Synergistic Mechanical Response of Nylon 6/Trogamid® T Blends

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ABSTRACT: Blends of semicrystalline Nylon 6 with a varying ratios of amorphous Nylon are studied for their morphological, thermal, dielectric, and mechanical behavior. Thermal analysis indicated a compositional dependant decrease in the melting and crystallization temperatures of Nylon 6. The blends exhibited a single compositional dependant glass transition temperature in dynamic mechanical thermal analysis and dielectrical relaxation spectroscopy over entire mixing ratio indicating miscibility between the blend components. The values of flexural modulus and tensile modulus of the blends are found to increase without significant loss in the impact properties. The water absorption of the blends is also lower than the values calculated by rule of mixtures. The observed synergistic behavior of the mechanical properties of the blends is indicative of presence of strong interactions in the blends components. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 65–72, 2013

INTRODUCTION

Polymer blending is an effective tool to obtain new materials with desired properties and with economic advantage. Promising future with blends is expected from large numbers of research articles published on the topic.[1–4] Most of the polymer blends reported in the literature are two phase systems or known as heterogeneous systems wherein the properties are governed by the phase morphology and the interface.[5–10] However, there are few miscible systems known, which represent a single phase and exhibit interesting properties such as single glass transition temperature, melting point depression, reduced crystallinity and crystallization rate.[11–15]

Commercial Nylon 6 made by ring opening polymerization of e-caprolactam, is a semi crystalline polymer with a very small range of processing window as the degradation temperature is very close to the melting point. Typically blending Nylon 6 with aromatic polyamide having higher glass transition temperature, more free volume, and lower water absorption can certainly of great interest.[16–18]

Blends of Nylons 6 (aliphatic) with Nylons (aromatic) have been a subject of interest because of the possible interactions between the amide groups and cross hydrogen bonding.[19–21] Miscibility of these components in blends can be described by negligible value of entropy of mixing in the free energy of mixing expression.[18]

$$\Delta G_m \approx \Delta H_m = kT\chi\phi_1\phi_2 \tag{1}$$

where ΔH_m is heat of mixing, k is the Boltzmann constant, T is the temperature, ϕ_1 and ϕ_2 are the volume fractions of first and second polymer, respectively. Miscibility requires exothermic mixing, i.e., a negative enthalpy of mixing.

In a series of publications, Ellis et al. have looked at the miscibility aspect of nylon blends prepared by solution blending and has derived various parameters, which define the interaction between the polymers.[16,18,22–27] The solution blends of semicrystalline Nylon 6 and an amorphous Nylon; poly (trimethyl hexamethylene terephthalamide) has been reported to be miscible.[18–25] It is therefore interesting to study the mechanical properties of these blends. Varieties of properties expected from these blends are completely governed by interaction between component chains. Predictions of miscibility range between blend components using binary interaction and intramolecular repulsion mode showed that the amide concentration was more important than compositional differences.[18] Nylon 6 and Trogamid exhibit different morphologies and incorporation of amorphous phase in semicrystalline polymer results in reduced crystalline component.

In such semicrystalline-amorphous blends, probable miscibility is obtained by interaction between amorphous phases of both components. Earlier studies validated this theory by showing

depression in T_m of crystalline component.[16] Crystallization behavior dependent on number of intrinsic and extrinsic thermodynamic variable. However in case of such blends it can be understood as interruption in growth of crystal morphology by means of amorphous component. Thus, many studies use this domain to estimate interaction parameters between semi crystalline-amorphous components.[26] Kambour et al. proposed that repulsive effect between comonomer units of copolymer leads to attractive forces for miscibility with other component in certain range of compositions.[28] In Ellis et al. work various polyamides grades had been taken to study miscibility. Interestingly, his study indicated that miscibility of aromatic amorphous nylons in aliphatic nylon is dictated by lower and upper critical concentration of amide functionality.[16,18,26] Further analysis revealed that 1-4 substituted phenyl isomers on aromatic nylon influence segmental interaction more than 1-3 substituted isomers of aliphatic component.[16]

On the basis of melting point depression in miscible polymer blends, Nishi et al. proposed estimation of interaction parameter for miscible blends. Simple form of equation to represent depression of melting temperature (T_m) is given as[29]:

$$\frac{1}{T_{mb}^0} - \frac{1}{T_{mp}^0} = -\frac{RV_2}{\Delta H_{fm}V_1}\chi_{12}(1-\phi_2)^2 \qquad (2)$$

