum for epoxidised SBS. Very recently Vijayan et al [47] observed higher volume shrinkage for epoxy/CTBN system compared with neat epoxy system. According to the authors CTBN increases the mobility of the epoxy phase allowing higher conversion. They also suggest the possibility of pressure induced shrinkage of CTBN and its effect on volume shrinkage. In line with reference [47], the highest normalized values for unepoxidised SBS may due to increase in the mobility of epoxy/amine system in the presence of unepoxidised SBS allowing higher conversion or it can be due to the pressure induced volume shrinkage of SBS. On the other hand the percentage volume shrinkage is decreased by the addition of the epoxidised eSBS. This can be explained by the plasticization effect and miscibility of epoxidised PB segments in epoxy resin [41], that is higher in the case of nanophase separated eSBS(47) blend systems, in comparison with the microphase separated, unepoxidised eSBS(0) blend system; therefore decreases the epoxy amine reaction and consequently, the decrease in the volume shrinkage, are in agreement with results of rheological tests.

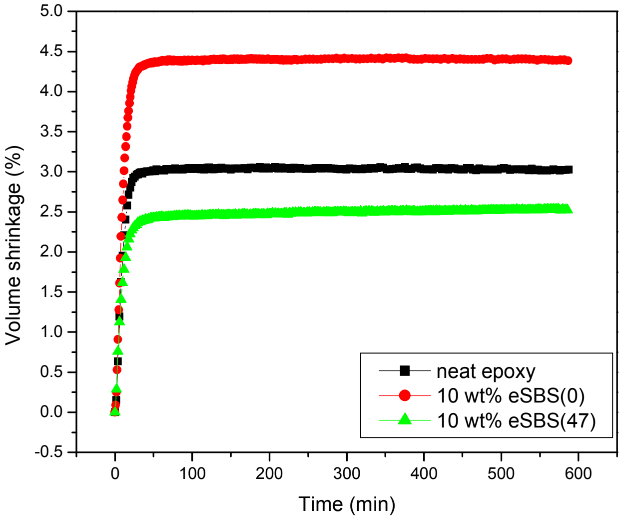


Figure 8. Influence of eSBS (0 and 47) content on the volume shrinkage during curing of epoxy/DDM blends.

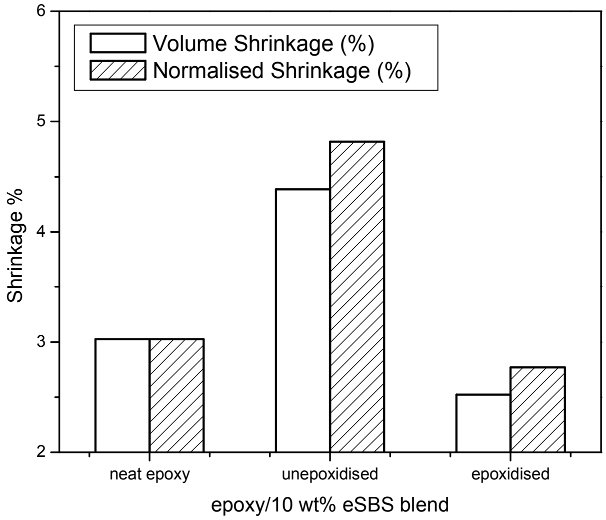


Figure 9. Volume shrinkage and normalized volume shrinkage values for epoxy systems

Conclusions

The synthesized epoxidised SBS was used for the modification of the highly brittle epoxy resin and the modification resulted by the formation of nanostructures within the epoxy matrix. The rheological and PVT analysis of the prepared blends was studied. The rheological studies showed a fluctuation in viscosity due to the nano phase separation of PS and unepoxidised PB domains in the continuous epoxy resin matrix and the results are in good agreement with the HR-TEM analysis. The gel time values are found to be increased with increase in modifier weight percentage and decreased with the isothermal curing temperature. The cure reaction is delayed by the addition of eSBS. The delay in cure reaction is due to the combined effects of plasticization and dilution and also due to the miscibility of epoxidised SBS in epoxy matrix. The miscibility of epoxidised SBS in epoxy resin and the viscosity is found to be increased with degree of epoxidation. The miscibility and viscosity increase is due to the plasticization effect and some specific type of interaction (hydrogen bonding) between the epoxidised SBS and the epoxy resin. The volume shrinkage analysis of block copolymer modified epoxy blends by PVT analysis reveals a decrease in volume shrinkage by the addition of block copolymer (eSBS), due to the dilution and nanophase separation of the PS and unepoxidised PB blocks of eSBS in the continuous epoxy matrix, while high volume shrinkage for unepoxidised SBS modified epoxy blends is due to immiscibility and pressure induced shrinkage of SBS.

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