

In Situ Growth of Multilayered Crystals in Amorphous Matrix: Thermal, Dynamic Mechanical, and Morphological Analysis of Nylon-6/Epoxy Composites

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ABSTRACT: A new procedure for processing of epoxy/polyamide blend was explored via solution polymerization of ϵ -caprolactam in *N*-methylpyrrolidone (NMP), which resulted in a suspension of nylon-6 in solvent at room temperature. The suspension was blended with water based epoxy resin using mechanical stirring at room temperature. Several films were prepared from blend by varying the amount of nylon-6 without curing agent. All films were fully characterized for thermal and dynamic mechanical properties using differential scanning calorimetry and dynamic mechanical analysis. The addition of nylon-6 had a plasticizing effect on epoxy evident by decrease in glass transition temperature (T_g). The reaction between nylon-6 and epoxy was studied using Fourier transform infrared spectroscopy by following the characteristic epoxy peak (914 cm^{-1}). The growth of nylon-6 crystals in epoxy matrix lead to spherulitic multiphase morphology, which was observed under scanning electron microscope. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2013

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INTRODUCTION

Epoxy resins are extensively used as coatings and adhesives in automotive, construction, and aerospace industries, primarily because of their excellent thermal and mechanical properties, such as high stiffness, high strength, chemical resistance, and dimensional stability with excellent adhesion to a variety of surfaces. In spite of outstanding properties, there are few drawbacks associated with epoxy, like inherit brittleness, low toughness, presence of microcracks, and poor fracture resistance. To overcome these drawbacks, incorporation of second phase, such as rubber or thermoplastic polymers, has often been successful to enhance the toughness and lower the brittleness of epoxy. The epoxy–thermoplastic composites have been studied since the 1980s with considerable progress in property improvement.^{1–3}

The modification of epoxy with rubber particles has shown significant increase in fracture toughness of brittle epoxy but at the expense of elastic modulus and glass transition temperature. Another major problem associated with rubbers such as polybutadiene is the presence of a high level of unsaturation, which provides sites for thermal and oxidative degradation. Moreover, the presence of double bonds in chain can cause further

crosslinking, which may result in a loss of elastomeric properties and ductility of precipitated particles.^{4,5}

To overcome the drawbacks in the use of rubber as a modifying agent, ductile engineering thermoplastics like polysulfone, polyester, poly(ether-imides), poly(ϵ -caprolactone), and polyamides have been studied as alternate modifiers. These thermoplastics are found to be promising since they do not decrease the inherent properties of the epoxy matrix.^{1,2}

Nylon-6 is a type of polyamide thermoplastic, which has been known to toughen epoxy not only by physical mixing but also by chemical interactions.^{6,7} Most of the previous research in the area of epoxy-nylon blends has been focused on mechanical properties but very little attention has been paid to prevailing chemical interactions. Gorton⁶ reported that the amide functional group in nylon backbone reacts with the epoxide functional group on the basis of swelling tests. Zhong and Guo⁷ studied the chemical reaction, cure kinetics and phase behavior of epoxy-nylon system using FTIR and differential scanning calorimetry (DSC). They found that curing reaction depends on composition and that curing decreases the crystallinity of nylon. This suggests that the chemical reaction has a profound effect on resulting multiphase structure, which controls the thermal

and mechanical properties, but there was no clear understanding of this phenomenon.

In a study by Kim et al.³ premade Nylon-6 powder was mixed with epoxy by heating the mixture above 200°C followed by cooling to room temperature. They found that the existence of multiphase structure, and hence ultimate properties of composite, depended on the mixing method. In another study by Jun Kyung Kim and Robertson, et al.,⁸ Nylon-6 powder was dispersed in epoxy resin mixed with the curing agent. They found that the inclusion of nylon-6 increase the fracture toughness without any loss of young's modulus or yield strength. Nylon-6, 6,⁹ nylon-4, 6,¹⁰ and nylon-12¹¹ have also been used as reinforcing agents with epoxy in order to modify epoxy resin properties.

For proper mixing of nylon-6 with epoxy, nylon-6 is desired in solution form. The known solvents for Nylon 6 are formic acid, hexafluoroisopropanol (HFIP) and *m*-cresol but acid may lead to corrosion in surface coating application while *m*-cresol is highly toxic and HFIP is very costly.

In this work, a novel nylon-6/epoxy resin reactive mixing process based on solution polymerization of Nylon 6 in NMP, a low volatility solvent, is explored. Nylon-6 was obtained in suspension form after polymerization and was then blended with water-based epoxy resin at room temperature at low shear with mechanical stirring. The obtained nylon-6 was found to react easily with epoxy resin. The morphology of the films was observed by using scanning electron microscope (SEM) while the transition temperature and mechanical property were determined by DSC and DMA.

The aim of this work is to develop a greater understanding of the processing-morphology-property relationship for nylon-6/epoxy resin composites. The effect of composition on the morphology and properties of the composites is presented in this article.

EXPERIMENTAL

Materials

Polyfunctional Water Dispersible DGEBA based Epoxy resin (EPIREZ 5522-WY-55) was purchased from Hexion Chemicals, Houston, TX. ϵ -caprolactam, 95% pure-dry sodium hydride, *N*-acetylcaprolactam and NMP solvent were purchased from Sigma-Aldrich, USA for solution polymerization ϵ -caprolactam.

Procedure

Synthesis of Nylon-6 in *N*-Methylpyrrolidone. Polymerization was carried out in an oil bath assembly. Hundred milliliter of NMP was taken in a three neck-flask and 30 g of monomer (ϵ -caprolactam) was added and stirred until it formed a colorless solution. Nitrogen supply was turned on and temperature was raised to 80°C. NaH (0.72 g) (catalyst) was then added to the solution and stirred till it dissolved completely. This process of dissolution was accompanied by a series of color changes from colorless to dark blue, which eventually turned black upon complete dissolution. Temperature was then gradually raised to 160°C and 0.396 g of *N*-acetyl caprolactam (initiator) was added to the solution while maintaining the stirring. After

addition of initiator, solution was stirred for 30 min, then nitrogen supply was turned off, and the black solution was observed to gently turning into a dark orange viscous solution. Nylon 6 existed as a homogeneous solution at higher temperature but while transferring to a glass jar at room temperature it began to phase separate and existed in a suspension form.