Here T_{mp}^0 and T_{mb}^0 are equilibrium melting temperature of crystallizable component of polymer and blend, V is the molar volume of respective component, ΔH_{fm} is the heat of fusion of per mole of repeating unit and ϕ_2 is the volume fraction of component 2. Equation can be further reduced by introducing interaction energy density term, B:

$$\chi_{12} = BV_1/RT \qquad (3)$$

Combining last two equations and substituting $T = T_{mb}^0$ gives the equation of the form:

$$\frac{1}{T_{mb}^0} - \frac{1}{T_{mp}^0} = -\frac{BV_2}{\Delta H_{fm}}(1-\phi_2)^2 \qquad (4)$$

Thus knowing the values of equilibrium melting temperature of crystallizable component of polymer and blend one can give interaction parameter of those blends. The miscibility for blend system under this investigation is reported with an interaction parameter of -0.005.[18,25]

MATERIALS

The aliphatic Nylon used in this experiment was Nylon 6; grade-Aegis[TM] H73QP supplied by Honeywell India (Melting point 220°C), semicrystalline in nature. Aromatic component used was nylon, poly(trimethyl hexamethylene terephthalamide), grade Trogamid® T-5000 (Trogamid) supplied by Daicel-Hulls Limited, containing terephthalic acid. This polymer was fully amorphous in nature.

Experimental Methods

Nylon 6 and Trogamid pellets were predried at 80°C and 110°C, respectively for 24 h in vacuum oven prior to blending. Two

polymer pellets were dry mixed in different compositions. These pellets were then fed in Berstoff ZE-25 intermeshing co-rotating twin-screw extruder with L/D 41.5:1 at a screw speed of 150 rpm. The temperature range was 225–265°C. Five blends compositions prepared for wt/wt ratio of Nylon 6 to Trogamid were 90/10, 80/20, 70/30, 60/40, and 50/50. The blend containing 100% Nylon 6 and Trogamid are abbreviated as N 6 and Trogamid® respectively; similarly, blends containing 10, 20, 30, 40, and 50% Trogamid of total composition are abbreviated as N6/10, N 6/20, N 6/30, N 6/40, and N 6/50, respectively.

Compounded pellets were predried at 80°C for 24 h in vacuum oven. The test specimens for tensile, flexural, and impact testing were molded using Arburg 220-90-350 injection molding machine at 220–260°C. The temperature profile for Trogamid[R] T-5000 was 240–280°C. Mold was kept at room temperature. Molded specimen of base polymer and blends were stored in vacuum-sealed desiccators prior to testing.

CHARACTERIZATIONS

Scanning Electron Microscopy (SEM)

Phase morphology of the prepared blends was examined by scanning electron microscopy (SEM), Leica model Steroscan 440. Injection molded samples fractured under impact testing were used to study morphology. The fractured surfaces were sputtered with gold to avoid charging under electron beam.

Differential Scanning Calorimetry (DSC)

The measurements of the crystallinity of nylon blends were carried out by using Perkin Elmer differential scanning calorimeter. Tests were conducted by placing sample in sealed aluminum pan over a temperature range of 50–250°C. A controlled heating rate and cooling rate was maintained at 10°C min^{-1}. The test was carried out in inert Nitrogen atmosphere. The melting point (T_m) and crystallization temperature (T_c) were determined from peak maxima of the reheating and cooling scans, respectively.

Dynamic Mechanical Thermal Analysis (DMTA)

Dynamic mechanical thermal analysis conducted using a dynamical mechanical thermal analyzer, DMTA IV Rheometric Scientific (Piscataway, NJ) in single cantilever bending mode with a strain of 0.02%. Temperature range subjected between 0 and 200°C with a heating rate of 5°C min^{-1}. The test performed at 1 Hz frequency. The size (length × width × thickness) of the test samples were 20 × 12 × 3.2 mm^3.

Dielectric Relaxation Spectroscopy (DRS)

Dielectric relaxation spectroscopy (DRS) measurements were performed on Novo control Alpha analyzer (Germany) at frequency of 1 Hz and temperature range of 30–200°C in 1 K steps. The temperature was controlled to ±0.1 K with Novo control Novotherm system. Dielectric measurements were carried out using gold coated copper electrodes; sample of thickness 1 mm and diameter 25 mm reside in between these electrodes.

