

Blends of Nylon with Polyethylene: Effect of Compatibilization on Mechanical and Dynamic Mechanical Properties

RUPALI GADEKAR, ASMITA KULKARNI, J. P. JOG

Chemical Engineering Division, National Chemical Laboratory, Pune Pashan 411008, India

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ABSTRACT: Blends of Nylon 6 with very low density polyethylene (VLDPE) have been studied. The blends exhibit two phase morphology wherein VLDPE is dispersed in the form of spherical domains in Nylon 6 matrix. The water absorption of the blends decreased with increasing VLDPE content. The mechanical properties of these blends show loss in tensile and impact strength due to poor adhesion at the interface. Addition of a compatibilizer containing MAH groups was found to result in improved properties. The tensile strength increased significantly whereas impact testing showed no break confirming better stress transfer across the interface. The dynamic mechanical analysis showed presence of microheterogeneity resulting into merging of tan delta peaks as a result of compatibilization. The observed results are ascribed to the possible reaction between reactive groups in Nylon 6 and the compatibilizer leading to compatibilization through copolymer formation. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 161–168, 1998

Key words: nylon; polyethylene blends; compatibilization; impact modification

INTRODUCTION

Nylon 6 is an important engineering thermoplastic having good wear, heat resistance, and high strength. However, it has poor dimensional stability, high water absorption, and poor impact strength. It is therefore generally blended with polymers having high impact strength, such as polyolefins, rubbers, etc., to widen its application potential. Blending with elastomers results in impact modification and lower water absorption. However, the extent of modification is dependent on the size of the dispersed phase, the glass transition of the dispersed phase, and the interfacial adhesion between the component polymers. Owing to the intrinsically different polarities, these blends are immiscible and represent two-phase morphology with poor interfacial adhesion and ex-

hibit poor mechanical properties. This problem can be alleviated by the addition of suitable compatibilizers or an interfacial agent or alternatively in situ formation of a copolymer that acts as a compatibilizer. The use of such compatibilizers ensure optimum bonding at the interface and thus improve the mechanical performance of the blends.

A lot of work has been reported on blends of Nylons with rubbers and polyolefins.^{1–9} The reported work has been dedicated to the study of Nylon 6 with polyolefins, such as high-density polyethylene, low-density polyethylene (LDPE), ethylene propylene rubber, and ethylene propylene dien monomer. All of these are basically ethylene-based polymers and the compatibilization has been achieved through use of carboxylated polyethylene, or an ethylene methacrylic acid random copolymer or elastomeric copolymers of ethylene with vinyl acetate containing maleic anhydride (MAH). The reaction between the terminal amine group of Nylon 6 results in graft copolymer forma-

Correspondence to: J. P. Jog.

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Table I Various Blend Compositions

Sample Code	Nylon 6	VLDPE	Compatibilizer
Nylon 6	100	—	—
NVA	90	10	—
NVB	85	15	—
NVC	80	20	—
NVD	75	25	—
NVE	70	30	—
NVLA	90	10	2
NVLB	80	20	4
NVLC	70	30	6

tion during extrusion, which acts as a compatibilizer in the blends. Use of commercial compatibilizers has also been tried, and the observed changes have been explained on the basis of possible interaction reactions between amine groups in Nylon 6 and the anhydride groups in the copolymers. In this article, we present the results of the study of blends of Nylon 6 with a novel polyolefin compatibilized using a commercial polymer.

Very low-density polyethylene (VLDPE) is a new class of polyolefins with very low density. These are special copolymers of α -olefins having low crystallinity and narrow molecular weight distribution, good elasticity, and good impact resistance at low and high temperatures. These polymers offer properties between those of ethylene propylene rubber and LDPE. It was therefore interesting to study the blends of Nylon 6 with VLDPE. In this article, we report the results of the study of mechanical and dynamic mechanical behavior of blends of Nylon 6 with VLDPE (Nylon 6/VLDPE). With VLDPE being nonpolar, these polymers form an immiscible polymer blend system and thus the properties are governed by phase morphology and stress transfer across the interface. An attempt has been made to improve the optimum bonding between the two phases and thus the mechanical properties. The significant achievement is the phenomenal increase in impact strength of Nylon 6, compared with the other reported work on Nylon 6/polyolefin blends.