Preparation of Nylon-6/Epoxy Blends. Epoxy was transferred to a glass jar, nylon-6 suspension was added in various amounts and NMP was further added to dilute the solution to reduce the viscosity for ease of processing in order to have defect-free films and coatings. Nylon 6 was added as 0, 5, 10, 15, 20, and 30 wt % with respect to solid content of epoxy resin. The mixture was then stirred using mechanical stirrer for 1 hr at room temperature to obtain homogeneous solution and then ultrasonicated for 5 min.

Preparation of Solid Nylon-6 and Free Standing Films of Epoxy/Nylon-6 Blends. Five milliliters of nylon-6 suspension was taken in a Teflon mold and gradually heated up to 200°C for 24 hr in vacuum oven to fully evaporate the solvent and likewise nylon-6 granules were precipitated from the solution.

Eight milliliters of blend was taken and casted in $1.5 \times 1.5 \times 1/4$ inches of teflon molds. The films were cured in vacuum oven in a stepwise manner, heating initially at 50°C for 13 h, 100°C for 4 h, 120°C for 2 h, and finally 150°C for 2 h and were then cut with a sharp razor blade to obtain rectangular films for dynamic mechanical testing.

The free-standing films were quenched in liquid nitrogen and broken to see the cross-section of fractured surface under scanning electron microscopy.

The films and coatings were prepared from the solution with different amounts of NMP. At low amount of NMP (high Viscosity), defects like pinholes, cracks, and bubbles were observed, thus solution was diluted (viscosity was reduced) until defect free films were obtained and that system was considered for further study, but the amount of NMP in all systems was kept constant.

Characterization

The viscosity of blend was measured by shear viscometry using the Brookfield Viscometer. The Viscometer spindle speed was varied from 0.5 to 100 rpm and temperature was maintained at 25°C.

Nicolet 6700 FTIR instrument, equipped with a smart orbit ATR accessory with diamond crystal, was used to determine the chemical composition of the samples. ATR was performed over a wave number range between 4000 and 400 cm^{-1} .

Dynamic mechanical spectroscopy (DMS) was used to study the variation of storage modulus and $\tan\delta$ of neat epoxy and epoxy/Nylon 6 composite films with respect to temperature. Dynamic mechanical analysis (DMA) was performed between -20 to 140°C by using DMS6000, Seiko Instruments. The test was performed under tensile loading at a heating rate of 5°C/min and a frequency of 1 Hz.

Differential scanning calorimeter (DSC) was used to measure thermal properties of Nylon 6 and modified epoxy. DSC was

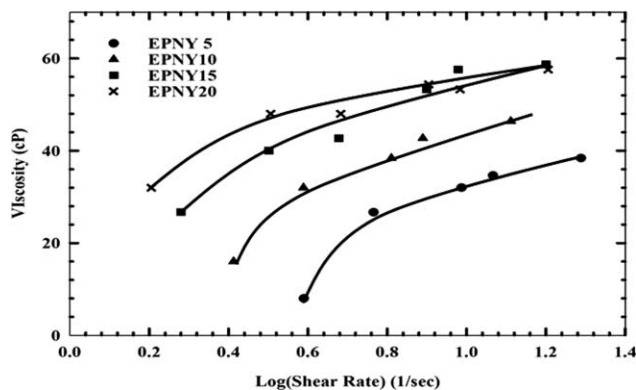


Figure 1. Variation of viscosity with shear rate for different nylon-6 wt % in epoxy solution.

performed at the heating rate of 5°C/min using DSC6200, Seiko Instruments.

SEM was a Philips model FEI XL 30 ESEM-FEG. The software used to capture images was Scandium. Aluminum stubs with carbon tape were used as sample holders, and the sample was coated with Au-Pd before subjecting to SEM.

RESULTS AND DISCUSSION

Rheological Behavior

Figure 1 shows the dependency of shear viscosity of epoxy/nylon-6 blend on shear rate with varying nylon-6 amount. The solution with greater amount of nylon-6 showed higher value of viscosity at all spindle speeds. The viscosity for all of the solutions increased with spindle speed indicating shear thickening. At low spindle speed there was a sharp increase in the viscosity with nylon-6 loading, while at high speed the increase was gradual as shown in Figure 2.

This kind of flow behavior suggests that an increase in Nylon-6 wt % in solution, results in more deviation from Newton's law of viscosity and the solution behaves more as a dilatant. The possible reason for this can be shear-induced particle migration or in other words, under stress nylon-6 tends to crystallize and behave more like a solid than solution.^{12,13}

There are two possible mechanisms for shear-induced particle migration during shear flow, heterogeneity of the stress field, and strong interparticle interactions. In first case, the particles

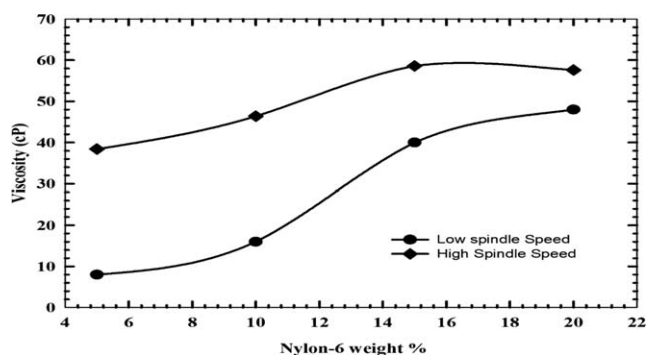


Figure 2. Viscosity at various nylon-6 wt % at spindle speed of 20 and 100 rpm.

