

The Effect of Zinc Oxide Addition on the Compatibilization Efficiency of Maleic Anhydride Grafted High-Density Polyethylene Compatibilizer for High-Density Polyethylene/Polyamide 6 Blends

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Received 30 April 2006; accepted 28 September 2006

DOI 10.1002/app.25565

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A high-density polyethylene with grafted maleic anhydride units has been investigated as a compatibilizer for high-density polyethylene with polyamide 6. The material acts as an effective compatibilizer, causing a marked reduction in dispersed phase size as well as an increase in tensile strength and toughness. Compatibilizer also affects the glass-transition temperature, crystallization kinetics, and amount of crystalline material for certain blend compositions. The addition of zinc cations, which

are effective in increasing ethylene-acid copolymer compatibilizer performance in low-density polyethylene/polyamide blends, has little, if any, effect on compatibilizer performance in these high-density polyethylene/polyamide blends. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3871–3881, 2007

Key words: ionomer; polyamide; blend; high-density polyethylene; maleic anhydride

INTRODUCTION

Commercial introduction of a polymer made from a new monomer is an extremely expensive, and risky, enterprise. One strategy to introduce new products into the market without a large investment is to take two or more different polymers and blend them together to make a new product with unique properties. However, the success of this strategy has been limited because the mechanical properties of the blend are typically far worse than a simple mixing law would predict. This situation arises because most polymers are not miscible in one another. Hence, the mixing two polymers together usually results in a material that consists of two separate phases, and the interface between the phases is very weak since polymer chains do not crossover the boundaries to form entanglements because of the aforementioned incompatibility.

Probably the most effective strategy to reduce this problem of immiscibility is to design blends so that a reaction can occur at the interface. The operative term

used here is *reduce*; in other words, certain mechanical properties, in particular toughness, are still below what would be predicted by a mixing rule. Polyamides (PAs) inherently have many attractive properties, and can react with many functional groups because of the terminal primary amines,¹ and, to a lesser extent, the possibility of chemical interchange reactions involving the amide linkage.² Further, if the other component has the appropriate functional group, there is a possibility of hydrogen bonding across the interface. Hence, polyamides have been extensively studied as blend components. One polymer that has been considered widely as a blend component with polyamides is high-density polyethylene (HDPE), because of its wide availability and uses in applications. Further, polyamides are known to have high water absorption, while HDPE has low water absorption; also, HDPE has a stiffness near that of the polyamide, which means that a blend should have a stiffness not too different than the starting components. This situation has led to many studies of blends of HDPE and polyamides.

Unfortunately, none of the favorable mechanisms that inherently make polyamides good blend components are relevant to high-density polyethylene. Hence, many approaches have been taken to add some functionality to HDPE to improve compatibility with polyamide. One common approach is to add acid functionality via the grafting of maleic anhydride (HDPE-g-MAH); blends made include

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Contract grant sponsor: National Science Foundation (Major Research Instrumentation grant and Instrument for Materials Research grant); contract grant numbers: DMR-0420626 and DMR-0315756.

Journal of Applied Polymer Science, Vol. 103, 3871–3881 (2007)
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HDPE-*g*-MAH/PA 12,³⁻⁵ and HDPE-*g*-MAH/PA6.⁶ Another approach is to add functionality to HDPE with a radiative treatment (γ , e-beam, photooxidation, etc.); blends have been studied with PA6.⁷⁻⁹ By and large, however, this approach is not desirable, since an extremely large amount of material must be modified, and this approach is completely impractical if the PA and HDPE are already mixed. A more practical approach is to add a third molecule, which can interact favorably with the polyamide and also interacts well with the HDPE, has been added. Table I shows an exhaustive list of the blends studied where a third molecule has been added, which interacts favorably with the polyamide and also interacts well with the HDPE.