EXPERIMENTAL

Materials

The materials used for this investigation include GULON M28RC injection molding, low-viscosity grade of Nylon 6 from GSFC, India; VLDPE; Norsolflex MW1920 injection molding grade from CdF

Chimie E.P having a density of 0.890 g cm^{-3} ; and Melt Flow Index (MFI) of 7.5 g/10 min . The compatibilizer used was an ethylene-based copolymer, Lotader 3200. A terpolymer of ethylene, acrylic ester, and MAH with a copolymer content of 9% and having MFI of 5 g/10 min .

Blend Preparation

Blends were prepared in different compositions by initially mixing the predried (80°C) material in a tumbler mixer for 15 min and then melt-blended in the extruder: ZSK 30 Werner & Pfleider corotating twin screw with 4 zones having L/D 30 at 33 rpm at temperature settings ranging from 230 to 250°C . The compatibilizer Lotader was used at 5% of the dispersed (VLDPE) phase. Table I shows the various blend compositions.

Injection Molding

For tensile, impact, and water absorption test specimens, pellets of the blends were dried for 8 h at 80°C and then injection-molded on an Arburg injection molding machine with a nozzle temperature of 220 – 250°C .

Differential Scanning Calorimetry (DSC)

Thermal analysis of the previously described blends were conducted on a Perkin-Elmer-2C DSC with cooling and heating rates of 10°C/min . The temperature and energy scales were calibrated as per the usual procedure. The temperature range used for scanning was 50°C to 300°C .

Water Absorption

The water absorption measurement was conducted per ASTM D570. All specimens used for study were disc specimens having a diameter of 54 mm and 3 mm thickness. Samples were weighed and immersed in water. After 24 h, specimens were removed from the water and wiped with a dry cloth and weighed again.

Scanning Electron Microscopy

Fractured surfaces of the injection-molded samples were characterized for the phase morphology using a scanning electron microscope, Leica model Steroscan 440. The surface of fractured samples was coated with gold to avoid charring under the electron beam.

Table II Melting Points and Crystallization Temperatures for Nylon 6/VLDPE Blends

Sample Code	Melting Point (°C)	Temperature of Crystallization (°C)
Nylon 6	231.5	184.3
NVA	229.5	183.5
NVB	231.7	188.1
NVC	230.9	185.8
NVD	227.7	185.7
NVE	229.1	185.3
NVLA	222.1	185.2
NVLB	224.4	183.1
NVLC	228.6	183.6

Mechanical Testing

Tensile

Tensile testing was conducted as per ASTM D638. The samples were tested using an INSTRON Universal Testing Machine model 4204 at room temperature with extensometer at a crosshead speed of 50 mm min⁻¹.

Izod Impact

The impact testing was conducted per ASTM D256. All specimens had dimensions of 63 mm × 12.6 mm × 3 mm with a notch of 0.025 cm radius.

Dynamic Mechanical Analysis

The dynamic mechanical properties of these blends were studied using a Rheometrics dynamic mechanical spectrometer RDS-7700. The storage modulus (G'), loss modulus (G''), and $\tan \delta$, was measured as a function of temperature at a frequency of 10 rads s⁻¹ and strain rate of 0.3%. The temperature range studied was from -170°C to 200°C, and the sample was heated at a rate of 10°C min⁻¹.