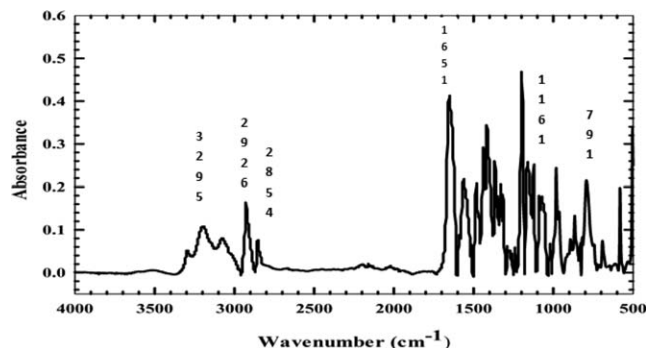


Figure 3. FTIR spectrum of nylon-6 precipitated from suspension in NMP.

tend to migrate to lower shear stress regions while in second case; the situation becomes more complex involving a coupled relationship between the thermodynamics and hydrodynamic forces.¹⁴

At low shear rate, interparticle force is more dominant in solution with low nylon-6 and shear force is dominant in solution with high nylon-6 loading. Hence, in the former case, suspended particles tends to remain in ordered layers as compared to solution with high nylon-6 loading, where particles tend to enter a state of flocculation and behaves more like a solid. This leads to a sharp increase in the viscosity of solutions at low shear rate. Whereas, at high shear rate, shear force is more dominant then interparticle force in all the solutions and thus there is a gradual increase in the viscosity.

Fourier Transform Infrared Spectroscopy

Figure 3 shows the FTIR spectra for the synthesized nylon-6. As expected, the characteristic amide peak was observed at 1651.6 (primarily due to carbonyl stretching vibration). CH₂ asymmetric and symmetric stretching was observed at 2926.6 and 2854.3, respectively. A small peak was observed at 3295, which can be attributed to hydrogen-bonded N—H stretching and peak at 1161.3 can be attributed to CONH skeletal motion.¹⁵ Peak at 791.3 belongs to N—H wagging and peak at 1351.6 corresponds to C—N stretch of amide linkage. This confirms that ϵ -caprolactam was successfully polymerized to form nylon-6 in NMP.

Figures 4 and 5 show the FTIR spectra for neat epoxy and epoxy/nylon-6 (20 wt %) composite, respectively. The

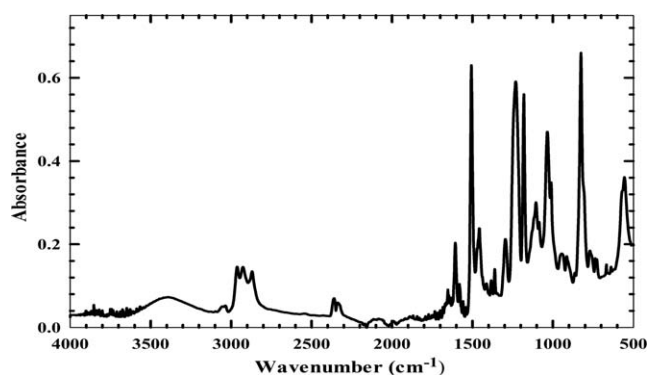


Figure 4. FTIR Spectrum of neat epoxy heated in oven for 9 h.

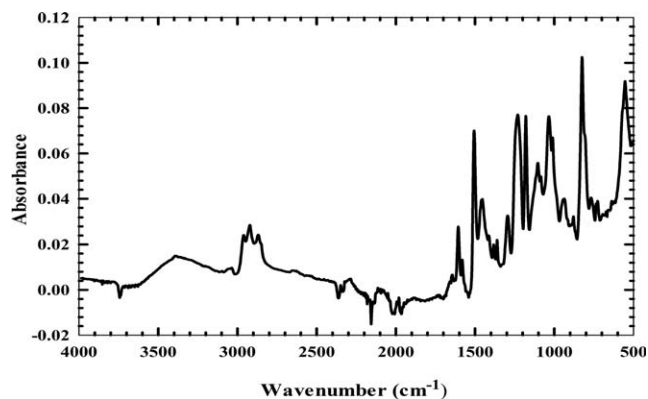


Figure 5. FTIR spectrum of epoxy/nylon-6 (20 wt %) heated in oven for 9 h.

characteristic peak of epoxide ring is observed at 914 and 863 cm^{-1} .¹⁶ On closely observing these two peaks in Figure 6, nylon-6 prepared in suspension form was found to be assisting in the curing of epoxy. All of the samples were cured under same conditions of time and temperature, but with the increase in nylon-6 wt % the peak corresponding to epoxide group gradually lowered, and at higher loading of nylon-6 (20 and 30 wt %) the peak completely vanished indicating complete curing. The broad peak corresponding to —OH stretching at 3393.5 in neat epoxy was found to be narrowed with a relatively sharp peak at 3392.5 in epoxy/nylon-6 blend indicating the presence of amine group in the system, which indicates hydrogen bonding.

Previously, many authors have done a time based study for curing of epoxy using FTIR, maintaining the same composition.^{17,18} Following the similar guidelines, a composition based study was carried out for the curing of epoxy as a function of wt % of Nylon 6.

All the samples were cured for same period of time and epoxy fractional conversion was calculated based on the peak area variation of epoxy group's absorption at 914 cm^{-1} . The internal standard was chosen as stretching vibration of C—C at 1506

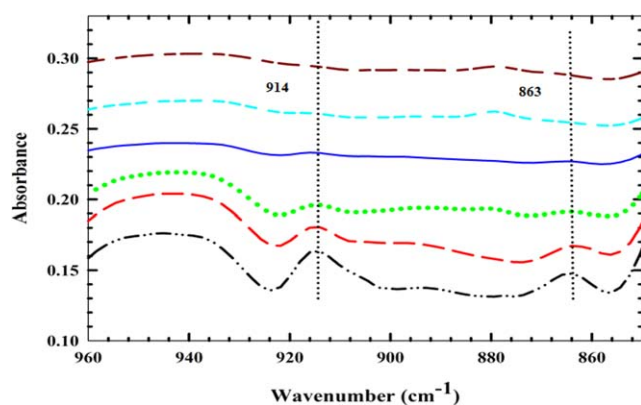


Figure 6. FTIR spectra of neat and nylon-6 filled epoxy (bottom—neat epoxy, 5 wt % nylon, 10 wt % nylon, 15 wt % nylon, 20 wt % nylon, top—30 wt % nylon). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

