Material Properties

Evaluation of non-Einstein rheology behavior of soft nanoparticles/epoxy nano-composites and their multifunctional effects on curing kinetics

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ABSTRACT

Non-Einstein rheology behavior is developed by using Polystyrene soft nanoparticles (PS-SNPs) in order to reduce viscosity and therefore the flow-ability of nano-composite during molding. PS-SNPs are synthetized by intramolecular crosslinking where the synthetized PS-SNPs' diameter is kept smaller than the diameter of epoxy chains to result the viscosity reduction through non-Einstein like behavior which is confirmed by DLS measurements. Also rheometric mechanical spectrometer (RMS) test showed about 50% viscosity reduction and the thermodynamic analysis showed that no phase separation will occur during curing process which is usual in epoxy/PS nano-composites. Also the effect of SNPs on epoxy crosslinking kinetic is studied by implementing non-isothermal differential scanning calorimetry (DSC). Using model-free approach to investigate the kinetic itself and its parameters, we have found that the activation energy is lowered by adding SNPs. Also as more conversion took place, the reduction of pre-exponential factor (showing the collision of reacting groups) occurred due to the linear growth of epoxy at early stages of the conversion and network growth is triggered at more conversions. These phenomena propose that for non-Einstein like behavior the polymer matrix molecular weight should be either more than critical molecular weight of entanglement or comparable with molecular weight among entanglements.

1. Introduction

Exciting nanoscale effects gives rise to a large decrease in melt viscosity of binary blends composed of high-molecular-weight polymer-A and polymer-A soft nanoparticles (SNPs). This idea is well-documented in the literature and interested reader may refer to [1–5]. Also addressed is the phase behavior of compressible, weakly interacting polymer-A and polymer-B SNP blends and their general strategies for better dispersion [1–3]. Pomposo et al. [5] have shown that the presence of SNPs in the PVME/PS-SNPs nanocomposite alters the thermodynamical behavior. They used a model equation for predicting free energy of soft nanoparticles [6] and showed that below a critical size of nanoparticles, the immiscible nanocomposite can be changed to complete miscible ones. Almost none of the previously introduced model equations of free energy for traditional hard nanoparticles could predict such changes in the thermodynamical behavior [7–10].

As approved by earlier studies, the presence of soft nanoparticles which are smaller than the matrix polymer chain radius of gyration decreases the viscosity through a complicated mechanism. Mackay et al. [1,2,11] suggested that the reduction occurs due to constraint release while Miller et al. [12] investigated the role of particle rigidity of SNPs by varying the crosslinking density of polystyrene nanoparticles. They observed that rigidity of nanoparticles affects the degree of viscosity reduction. However, the glass transition temperature was increased in some cases which are incommensurate with an increase in free volume. This phenomenon shows that SNPs are not a simple plasticizer and the mechanism of reduction can be more confusing. Also Li et al. [13,14] have recently showed that adsorption of polymer chains on nanoparticles depends on the ratio of diameters of nanoparticle and polymer matrix chain. All these reasons prove the enhancement of the chain dynamic in presence of SNPs leading to viscosity reduction. Tuteja et al. [2] have summarized the conditions for occurrence of non-Einstein behavior: (i) the radius of the SNPs should be smaller than the radius of gyration of the matrix polymer chains, (ii) the concentration should be such that the interparticle half-gap becomes less than Rg (radius of gyration) and (iii) the molecular weight of polymer should be higher than the entanglement weight.

Epoxy resins are widely used as adhesives, coatings and composite materials [15]. Some of the most challenging issues in these composite resins are the impregnation of reinforcements, curing behavior and

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stress residue of the molded article which all are influenced by resin viscosity [16–18]. The uncured resin behaves as a viscous liquid. As the curing reaction proceeds, the chains start to cross-link in a linear growth at early stages while the resin loses its processability at the end of this stage. At middle stages of curing reaction, resin's chains start to make 3-dimensional networks to reach diffusion stage of curing [19–21]. During the process, the low viscosity of initial stages helps molding process by decreasing molding pressure, shrinkage and increasing the middle stage time of the curing process. In spite of the good properties, applications and performance of epoxy resins, it is well known their fragility and poor resistance to the initiation and propagation of fissures or cracks. It is also known that brittle thermoset materials can be toughened by the incorporation of a thermoplastic or elastomeric additive, which can be dispersed in the epoxy matrix. In most cases, these mixtures are prepared from a homogeneous solution of the thermoplastic modifier in the precursor thermoset (monomer–epoxy), by inducing phase separation. But there are a lot of researches which are attempted to make complete solubility without affecting curing mechanism or conditions [17,22].

In addition, tracing of curing behavior is a method to evaluate the variation of viscosity on different stages of curing process. To reach this purpose, there are different tracing methods to study the curing kinetic of the resins, among which the differential scanning calorimeter (DSC) is the most common one [23–26]. By using this information and phenomenological methods, parameters like activation energy, pre-exponential factor can be calculated. Also, the activation energy of a curing resin directly depends on activation energy barrier of individual steps of curing reaction and pre-exponential factor which illustrates the collision of reacting groups [27,28].