RESULTS AND DISCUSSION

Melting and Crystallization Behavior

The melting and crystallization parameters determined from the DSC heating, and cooling scans of the blends are presented in Table II. As expected in the case of immiscible blends, the melting point and the crystallization temperature

remained constant. The second component, VLDPE, did not show any melting or crystallization peaks. The constant values of melting and temperature of crystallization of Nylon 6 in the blends also confirm little degradation of Nylon 6 during processing. For blends containing compatibilizer, a decrease in the melting point ($\sim 5-6^\circ\text{C}$) has been observed. Such a melting point depression has also been reported for Nylon 6/EVA alcohol blends that was ascribed to the possible miscibility between the two polymers.²

Water Absorption

It is well known that the properties of Nylon 6 are very sensitive to the humidity. This is because of absorbed water. Water absorption also becomes a critical parameter in the processing of Nylon 6, because its presence leads to molecular weight degradation of Nylon 6 and thus deterioration of properties. It was therefore necessary to reduce water absorption in Nylon 6 by blending. Figure 1 illustrates the percentage of water absorption of the blends as a function of VLDPE composition. It is observed that the water absorption decreases linearly with VLDPE content for blends, compared with plain Nylon 6. The sorption of water at room temperature has been studied by Puffer and Sebenda.¹⁰ They have suggested the sorption of water in Nylon 6 was mainly due to the amide groups in the water-accessible region. It was also suggested that three water molecules are sorbed

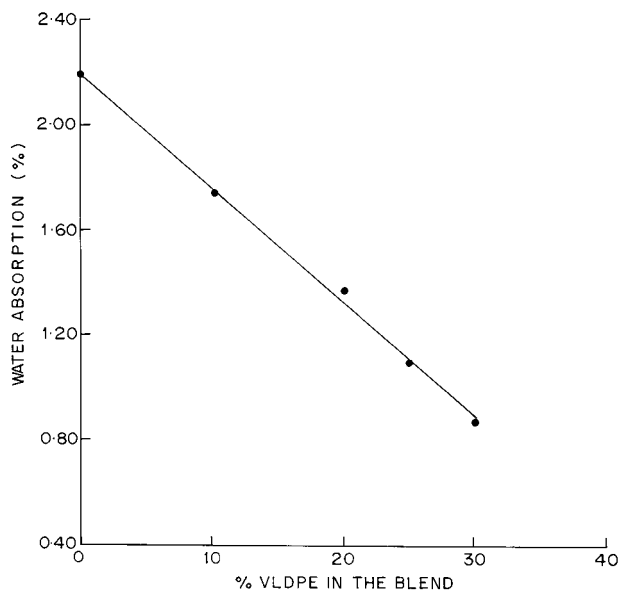
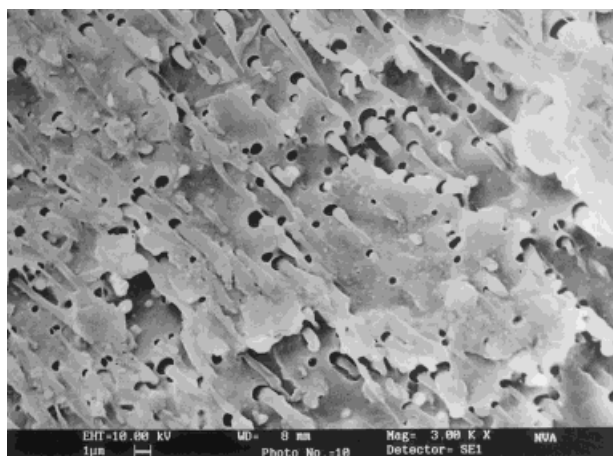
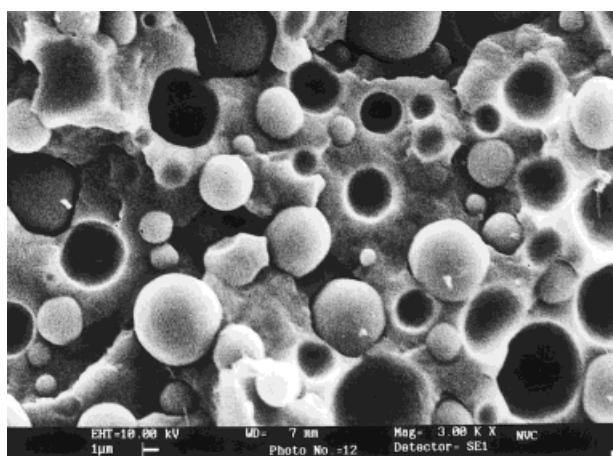