Mechanical Testing. Computerized STAR make universal testing machine (UTM) was used to carry out the tensile and flexural tests. The tensile test conditions were maintained as per

ASTM D 638, using type I specimen at a strain rate of 50 mm min^{-1} with load cell of 10 kN. The flexural testing was carried out as per ASTM D 790 for three-point bending with span length 60 mm at the strain rate of 1.3 mm min^{-1} with load cell of 500N. The Izod Impact (Notched) tests were carried out as per ASTM D 256 by using ZWICK (Germany) digital Impact tester with impact hammer of 0.5 J. All samples were tested at 50% RH and at room temperature.

Water Absorption. Water absorption test was carried according to ASTM D 570. Specimens were dried at 60°C for 24 h and cooled to room temperature in desiccators. The specimens were weighed to ±0.001 g by using electronic balance and then were immersed in distilled water for 24 h. The specimens were again weighed after wiping. The percentage of water absorption was calculated as follows:

$$\text{Increase in Weight} = \frac{\lfloor \text{Wet Weight} - \text{Conditioned Weight} \rfloor}{\text{Conditioned Weight}} \times 100 \qquad (5)$$

RESULTS AND DISCUSSION

Morphological and Thermal Characterization of Prepared Blends

The morphology of the phases in a blend is critical to property development and is well investigated with SEM. Figure 1 shows the SEM micrographs of fracture surfaces for Nylon blends.

As can be seen, the blends show homogeneous structure for all the blend compositions. The presence of such homogeneity can be attributed to the possible miscibility in the blends. Similarly fracture mechanism in the Figure 1 shows strong composition dependency. Fracture surface shows the formation of steps along the crack growth direction in all samples except N6 where flat surface is evident. These fracture steps are characteristics of brittle failure. Fracture steps moving in the direction of crack in all cases except Trogamid. This is due to bridging mechanism by Nylon 6 in all cases which is absent in Trogamid. Under the cracking mechanism it could found that both blends suggest miscible behavior.

This probable miscibility is investigated by thermal analysis of phase component in differential scanning calorimetry. Overall depression in crystallization of Nylon 6 expected by incorporation additional amorphous domain.

Figure 2 shows the crystallization and melting temperature (second heating thermograms) of both Nylons and their blends obtained in DSC as a function of Nylon 6 ratios in blends. The endothermic melting peak (T_m) of Nylon 6 shows depression with addition of amorphous component over the entire range. However, actual melting temperature is sufficiently high for Trogamid$^®$ than projected model. Crystallization kinetics of crystalline component follows the trends but shows a drop in crystallization temperature (T_c) after loading of amorphous component more than 20 wt %. In Figure 3, the plot of ΔH_f versus blend composition shows linear behavior leads to the conclusion that overall crystalllinity of samples following rule of mixing. Thus major rearrangement occurs in amorphous components due to very strong intermolecular interaction, in the form of electron donor–acceptor complexes.[30–34] Ellis et al. and Myres et al. discussed these interactions for number of miscible and immiscible nylon blends in details.[18,30] Observed reduced thermal behavior analysis of blends can be studied in more details by understanding amorphous domain of system at transition temperature which can be better represented by Dynamical mechanical thermal analysis.

Dynamical Mechanical Properties

The phase behavior of binary blends is usually studied by dynamic mechanical thermal analysis, as the technique is very sensitive to molecular relaxation processes. The degree of mutual solubility of the component polymers leads to changes in the transitions providing direct evidence of the miscibility. The dynamic mechanical thermal analysis provided confirmation of the phase behavior of Nylon 6 and Trogamid blends and replicate true nature of segmental transition of blends. All blend compositions exhibited a single tan δ peak over temperature spectrum of 0–200°C as evident in Figure 4.

Generally the occurrence of a single tan δ peak in blend is indicative of miscibility at a molecular level. The presence of single tan δ peak for all the blend compositions thus confirms miscibility in component, which shows complete agreement with DSC results. Nylon 6 exhibits a single tan δ peak at about 75°C and Trogamid at about 162°C corresponding to the glass transition where as the blends exhibited peaks in the temperature range of 90–135°C. Relaxation dynamics of glass transition of blends reveals higher T_g than Nylon 6. Also the broader peaks changed to sharper peaks with higher tan δ values indicating increased amorphous content.[35] This is also consistent with the observed reduction in crystallinity of blends in DSC results. This behavior reflected in dynamical flexural modulus value in amorphous as well as crystalline regions.