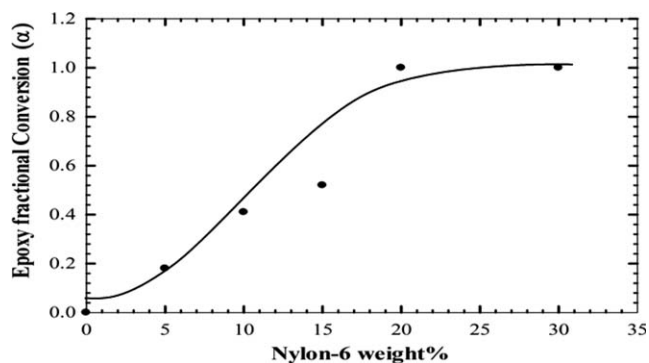


Figure 7. Epoxy fractional conversion as a function of nylon-6 wt %.

cm^{-1} characteristic peak of benzene to quantify the variation. The epoxy fractional conversion is calculated as:

$$\alpha = 1 - \left(\frac{\left(\frac{A_{\text{epoxy}}}{A_{\text{benzene}}} \right) \text{with nylon}}{\left(\frac{A_{\text{epoxy}}}{A_{\text{benzene}}} \right) \text{without nylon}} \right) \quad (1)$$

where A is the area under absorption peak.

Figure 7 gives the variation of epoxy fractional conversion as a function of weight % of nylon-6 in epoxy resin and was found to be increasing with the loading of nylon-6. The conversion is found to be low at low loading (5%), which increases sharply at 10 and 15% and then reaches a plateau at 20%, after which the conversion becomes almost constant.

Dynamic Mechanical Analysis

Figures 8 and 9 shows the dynamic mechanical properties for the neat and nylon-6-loaded epoxy films. The storage modulus and tangent-to-loss modulus are studied as a function of temperature beginning in the glassy state, through the T_g , and ending as a rubbery plateau.

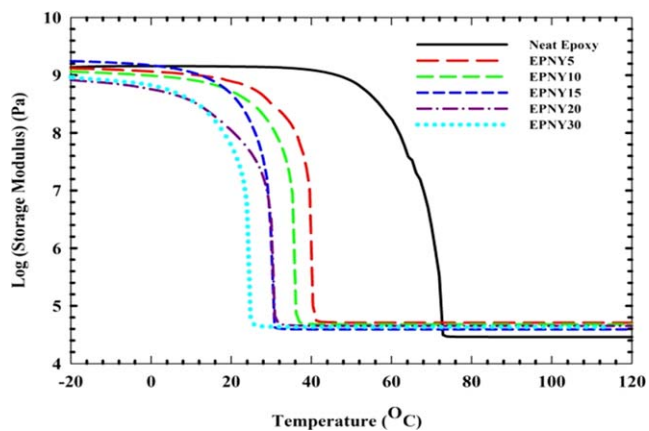


Figure 8. Variation of storage modulus with temperature for various nylon-6 loading of composite films (a: neat epoxy, b: 5 wt % nylon, c: 10 wt % nylon, d: 15 wt % nylon, e: 20 wt % nylon, f: 30 wt % nylon). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

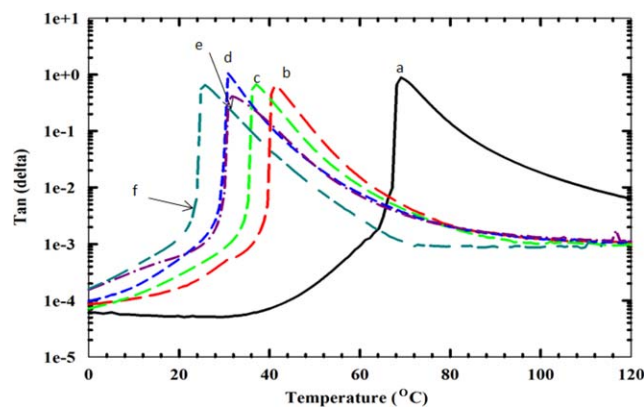


Figure 9. Variation of tan delta with temperature for various Nylon-6 loading of composite films (a: neat epoxy, b: 5 wt % nylon, c: 10 wt % nylon, d: 15 wt % nylon, e: 20 wt % nylon, f: 30 wt % nylon). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The storage modulus, which provides a measure of material stiffness under tensile deformation of a solid sample at room temperature, was highest for the neat epoxy, whereas the systems with nylon-6 showed lowering of storage modulus in glassy region. The variation of storage modulus with different nylon-6 loading in glassy region is shown in Figure 10. The fall of storage modulus in this region confirms the plasticizing effect of nylon-6 with an increase in flexibility of epoxy, which is inherently brittle by nature. As can be seen figure, the storage moduli of composite decreased almost linearly with addition of nylon-6. In glassy state, stiffness is related to changes in the stored elastic energy upon small deformation as the molecular segments resist motion.¹⁹ The composites with nylon-6 appear less able to resist segmental motion and thus are not able to store elastic energy, resulting in lower glassy modulus.