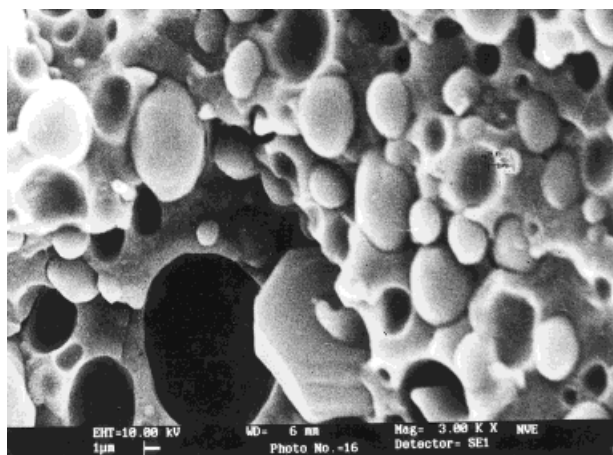
Figure 1 Percentage of water absorption for Nylon 6/VLDPE blend compositions.



(a)



(b)



(c)

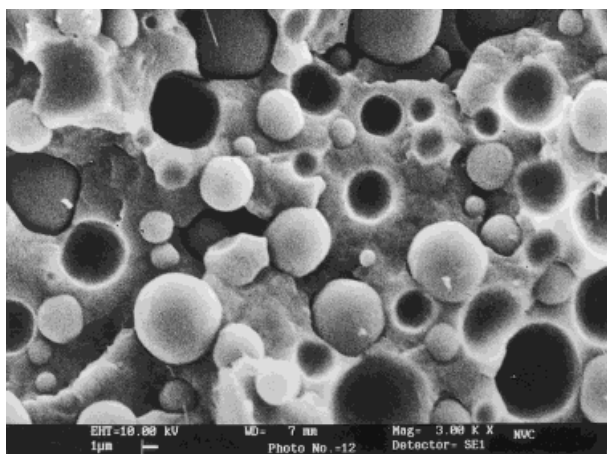
Figure 2 Scanning electron micrographs for Nylon 6/VLDPE blends. (a) 90/10; (b) 80/20; and (c) 70/30.

by two neighboring amide groups that form a sorption center. Considering this model, the results of the present study indicate that the addi-

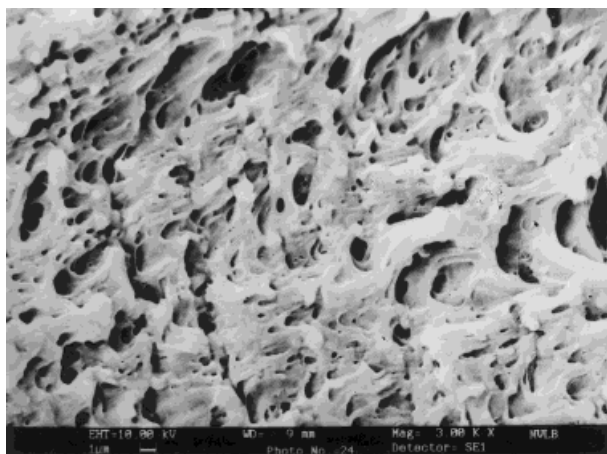
tion of VLDPE, which is a nonpolar polyolefin, may be resulting in a decrease in the number of amide groups in the accessible region due to dilution effect, thus leading to a significant drop in the percentage of water absorption. Such a decrease in water absorption is already reported for Nylon 6/polyolefin blends.⁴ The addition of compatibilizer was found to increase the percentage of water absorption of the blends marginally. For 90/10 composition, it was found to increase from 1.74 to 1.79, whereas for 80/20 composition it increased from 1.37 to 1.46. However, it was found to decrease almost linearly with composition.