The elastic modulus (E') was obtained over the temperature range of 0–200°C. Figure 5 represents the elastic moduli of semicrystalline Nylon 6, Trogamid and their blends. It can be observed from the Figure 5 that Trogamid shows higher flexural modulus than all compositions in glassy state. Lowest values of storage modulus are observed for Nylon 6 in glassy state. DMTA plots are more descriptive than static mechanical behavior. It clearly describes changed mechanical performance over entire temperature range with respect to altered amorphous content. In all plots except Trogamid storage modulus shows flatten behavior of curve after sharp drop in glass transition region which is due to restriction to the flow by crystals, which is not the case in Trogamid where entire polymer is amorphous and shows sharp drop in the modulus leading to significant mobility of chains. These results are in accordance with the DSC and tan δ results.

Dielectric Relaxation Spectroscopy

Temperature dependant dielectric behavior of prepared blends can be understood at constant frequency. At given condition of 1 Hz frequency in the temperature range of 30–200°C only one relaxation process observed which can be attributed to α-relaxation (glass transition) and an increase of the imaginary part (ε'') of the dielectric permittivity associated with an ionic
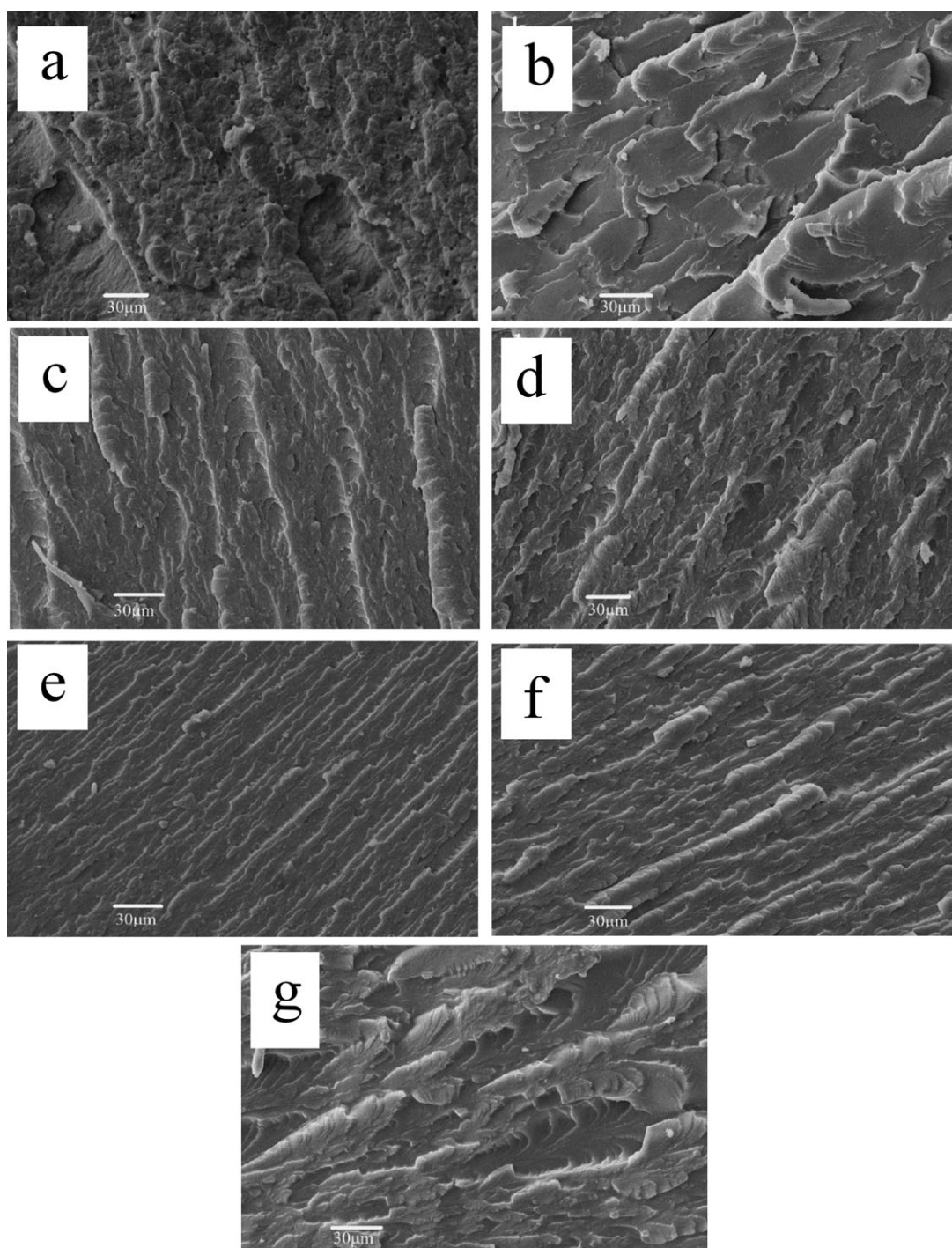
Figure 1. SEM micrograph of fractured surface under impact testing of Nylon 6, Trogamid and their blends with different composition range. Sample (a) and (b), respectively represent fracture surface of Nylon 6 and Trogamid. Sample (c), (d), (e), (f), and (g), respectively stand for N6/10, N6/20, N6/30, N6/40, and N6/50.