An increase in storage modulus in rubbery region was observed from neat epoxy to epoxy/nylon-6 blend. In composite systems, storage modulus was highest for 5% but decreased gradually with increase in nylon-6 weight % though it was greater than neat epoxy for all blends as shown in Figure 11. This phenomenon can be attributed to reaction between epoxy and nylon-6, which causes increase in crosslink density evident by the rise in elastic modulus. The presence of unreacted nylon-6 for higher

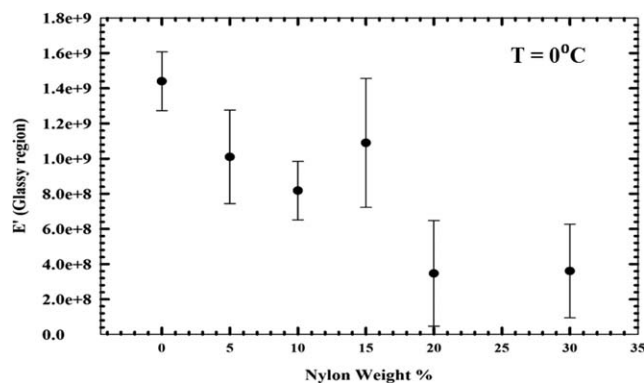


Figure 10. Storage modulus in glassy region as a function of nylon-6 wt %.

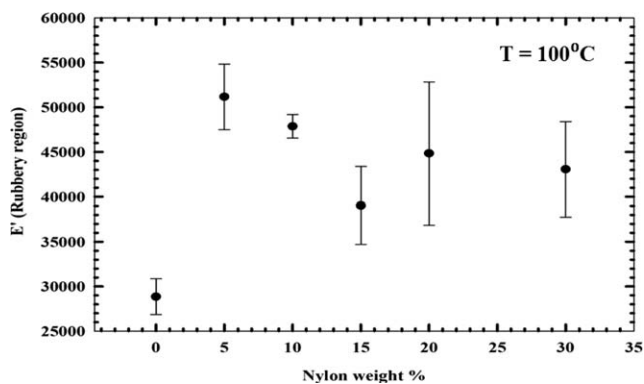


Figure 11. Storage modulus in rubbery region as a function of nylon-6 wt %.

amounts acts as plasticizer,²⁰ which causes fall in T_g , with increase in fraction of nylon-6. The curve for T_g as a function of composition is shown in Figure 12. The T_g drops sharply from neat epoxy (70°C) to 5% (41.2°C), then decreases gradually from 5 to 30% (25.7°C).

The reason for drop of T_g has been cited as under-curing of epoxy due to partial miscibility of second phase in epoxy²⁰; another reason can be flexible aliphatic nature of thermoplastic backbone.² In the present case increase in nylon-6 loading leads to increase in crosslink density as indicated by increase in storage modulus in rubbery region. Moreover, FTIR results also suggest increased curing of epoxy. Hence, a possible reason for lowering of T_g by addition of nylon-6 should be its plasticizing effect, i.e., it reduces the intermolecular forces among chain of epoxy and essentially lubricates the macromolecular chains.

Furthermore in the given temperature range, presence of single peak for tan (delta) indicates the existence of a single amorphous phase in cured epoxy/nylon-6 blend. If the two starting materials had different phases in amorphous region and prevented reaction, then two T_g peaks would be expected, one for each amorphous phase, which is observed for immiscible or partially miscible thermoplastic blends.

The observed T_g from DMA was compared with the theoretical linear model given by Fox equation, which predicts the

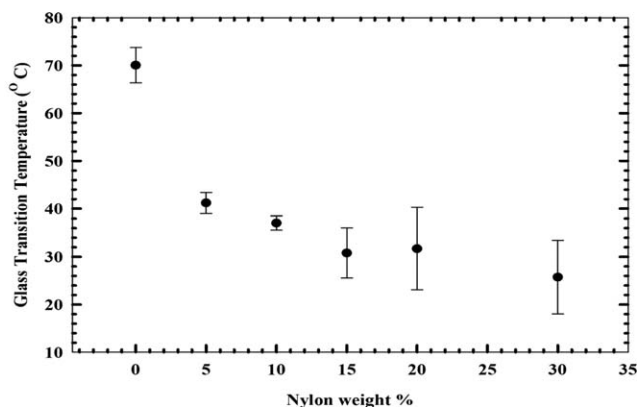


Figure 12. Variation of T_g of the composite with increased loading of nylon-6 in epoxy.

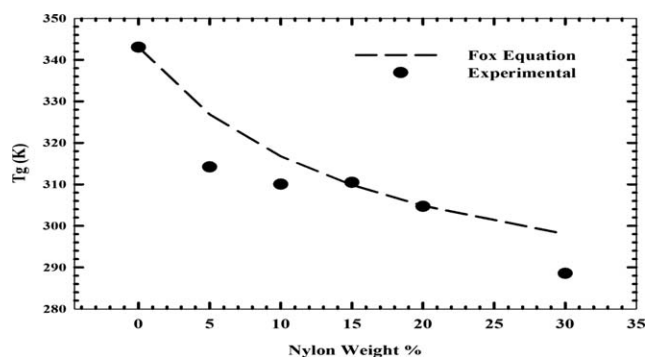


Figure 13. Comparison of experimental dependency of T_g on composition with fox equation.

dependency of T_g on composition. The Fox equation is a simple additive law, which does not account for any kind of interaction between two polymers in the systems. The comparison can be seen in Figure 13. A negative deviation was observed from the ideality, which suggests the presence of strong hydrogen bonds and chemical interaction between two participating polymer entities.

Differential Scanning Calorimeter

Thermal transitions in nylons have been widely studied by previous researchers using DSC.²¹ Nylon-6 and its blends with epoxy were subjected to DSC to investigate thermal transitions. Figure 14 is the DSC thermogram for nylon-6, which shows glass transition temperature (T_g), Melting point (T_m), and crystallization temperature (T_c). The nylon-6 and composite samples were first heated to 60°C from room temperature followed by quenching with liquid nitrogen and the second run was started from -20 to 250°C. They were then cooled rapidly to room temperature and were reheated from -20 to 250°C and then cooled to monitor the crystallization peak.