Scanning Electron Microscopy

Scanning electron micrographs of fractured blend samples showed clear-cut, two-phase mor-



(a)



(b)

Figure 3 Scanning electron micrographs for Nylon 6/VLDPE blends. (a) 80/20 and (b) 80/20 with compatibilizer.

phology with phase separation between Nylon 6 and VLDPE phases as illustrated in Figure 2. The domain surface and the cavities created by a large number of domains during fracture seem to be very smooth, suggesting lack of adhesion between Nylon 6 and VLDPE phases as expected. The particle size of the droplet was found to increase with an increase in VLDPE content. Particle size for the samples that are rich in VLDPE showed a tendency to deform elliptically from spherical shape. In case of compatibilized blends, a considerable difference is observed in morphology, compared with the binary blend as shown in Figure 3(a, b) for Nylon 6/VLDPE blends without and with compatibilizer, respectively. It has also been observed that the size of dispersed particle is greatly reduced in case of compatibilized blends. Similar change in the phase morphology has already been reported for compatibilized Nylon 6 blends.^{5,7,8}

Tensile Properties

The variation of tensile strength at yield with composition for Nylon 6/VLDPE blends is shown in Figure 4. It is observed that the values of stress at peak vary linearly with composition. In blends, such a decrease in tensile strength is generally observed in incompatible blends and has been attributed to the softening effect of the second component.⁴ In case of blends containing compatibilizer, the values of tensile stress were still lower than

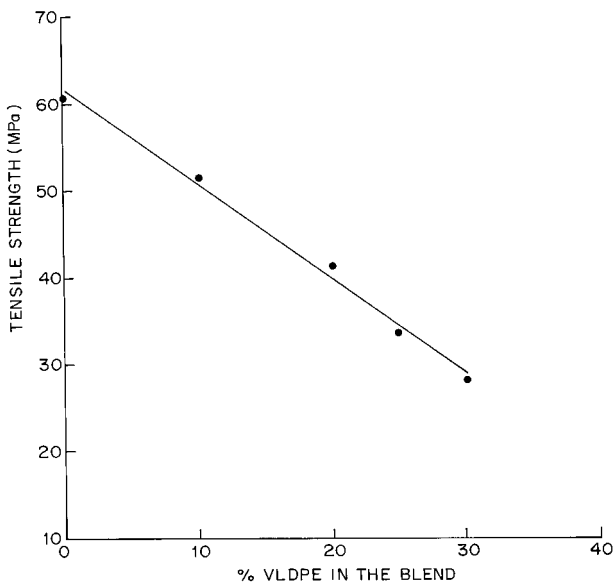


Figure 4 Tensile strength at yield for Nylon 6/VLDPE blend compositions.

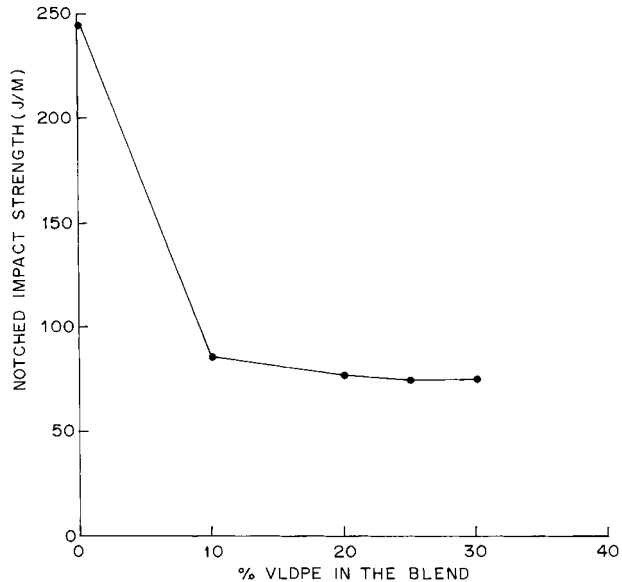


Figure 5 Impact strength for Nylon 6/VLDPE blend compositions.