conductivity which is prominent after α-relaxation. This higher conductivity contribution masks the dipolar relaxation process at glass transition.

The electric modulus formalism introduced by McCrum et al. is used to study electrical relaxation phenomena.[36] Accordingly, the loss modulus spectra (M'') represents the temperature de-

pendent dielectric transitions. Figure 6 shows loss modulus spectra (M'') versus temperature plot for different blends compositions.
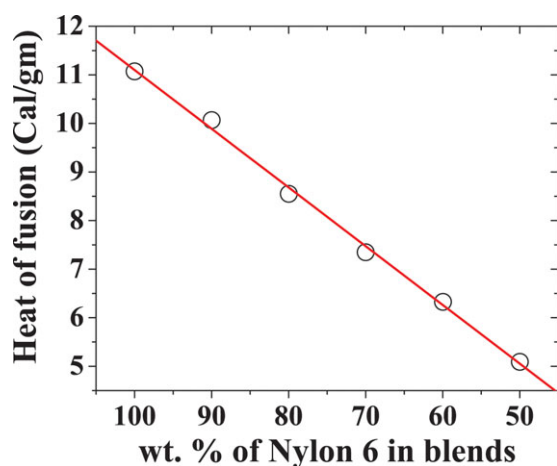
The position of the α-relaxation peak in the loss modulus plot of dielectric spectroscopy is influenced by the amount of increased amorphous content.[37] It represented increased value
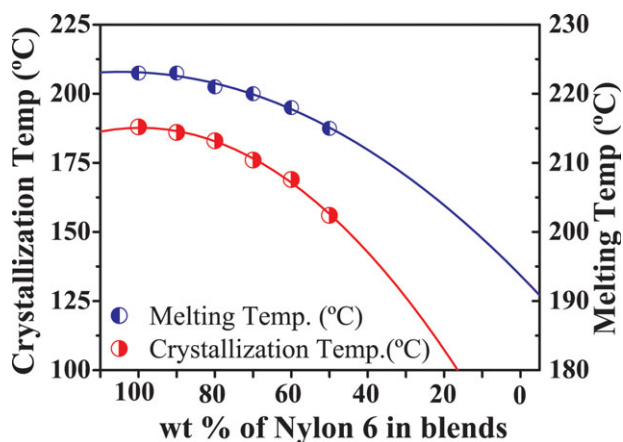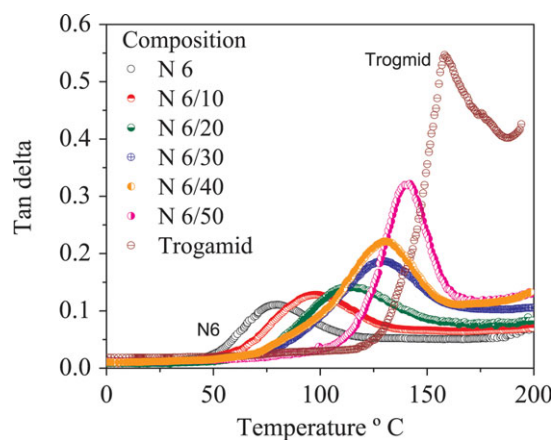
Figure 2. Schematic representation of melting point and crystallization temperature versus weight percentage of Nylon 6 presented in blends obtained by DSC. Zero weight percentage stands for Trogamid and 100% stands for Nylon 6 sample. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 4. Dynamical mechanical dissipation factor (tan δ) as a function of temperature for nylon blends. Peak associated with glass transition (T_g) relaxation of systems. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of loss modulus up to 80% of nylon 6 loading after which it remain uniform. The T_g values obtained for blends compositions in dielectric relaxation spectroscopy are in good agreement with those obtained in DMTA for the loss modulus. This comparison is represented in Figure 7.