A sharp fall in the baseline was observed for neat nylon-6 from 9°C to 32°C suggesting T_g to be around 25–28°C. The onset temperature for melting of nylon-6 was 188°C, the peak was observed at 209°C, and the offset temperature was around 215°C. The crystallization begins to occur at 177°C, reached a

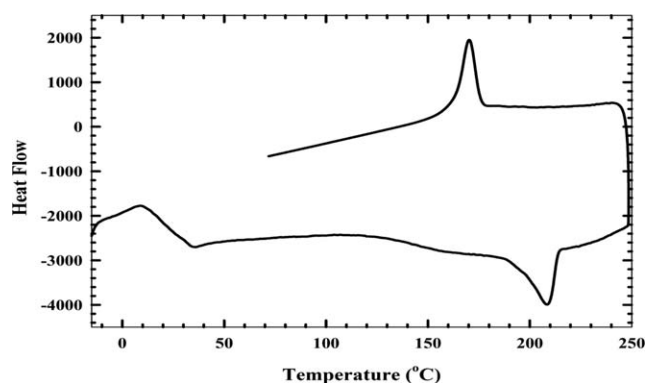


Figure 14. DSC thermogram for nylon-6 showing glass transition temperature, melting temperature, and crystallization temperature.

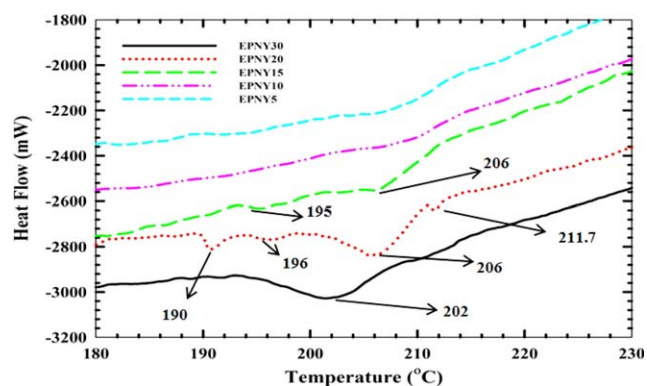


Figure 15. DSC curve for epoxy-nylon composites films showing T_m . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

peak at 170°C and the peak dropped at 160°C. The % crystallinity was calculated on basis of the following formula:

$$\% \text{ Crystallinity} = \frac{\Delta H_f}{\Delta H_f^0} \times 100 \quad (2)$$

Where ΔH_f is measured heat of fusion from DSC and ΔH_{f0} is heat of fusion of equilibrium crystals (totally crystalline polymer). A commonly accepted average value of 230 (± 20) J/g for nylon-6 was used as ΔH_{f0} for calculating crystallinity.²¹ The approximate value of ΔH_f calculated from melting peak of nylon-6 was 89.71 J/g.

The calculated crystallinity was around 35–42%.

For the composites with loading of nylon-6, associated melting peak was well observed, but with the reduction in nylon-6, the melting peak began to broaden and no clear and distinct peak was observed at lower loading of nylon-6 (5 and 10%) suggesting significantly low crystallinity. Figure 15 is the DSC thermogram showing the melting peak of epoxy/nylon-6 composites and Figures 16 is a comparison between glass transition

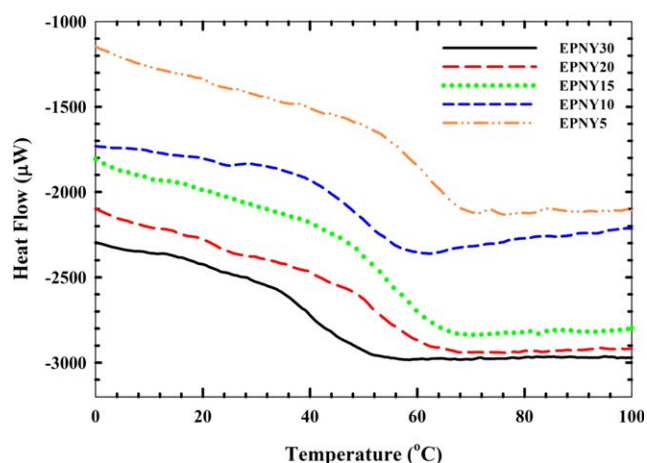


Figure 16. DSC curve for epoxy-nylon composites films showing T_g . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. The Peak Value of Melting Depression for Different Composition

Composition	Melting onset temperature (°C)	Melting peak temperature (°C)	Melting offset temperature (°C)	T_g (°C)
Neat Nylon-6	188	209	215	25
EPNY30	193	202	209	42
EPNY20	189	190	193	54
	194	196	198	
	200	206	210	
	210	211.7	213	
EPNY15	193	195	200	57
	202	206	212	
EPNY10	204	208	213	50
EPNY5	189	194	200	61
	202	208	214	

temperatures. Table I shows the onset melting point, peak melting point, offset melting point and T_g of neat nylon-6 and its blends with epoxy.

The T_g shown in Figure 16 was calculated in the third run of DSC, where solvent was evaporated and curing was complete. Hence, T_g observed by DSC was higher than that of DMA. In few compositions of epoxy/nylon-6, distinct multiple peaks over a broad range were observed. This suggests a wide distribution of nylon crystals in epoxy matrix.

As nylon-6 was crystallized in a solution of epoxy and NMP, epoxy can be considered as a diluent in present case. The results on melting were in accordance with Flory's theory of depression of melting point in presence of diluent. The T_m for neat nylon-6 was 215°C, which was more than T_m of nylon-6 in epoxy for all compositions. But when T_m was analyzed only for composites, it was found to decrease with increase in nylon-6 concentration (decrease in epoxy as diluent), which is in opposition to Flory's theory, where T_m is expected to decrease with increase in diluent. Figure 17 shows a variation in onset, peak, and offset