that of neat Nylon 6 for all of the compositions. For 90/10 composition, the change was marginal whereas for 80/20 composition the tensile strength was found to increase from 39 to 45 MPa as a result of the addition of compatibilizer. The effect of compatibilization was more predominant in 70/30 composition, compared with other two compositions, in which the tensile stress increased from 28 to 40 MPa. From the values of percentage elongation, it was observed that the percentage elongation remained almost constant (280%), up to 20% of VLDPE in case of binary blends. However, for the 70/30 blend composition, the percentage elongation dropped drastically from about 280% to 185%. This may be due to the large-sized dispersed particles [Fig. 3(a)] causing the premature rupture of material.⁴ However, with the addition of Lotader, the percentage elongation for the 70/30 composition increased from about 185 to 264% as a result of compatibilization. The increase in elongation suggests better stress transfer across the interfaces. The enhancement in the mechanical properties suggests the occurrence of strong interaction at the interface due to the presence of compatibilizing agent Lotader 3200. The tensile modulus exhibited significant increase only for the 90/10 composition. With an increase in VLDPE content, the modulus decreased and the addition of compatibilizer resulted in the marginal increase in the values of modulus.

Impact Strength

The impact properties are generally measured in two modes (i.e., notched and unnotched) to get

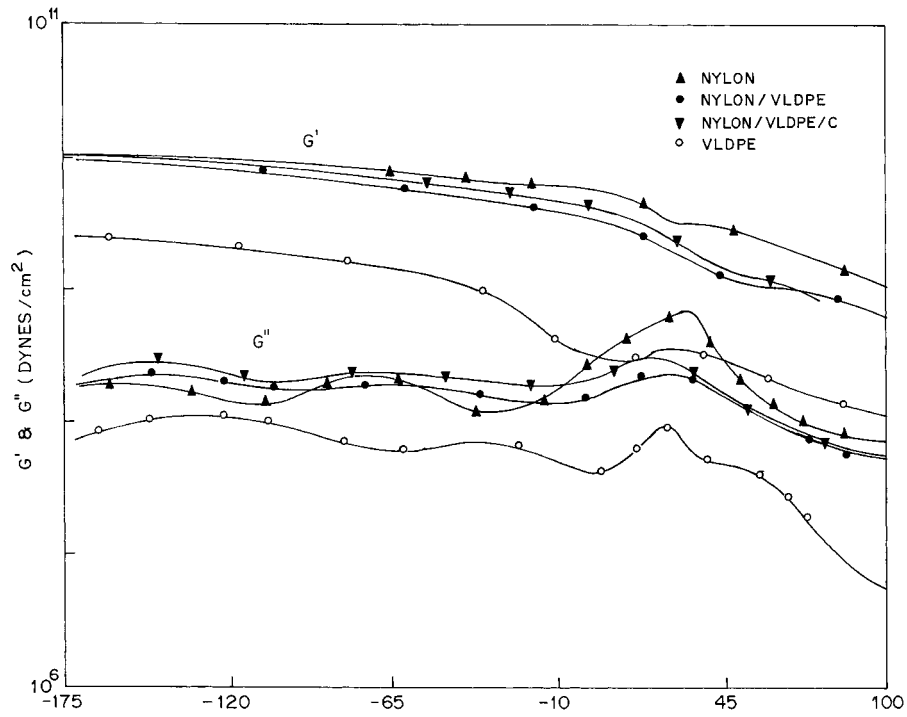


Figure 6 Temperature dependence of dynamic storage modulus (G') and loss modulus (G'') for blends.

better insight about the fracture mechanism in the blends. The impact strength of an unnotched specimen is dependent on the contributions of the

energy required for initiation and propagation, whereas for notched specimens the impact strength is dependent on the resistance to propagation. Ny-