In Nylon 6, a broad α-relaxation peak in loss modulus spectra ascribed to Brownian motion of the amorphous component which is under the constraint of crystalline domain. Magnitude and shape of this peak is distinct features of amount and distribution of amorphous component. Figure 6 observed systematic increase in peak position (T_g value) of loss modulus spectra as function of increased amorphous content. Magnitude of these spectral does not show any increase after 80 wt % of Nylon 6. This can be understood as significant drop in constrain applied by crystalline component. After 80 wt % of Nylon 6, backbone

chain is sufficiently mobile to allow dipole to orientation in applied electric field.

Many papers reported single or two (dynamic heterogeneity) transitions in dielectric study for miscible blends.[38] Here difference in T_g of Nylon 6 and Trogamid are sufficiently large. Components of miscible blends does not always share same segmental dynamics as off pure polymer this gives broad nature of loss modulus peak leads to broad relaxation time which is also evident here upon comparing Trogamid (pure polymer) with other blends. Amorphous Trogamid shows sharp peak over blends. Component containing 80–50 wt % of Nylon 6 shows coupled nature of segmental relaxation which shows identical relaxation spectra at changing relaxation temperature. Thus, these blends show homogeneity on segmental level.

Static Mechanical Properties
The mechanical properties of blends often reflect the miscibility/immiscibility and presence of specific interactions between

Figure 3. Schematic representation of ΔH_f as a function of blend composition. Values of heat of fusion taken from reheating scan during melting. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
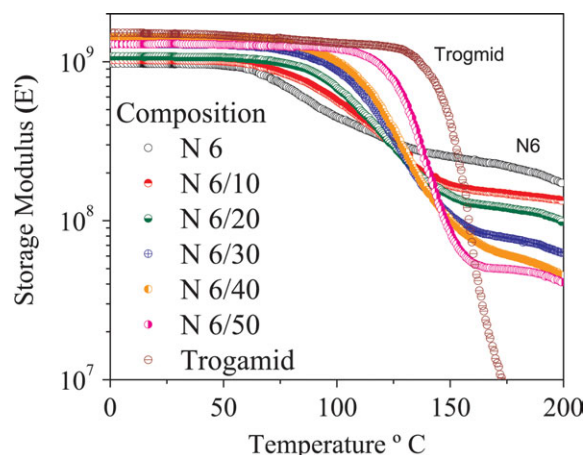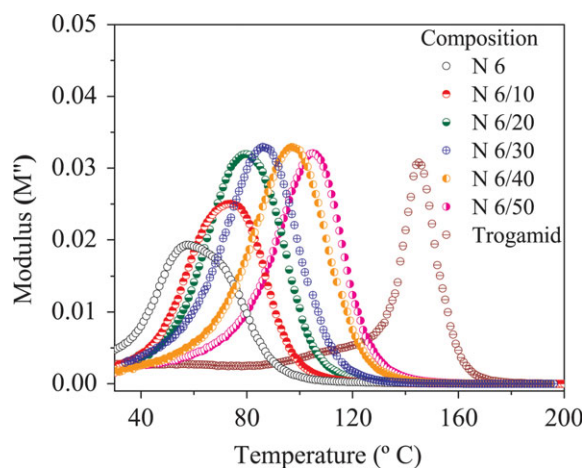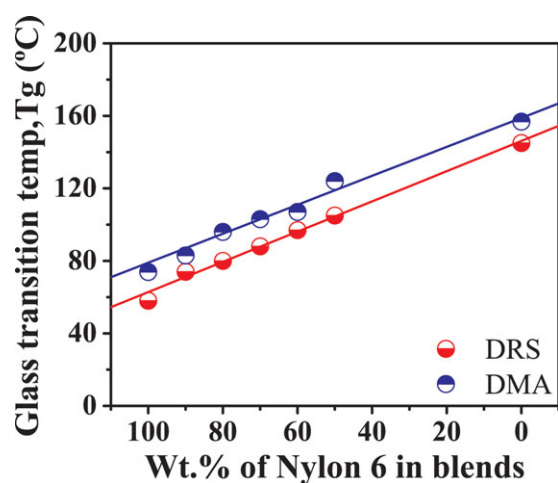