In this study polystyrene SNPs are used as a multifunctional filler of epoxy resin in order to reduce viscosity and shrinkage through non-Einstein like behavior. The SNPs were synthetized by intramolecular method [29,30]. Thermodynamic equations are also used to investigate the miscibility of the synthetized SNPs [3]. Furthermore, the multifunctional effect of SNPs as a viscosity and profile reducer is studied by evaluating the curing kinetic and rheology behavior of the epoxy/PS-SNP nanocomposite.

2. Materials and methods

2.1. Materials

Styrene monomer and 4-vinylbenzylchloride were purchased from Sigma-Aldrich Co. TEMPO-OH (4-hydroxy-2,2, 6,6-tetra-methylpiperidine 1-oxyl), Sodium Azide, Benzoyl peroxide (BPO) and solvents were purchased from Merck Co. Epoxy resin was a product of Khalij-e-Fars Petrochemical under the commercial name of EP010 and EEW of around 660 g/eq. An anhydride curing agent was selected to cross-link the epoxy resin. All materials were used without any purification.

2.2. Synthesis of azide functionalized polystyrene

Random copolymer of poly(styrene-*co*-4-vinyl benzyl chloride) was synthesized using nitroxide mediated radical polymerization (NMRP) method [31] which is a controlled/living radical polymerization technique enabling the design of a well-defined copolymer [32]. Briefly, 10.8 g of styrene monomer and 1.74 g of 4-vinylbenzylchloride were added to a glass reactor and stirred for a short period, then 20.8 mg ofTEMPO-OH and 15 mg of BPO (Benzoyl peroxide) were added and stirred for 3.5 hr at 95 °C under the nitrogen blanket. Next, the temperature was raised to 125 °C and the mixture was stirred at this temperature for around 5 h. The resultant random copolymer was poly (styrene-*co*-4-vinyl benzyl chloride) which has 10% of chloride function. Percentage of this chloride function controls the percentage of further azide functions which, in turn, manipulates the cross-linking

degree of final intramolecular SNPs.

To change the functional groups of chloride to azide, 0.8 g of synthetic polymer was solved in 50 ml of Dimethylformamide (DMF) and then 0.06 g of Sodium azide was added, heated to 80 °C and stirred for 15 h. The reaction was held in opaque cell to prevent any light-mediated decomposition of Sodium azide.

2.3. Synthesis of polystyrene soft nanoparticles

The produced Azide functionalized PS was dissolved in DMF and a 10^{-7} M concentration of PS solution was prepared. The solution was placed in ultrasonic bath and subjected to the UV irradiation in order to proceed the intramolecular reactions. Ultrasonic bath is used to have a well-mixed sample and prevent intermolecular cross-linking of Azide groups. The resultant solution was concentrated in 60 °C for a day. Concentrated solution was precipitated by distilled water and filtered. Finally, the obtained powder was dried for further usage.

2.4. Preparing the Epoxy/PS-SNP nanocomposite

To prepare the epoxy/PS-SNP nanocomposite, the epoxy resin was dissolved in Dichloromethane (DCM) and SNPs were added and sonicated to ensure well dispersion. Also the thermodynamic evaluation predicts the miscibility of SNPs in epoxy resin which has been discussed in section 3.2. After 20 min of sonication, the anhydride curing agent was added and stirred in order to get a homogenous solution. Eventually, DCM solvent was evaporated by vacuum over the night.

2.5. Instruments

Fourier transform infrared (FT-IR) spectra were used to characterize the nanoparticles and functionalized polystyrene on a BOMEM spectrometer using KBr pellets. Also hydrodynamic diameter of synthesized SNPs was evaluated by Dynamic Light Scattering (DLS) on a Mastersizer 2000 (Malvern Instruments Ltd., UK, Model: 11029). To evaluate the surface topology of nanocomposite and miscibility of PS-SNPs in epoxy resins, we employed atomic force microscopy (AFM) with an Ambios Technologies USPM instrument in tapping mode.

To trace kinetic behavior of epoxy resin during curing, dynamic scans were performed using a differential scanning calorimeter instrument (DSC Toledo Mettler instrument, USA) from 25 °C to 200 °C by the rates of 5, 10, 15 and 20 °C/min. Samples preparation for DSC tests were similar to what describe above for nanocomposite.

To measure the impact of SNPs on rheology of epoxy resin, rheometric mechanical spectrometer (RMS, PaarPhysica, model UDS 200) was used at 80 °C which is the softening temperature of epoxy.

2.6. Thermodynamic analysis

The size of nanoparticles, or in another word, the ratio of nanoparticle radius to that of polymer chain radius of gyration affects the miscibility and stability of polymer/nanoparticle mixture [3,33]. As Pomposo et al. [3] showed, the replacement of the state of a polymer to its nanoparticle form could change the phase behavior of its blends so that an un-miscible blend of two polymer can change into miscible one when one of the species become nanoparticle with an ultra-small size. They proposed a free energy equation for compressible blends of polymer-B and polymer-A SNPs:

$$F = F_m^{co} + F_m^{int} + F_m^{np-np} + F_m^{np-p} \tag{1}$$

where

$$F_m^{co} = kT \left[\frac{\varphi_A \hat{\rho}_A}{\upsilon_P} \ln \varphi_A + \frac{\varphi_B \hat{\rho}_B}{N_B \upsilon_B} \ln \varphi_B \right] \tag{2}$$