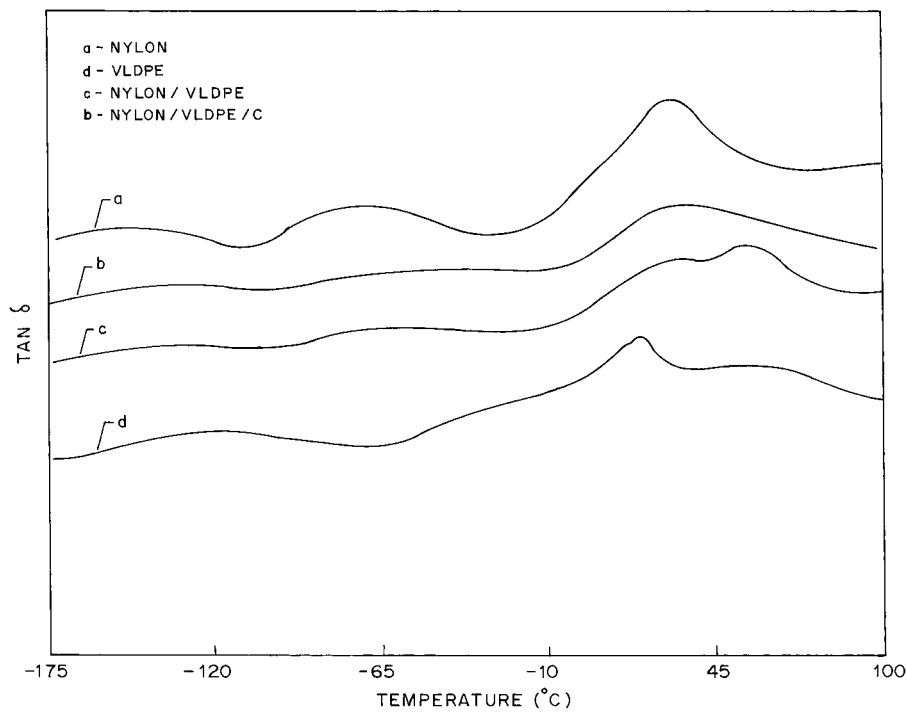


Figure 7 Temperature dependence of $\tan \delta$ for blends.

lon 6 has been classified as a pseudoductile material that usually fails by yielding and thus has high crack initiation energy. However, notched strength is very low because of the low crack propagation energy. It is therefore necessary to improve the notched impact strength of Nylon 6 by blending it with rubbery polymers.

As illustrated in Figure 5, in the case of binary blends, a drastic decrease in notched impact strength with increasing VLDPE content was observed, compared with pure Nylon 6. This indicates poor adhesion between the two phases. In case of blends containing Lotader, for the first composition (90/10), the impact strength instantly increased to about twice than that of pure Nylon 6, and with further increase in VLDPE percentage the impact samples did not show break. The presence of the third-phase Lotader seems to ensure optimum stress transfer at the interface, thus enhancing the properties of these blends.

The incorporation of a graft copolymer as a compatibilizer has been reported to increase the impact strength of blends. Raval and colleagues⁴ have found that the impact strength increased from 4 to 6 kg cm cm⁻¹ for the 90/10 composition in case of Nylon 6/LDPE blends. It was also noted that further increase in LDPE resulted in a decrease in impact strength. In case of blends of Nylon 6 with PP using PP-g-MAH as a compatibilizer, Speroni¹¹ has reported an increase from 50 to 80 kg cm cm⁻¹ for blends containing 30% of PP. Similar results have been reported by Sathe and colleagues¹³ for Nylon 66/PP blends compatibilized with PP grafted with various percentages of MAH. They found that the impact strength increased when the MAH content increased from 2.4 to 4.8%. However, further increase in MAH percentage resulted in a decrease in impact strength.

The reaction between MAH containing polymer and Nylon 6 has been well established in the literature.^{3,5,9,14,15} The presence of such reactions has already been reported for Nylon 6/SMA and Nylon 6/PP blends containing MAH.