The following are general points about the effect of the addition of third molecules to the HDPE/PA blends

1. A small amount ($\sim 1\%$) is required for the maximum improvement in room temperature mechanical properties and maximum reduction in dispersed phase size. Adding more than this amount does not, in general, improve performance,^{10,22,28} although higher levels of compatibilizer were found to be necessary in certain cases.²⁷
2. Some studies investigated changes in room temperature mechanical properties with compatibilization^{22,25,27,28}; however, some studies were interested primarily in rheological behavior.^{27,29,30,33} The addition of compatibilizer raises G' at low frequencies,²⁹ reduces the interfacial tension,¹¹ and increases the steady-shear melt viscosity.^{17,22}
3. The addition of compatibilizer raises the melting temperature of the PE phase and reduces the melting temperature of the PA phase.¹⁷

The purpose of this study is to examine the effect of maleic anhydride grafted high-density polyethylene compatibilizers on HDPE/nylon 6 blends. Although there are some points of duplication with previous studies, there are a couple of significant differences. The first is that a much more careful study on the effect of compatibilizer on crystallization has been performed, which includes effects that compatibilizer has on crystallization kinetics. The second unique aspect is a study on how the glass-transition behavior is affected by the addition of compatibilizer.

A third unique aspect is that the effect that partial zinc neutralization of the hydrolyzed anhydride acid groups is studied. The addition of zinc on the surface should reduce compatibilization efficiency, since neutralized acid endgroups cannot be reacted with amine endgroups and cannot participate in any hydrogen bonding. However, partially zinc-neutralized ethyl-

TABLE I
Blends with Polyamide Using Compatibilizer Molecule that Reacts with Amine

Blend	Third component	References
HDPE/ polyamide 6	EMAA-based zinc ionomer	10-16
	HDPE- <i>g</i> -MAH	17-21
	HDPE- <i>g</i> -GMA	16
	SEBS- <i>g</i> -MAH	22
	Ethylene-various acid copolymers	23
HDPE/ polyamide 12	Ethylene- <i>co</i> -vinyl acetate- <i>g</i> -MAH	24
	HDPE- <i>g</i> -MAH	25, 26
HDPE/ polyamide 6,6	EMAA-based zinc ionomer	27
	HDPE- <i>g</i> -MAH	28
	SEBS- <i>g</i> -MAH	29
HDPE/ polyamide 11	Ethylene-MAH copolymer	30
	Ethylene-propylene-diene terpolymer- <i>g</i> -MAH	31, 32

EMAA, ethylene-*co*-methacrylic acid; SEBS, [polystyrene-poly(ethylene-butylene)-polystyrene block copolymer].

ene-acrylic acid or ethylene-methacrylic acid copolymers are reported to be better compatibilizers than the acid form for LDPE/PA6 blends,^{34,35} so we thought to see whether the same was true with partially zinc-neutralized HDPE-*g*-MAH materials.

EXPERIMENTAL

Materials

The polyamide 6 employed in this study was an injection molding grade, 1013B, supplied by UBE Nylon (Thailand). The molecular weight of this material is 12,000 g/mol (as reported by the supplier) and is reported to have approximately equal numbers of amine and carboxylic acid end groups. High-density polyethylene, H5480S grade, was also an injection molding grade polymer (density 0.954 g/cm³) graciously supplied by Thai Polyethylene. Zinc oxide was obtained from Aldrich and used as received. High-density polyethylene-graft maleic anhydride, Fusabond[®] grade E MB100D, was graciously supplied by DuPont. The grafting fraction was determined by titration. About 1.0 g of the HDPE-*g*-MAH was dissolved in 100 mL of hot xylene; the solution was refluxed for 40 min. Successively, 3 mL water was added to hydrolyze the anhydride groups. After 25 min, the hot solution was added with excess KOH solution in ethanol (0.025N) and back titrated with HCl in ethanol (0.025N), with phenolphthalein as an indicator. The weight fraction of grafting was 0.9%, i.e., an equivalent weight (weight of polymer per mole acid) of 5000 g/mol.