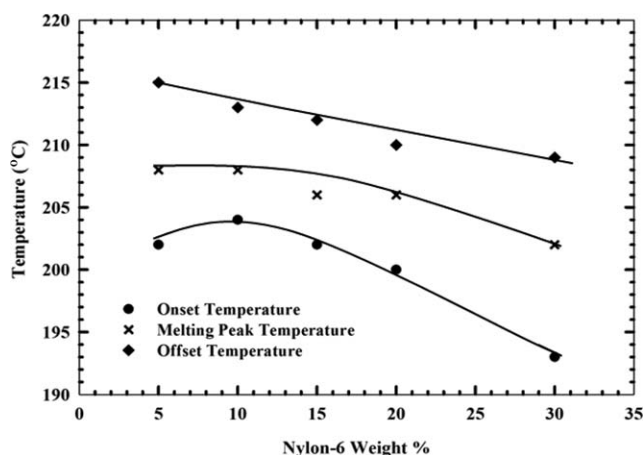


Figure 17. Comparison of onset, peak, and offset melting temperature of nylon-6 in epoxy.

melting points. All of them showed a decrease with increase in composition. This phenomenon can be explained on the basis of thermodynamics. The equilibrium melting point is given by following equation¹²

$$T_m = \frac{\Delta H_f}{\Delta S_f} \quad (3)$$

The addition of nylon-6 in epoxy can be viewed as increase of nylon-6 chains in epoxy. During processing of composites, two phenomena take place: reaction (curing) and crystallization. At higher concentration, more chains of nylon-6 react with epoxy and reacted chains of nylon-6 exist in amorphous state.⁷ Molecular weight of epoxy resin increases, i.e., at higher composition epoxy acts as more effective diluent. Second, melting point depends on change in enthalpy and entropy of the system according to eq. (3). The melting point depends upon the ratio of ΔH_f to ΔS_f . Once melting initiates, there are more number of crystalline chains going through transition to liquid state at higher composition. The more are chains, the more is number of conformations, which will lead to increase in entropy of system according to Boltzman's equation:

$$S = K \ln \omega \quad (4)$$

Melting temperature is inversely dependent on entropy, hence at higher composition, more number of chains lead to increased entropy, which results in lowering of melting point.

Morphology

The structure of crystals grown from solution has been reported for higher density polyethylene, slightly branched polyethylene, polypropylene, poly(4-methylpentene-1), polyoxymethylene. In all aforementioned polyolefins and polyoxymethylene, only weak secondary forces exist between neighboring chain segments, but polyamides have relatively stronger hydrogen bonds, which greatly influences the nature of crystal growth. Previous studies were limited to precipitation of polyamides from formic acid near room temperature, where spherulitic structures were obtained composed of lathlike lamellae. Later, growth of single crystals of alcohol soluble nylon from solution was thoroughly investigated by Geil.²² The crystal structure of nylon-6 crystals has been demonstrated as dendrite or febrile with the appearance of being a bundle as ribbon twisted together in the middle while some of them being a radial array by previous authors.^{22,23}

The crystalline morphology of neat nylon-6 obtained by solution polymerization and then precipitated from suspension in NMP was observed under SEM (Figure 18). A unique morphology was observed with fiber like crystals; hence it was vital to see the growth and nature of crystals in epoxy matrix.

It was observed that crystals grow in distinct crystalline zones within the amorphous epoxy matrix. As the nylon in composition increases, the number of crystalline zones increases and after certain composition phase inversion takes place. Three distinct SEM images have been shown for comparison in Figure 19. The first one is of neat epoxy, which represents only

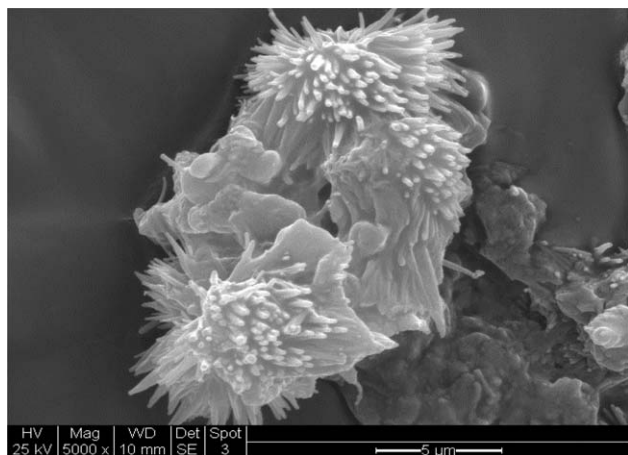


Figure 18. SEM image of nylon-6 crystallized from nylon-6-NMP solution.

amorphous phase. The second image is of epoxy/nylon-6 (10%), which shows nylon-6 crystals growing within the amorphous matrix and protruding out of the fractured surface. In this case, epoxy can be considered as diluent, which dilutes nylon-6, causing growth of large crystals during the process of curing. The third SEM image is of epoxy/nylon-6 (20%), which shows various crystals distributed uniformly among the amorphous matrix. This can be considered as composition where phase inversion initiates.

The process of crystal growth in epoxy matrix can be visualized as a series of events that occurs during the process of curing. All the epoxy/nylon-6 blends initially exist as a miscible solution. In the state of solution, polymer chains are free to move in any direction i.e., chains are in their random state. As the heat is supplied to initiate the curing process, the solvent begins to evaporate. Because of lack of solvent and dilution, polymer chains realign themselves to acquire the most stable state. Epoxy being the amorphous polymer forms a crosslinked network, but nylon-6 is able to crystallize because of presence of amide group, which tends to hold up the chain in an orderly fashion via hydrogen bonding. Hence, surface of epoxy chain acts as an impurity or nucleating agent for crystals of nylon-6 and the thermoplastic chains begin to fold over the surface leading to formation of crystal lamellae. Their radial growth leads to formation of spherulites. Hence, the cured film of homogeneous blend exists in two phases: a crystalline nylon-6 phase with fibrillar crystals and an amorphous epoxy and reacted nylon-6/epoxy phase. The nylon-6 chains, which were able to crystallize represent the part of nylon-6 that could not take part in the reaction with epoxy. It has been reported that the reaction of nylon with epoxy leads to decrease in its crystallinity. The amorphous part of nylon-6 reacts with epoxy leading to a single amorphous phase indicated by presence of one T_g .