Because Lotader contains MAH groups, it seems that the addition of Lotader to the blends results in copolymer formation during compounding. The reaction between the component polymers and compatibilizer was confirmed on the basis of a solubility test using formic acid. Binary blends showed a clear solution and the insoluble VLDPE phase at the top. This clear phase separation confirmed the lack of adhesion between the phases. On the other hand the blends containing compatibilizer formed a stable emulsion indicating formation of copoly-

mer with compatibilizer. Similar results have been reported in Nylon 6/LDPE and Nylon 6/PP blends by other workers.¹¹⁻¹³

Thus, phenomenal improvement in the impact strength of Nylon 6/VLDPE blends as a result of addition of Lotader suggests the presence of similar reactions between the component polymers.

Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) is often used to study polymer/polymer miscibility in polymer blends. The glass transition region can be studied using $\tan \delta$ or the loss modulus curves. The results of dynamic mechanical testing thus add information to the behavior of the blends and the phase morphology. The DMA scans illustrating the temperature dependence of dynamic storage modulus, G' , dynamic loss modulus G'' , and $\tan \delta$ of the blends along with the base polymers are shown in Figures 6 and 7. Seen from the figures, the Nylon 6 sample exhibits three peaks, namely α , β , and γ at temperatures of 35°C, -71°C, and -140°C, respectively. The low temperature transition observed at about -140°C has been attributed to the relaxation of methylene groups and also amide groups.¹⁴⁻²² The β transition, which is observed at about -70°C, has been explained on the basis of the rotational motion of water molecules¹⁹ and/or the water/polymer complex.²⁰ It has also been observed that the position and height of the β peak depends on the concentration of absorbed water.²² The third and high temperature α peak observed at about 35°C is ascribed to the glass transition temperature or to the onset of micro-Brownian motion of the chain segments. These temperatures are in good agreement with the reported data on Nylon 6.¹⁷⁻²² For the VLDPE sample, three peaks were recorded in the temperature range of -170°C to 70°C. The results for VLDPE can be compared with those for polyethylene samples, and it has been observed that these relaxations are similar to those observed in case of branched polyethylene. For branched polyethylene, three relaxation peaks have been reported. The peak at about -110°C has been associated with the mobility of at least 3 to 4 CH₂ groups in the amorphous region, and its magnitude depends on the density of polyethylene. Another peak that appears as a shoulder at about -25°C is associated with the motion of the main chain containing branches. The two high temperature peaks at about 30°C and 65°C can be attributed to the crystalline phase. These temperatures are in good agreement with those reported values.²³ In case

of the Nylon 6/VLDPE blend from data of $\tan \delta$ vs temperature, the intensity of the low temperature relaxations is found to be diminished significantly. The β relaxation peak, which is observed for Nylon 6, is not well defined. It is understood that this peak corresponds to the presence of water in the sample. The suppression of the β relaxation peak reveals that the number of amide groups contributing toward water absorption is lower for compatibilized blends. This observation is consistent with the earlier results on water absorption. The high temperature relaxations, however, are well defined and two relaxation peaks are observed at 35°C and 55°C. The transition at 35°C is corresponding to the Nylon 6 phase, whereas that at 55°C is related to transition in VLDPE in case of blend samples. The presence of two well-defined peaks in the blends thus establish the immiscibility of the two phases. Although a decrease is observed in the transition temperature of VLDPE, no change is observed in glass transition temperature for Nylon 6 when blended with VLDPE. The addition of compatibilizer resulted in modification of the high temperature relaxation process as can be seen in Figure 7. The two peaks corresponding to each of the component polymer merged into one peak. Such a behavior has been ascribed to microheterogeneous blends in which homogeneity exists in the microphase region.²⁴

CONCLUSIONS

Nylon 6/VLDPE are immiscible blends and exhibit properties that can be further modified using a suitable compatibilizer. Blends exhibit lower water absorption. The mechanical properties of these blends were poor due to lack of adhesion between the two phases. The addition of compatibilizer resulted in a significant increase in the impact properties with marginal changes in the tensile properties. The use of VLDPE with the compatibilizer has been found to result in enhanced properties, compared with other Nylon 6/polyolefin systems reported previously.

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