Figure 5. Dynamical mechanical storage modulus (E') as a function of temperature for nylon blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6. Temperature dependence of dielectric loss modulus (M'') for Nylon 6/Trogamid blends at frequency of 1 Hz. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

component polymers. Presence of the second component has been known to modify the mechanical properties to a great extent. Miscible polymer blends form single-phase materials as a result of presence of specific interactions. The presence of specific interactions between component polymers also causes volume contraction and loss of free volume leading to higher modulus and strength. It is expected that the mechanical properties of such blends will follow or exceed the values predicted by plain rule of additivity.

The effect of blending on the tensile, flexural and impact properties of Nylon 6 was systematically studied. The composition dependence of tensile and flexural modulus is shown in Figures 8 and 9, respectively. It is observed that the tensile modulus increased with increase in amorphous Trogamid content. This is particularly interesting, as the tensile modulus values increased

Figure 7. Comparison of glass transition temperature (T_g) values observed for different blends compositions from loss modulus spectra in dynamical mechanical thermal analysis and dielectric relaxation spectroscopy. Experiments conducted at 1 Hz. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
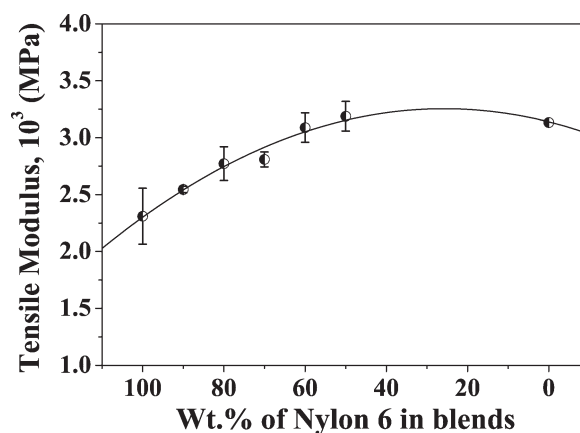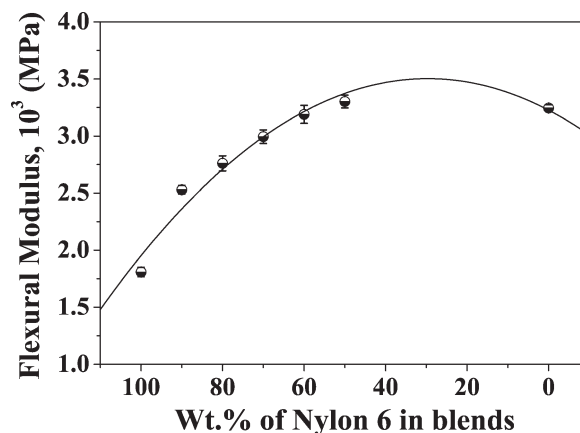

Figure 8. Static tensile modulus as a function of blends composition.

in blends higher than those expected. The flexural modulus of blends also shows similar behavior. The tensile modulus for 50/50 compositions is almost equal to that of amorphous nylon and the increase is about 40% over tensile modulus of Nylon 6. The flexural modulus is also found to increase with amorphous Nylon content as shown in Figure 9. However, at 50/50 composition the flexural modulus of the blends is 80% higher than Nylon 6 and almost comparable to that of amorphous Trogamid. Even for 90/10 composition about 38% increases in the flexural modulus is observed.

Nylon 6 has been recognized as a tough plastic but is found to be notch sensitive. In blends, we find that the impact resistance decreases from 81 J m^{-1} for Nylon 6 to 73 J m^{-1} for Nylon 6 / 50 (50/50) compositions as shown in Figure 10. The results indicate that the incorporation of amorphous component in Nylon 6 leads to a small decrease in crack propagation energy.