Infrared spectroscopy suggests the presence of chemical linkages between two entities, on the other hand DSC and Morphology suggests the presence of nylon-6 crystals in product formed. Hence, the novel product can be considered as a copolymer of epoxy and nylon-6, which contains crystallite domains in the

long chain. The resultant product can either be semicrystalline network structure or semicrystalline branched structure or non-interacting network structure. The schematic of proposed modified epoxy is shown in Figure 20.

CONCLUSIONS

A nonconventional method to synthesize nylon-6 was successfully explored via ring-opening polymerization of ϵ -caprolactam in *N*-methylpyrrolidone solvent leading to a very simple and efficient blending of nylon-6 with water-based epoxy. The increase in concentration of nylon-6 in epoxy leads to lowering of T_g with increase in flexibility indicating the plasticizing effect

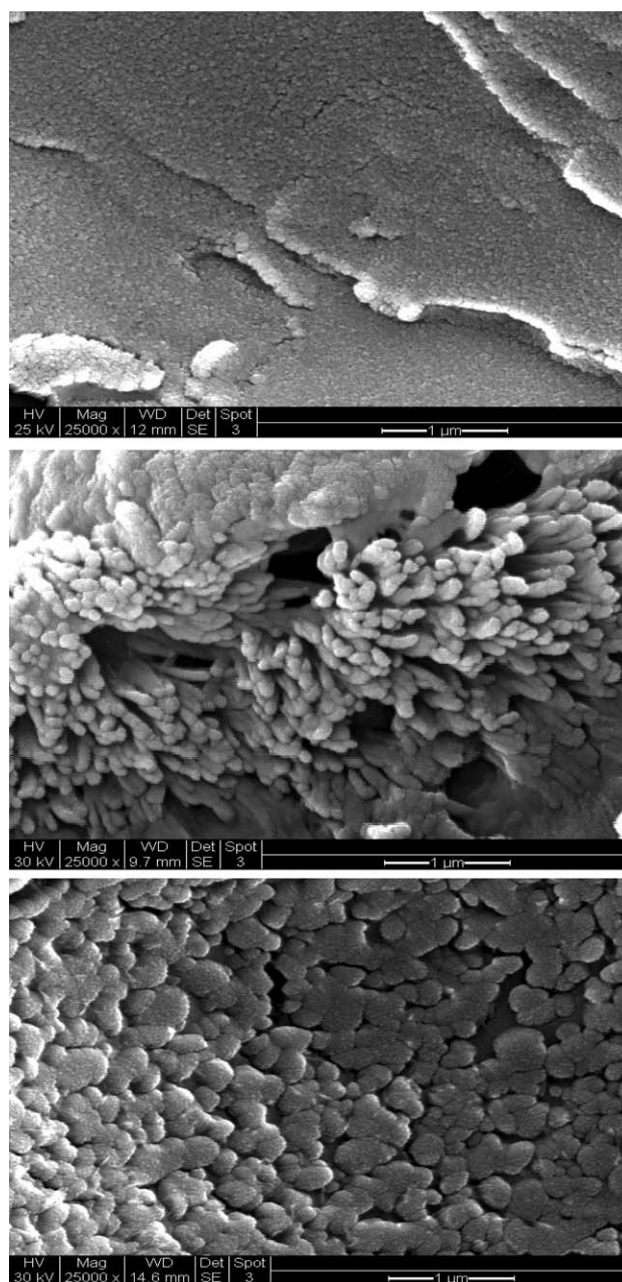


Figure 19. SEM Images of cross-section of fractured surface for neat epoxy, epoxy/nylon-6 (10 and 20%).

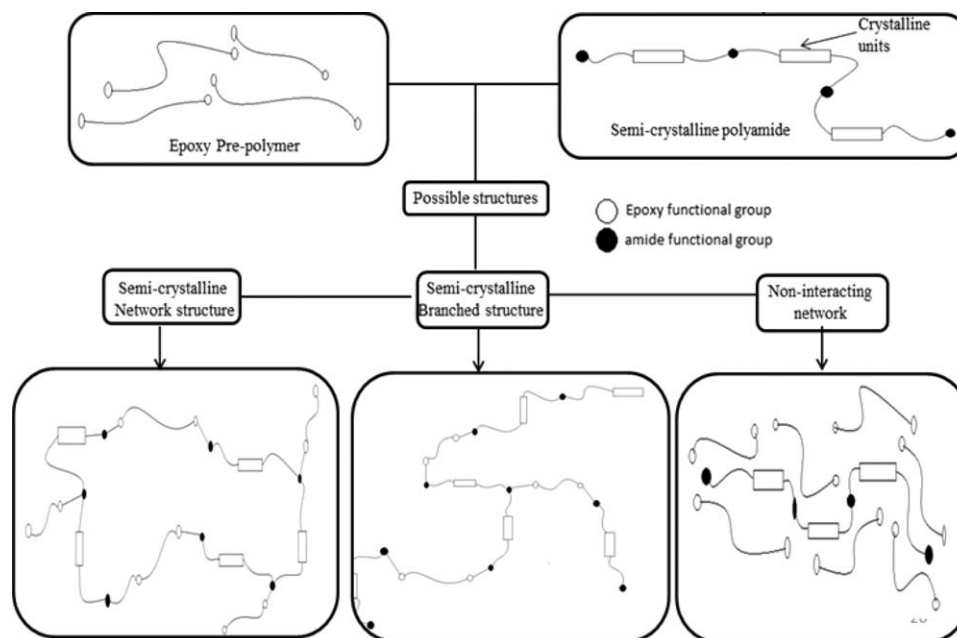


Figure 20. Schematic of possible structures of modified epoxy.

on epoxy. Nylon-6 was found to be assisting in the curing of epoxy as confirmed by FTIR studies and an increase in storage modulus in rubbery region. All the prepared systems exhibit heterogeneity and the morphology changes considerably with variation in thermoplastic component. The thermal transitions studied using DSC revealed that nylon-6 prepared by this method attains a high crystallinity. During the processing of composite, curing of epoxy and crystallization of nylon-6 occurs simultaneously leading to formation of crystalline zones in amorphous matrix.

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