Water Absorption

It is well known that properties of Nylon 6 are very sensitive to the humidity whereas amorphous Trogamid has very good moisture resistance. The blends showed improvement in the water resistance properties of Nylon 6. Figure 11 illustrates the percentage of water absorption of the blends as a function of composition.

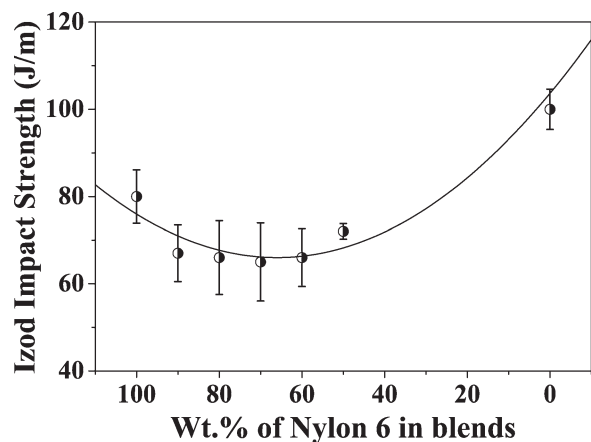**Figure 9.** Static flexural modulus as a function of blends composition.

Figure 10. Izod impact strength as a function of blends composition.

It is observed that the water absorption decreases drastically with increase in Trogamid content. It is also noted that the water absorption values are lower than those calculated by of rule of mixtures which is proposed in Figure 11.

The absorption of water at room temperature has been studied by Puffr and Sebenda.[39] They have suggested that the sorption of water in Nylon 6 was mainly due to the amide groups in the water accessible region. In Nylon 6, three sites available for water molecule absorption. First absorption takes place via double hydrogen bond between two carbonyl groups, which are firmly bound. The two more sorption center can be formed at already present hydrogen bond between carbonyl group and hydrogen atoms of amide group, regarded as loosely bound water molecule. Comparatively sorption centers in Trogamid are not easily accessible as Nylon 6 due to strong interaction of hydrocarbon segment in backbone. Therefore only one water molecule can remain as firmly bound water molecule. Considering this model, the results of the present studies indicate that the addition of Trogamid, results in the gradual reduction of the accessible amide groups.
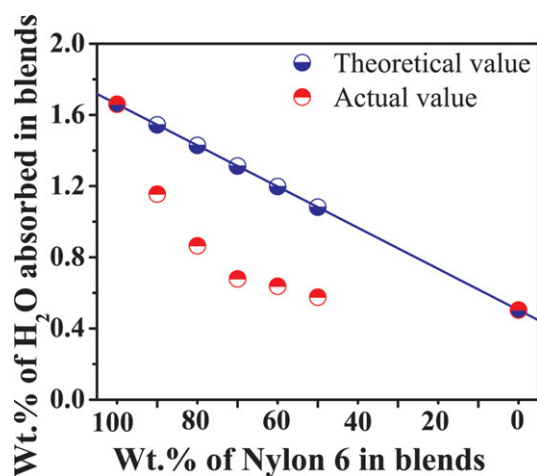

Figure 11. Weight percentage of water absorbed in base polymer and blends after 24-h exposures to water, as function of blend compositions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSION

The static and dynamic mechanical properties of blends of semicrystalline Nylon 6 with an amorphous nylon Trogamid were studied. The phase morphological study of fractured surfaces using scanning electron microscopy showed absence of two-phase morphology. The blends are known to be miscible over the entire range and exhibit reduced crystallizability as evidenced by the decrease in crystallization temperature. The tensile strength and modulus are found to increase as a result of blending. The dynamic mechanical thermal analysis indicated presence of miscibility in component polymers as evidenced by a single tan δ peak. The results of dielectric relaxation spectroscopy are concurrent with the DMTA results. The water absorption of Nylon 6/ Trogamid blends is lower than that of Nylon 6. Thus the improved mechanical performance along with reduced water absorption of these blends can make these blend a better candidate for applications wherein Nylon 6 is presently being used. The results of the present investigation offer a deeper insight to the mechanical behavior of Nylon 6/Trogamid blends which may augment its practical applications.

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