Blend preparation

Pellets were mixed in a tumble mixer for 10 min, followed by drying under vacuum at 60°C for 24 h. The materials were blended in a Collin D-8017 T-20 twin-screw extruder using a screw speed of 35 rpm, corresponding to a residence time of approximately 1 min in the extruder. The blends were extruded through a single-strand die; the extrudates were cooled in a water bath, dried at ambient temperature and then pelletized. The pellets were dried and kept in sealed plastic bags before compression molding, to minimize moisture absorption. Compatibilized blends were made in a 2-step process; first the HDPE-g-MAH and HDPE were extruded together with or without the appropriate amount of zinc oxide, followed by extrusion with the PA6. Extrusion of the acid copolymer with zinc oxide is one method used commercially to neutralize ethylene-acid copolymers, and this method is expected to work equally well with maleic anhydride grafted materials. The amount of zinc oxide was adjusted, so that 50% of the acid groups would be neutralized with zinc. In all cases, compatibilizer amount is stated in parts per hundred (phr), i.e., HDPE/PA6 80/20 with 10% compatibilizer actually means a composition of 80 parts HDPE, 20 parts PA6, and 10 parts HDPE-g-MAH copolymer (zinc weight is not included in any calculations). Infrared spectra and X-ray diffraction patterns of the compatibilized blends show no presence of zinc oxide, while the former indicates zinc neutralization of some carboxylate groups.

Specimen preparation

Test specimens are prepared using a Wabash V 50 H 50 ton compression molding machine. Pellets are placed in a picture frame mold, and the mold is preheated at 240°C for 3 min in the press without application of pressure. The mold is then compressed under a force of 10 tons for a further 3 min, after which the mold is cooled to 40°C under pressure. Test specimens were cut from the molded sheets using a die cutter.

Scanning electron microscopy

Scanning electron microscope (SEM), JEOL 5200-2AE (MP152001), was used to study phase morphologies of the blends. The specimens were fractured in liquid nitrogen and etched using (i) hot decalin (for HDPE minor phase blends) and (ii) formic acid (for PA6 minor phase blends). The specimens were then coated with gold under vacuum. All scanning electron micrographs studied were characterized using magnification of 1500× at 20 kV.

Dynamic mechanical analysis

A Solids Analyzer RSA II (Rheometric Scientific) was used to measure the storage and loss moduli as a function of temperature. The 3-point bend fixture was used to mount the samples, and 4°C temperature steps were used. Samples were molded (same as shown earlier) to a thickness of around 2.5 mm. All experiments were performed with a 1 Hz frequency, 0.03% strain, and with static force tracking dynamic force. Peak heights were determined by fitting the curve with a cubic spline, and finding the derivative of the spline. The error in the measurement was determined by running duplicates of selected samples; error bars in DMA plots and all plots that appear in this article represent one standard deviation.

Tensile testing

A D1708 microtensile die was used to cut the samples for tensile testing, and an Instron universal testing machine was used to measure tensile strength using a crosshead speed of 1.30 mm/min. Samples were molded to a thickness of approximately 0.5 mm. At least five samples were used for each composition to determine an average and standard deviation.

X-ray diffraction

Wide angle X-ray diffraction (WAXS) investigation of the neat PA6 and HDPE as well as their blends was carried out at room temperature using a Bruker AXS D8 Discover system with a 2D wire detector. Samples were measured in symmetric transmission; two different source-detector angles were used, and the data were combined by matching the intensities in the overlap region. Within experimental error, this procedure was identical to matching the two spectra by using the known angular correction for the two angles. No angular correction was performed for different sample absorption depending on angle for a given source-detector angle; the transmittance of all samples was fairly high (~80%), and no distortions were apparent in the overlap region. A measured transmittance was not used to subtract the background spectra from the sample spectra, rather the transmittance was set at a value that gave a flat profile at low angles.

Differential scanning calorimetry

Samples were cut from the same sheet used to cut samples for tensile testing. For melting and glass-transition temperature determination, samples were placed in aluminum DSC pans, and were scanned at

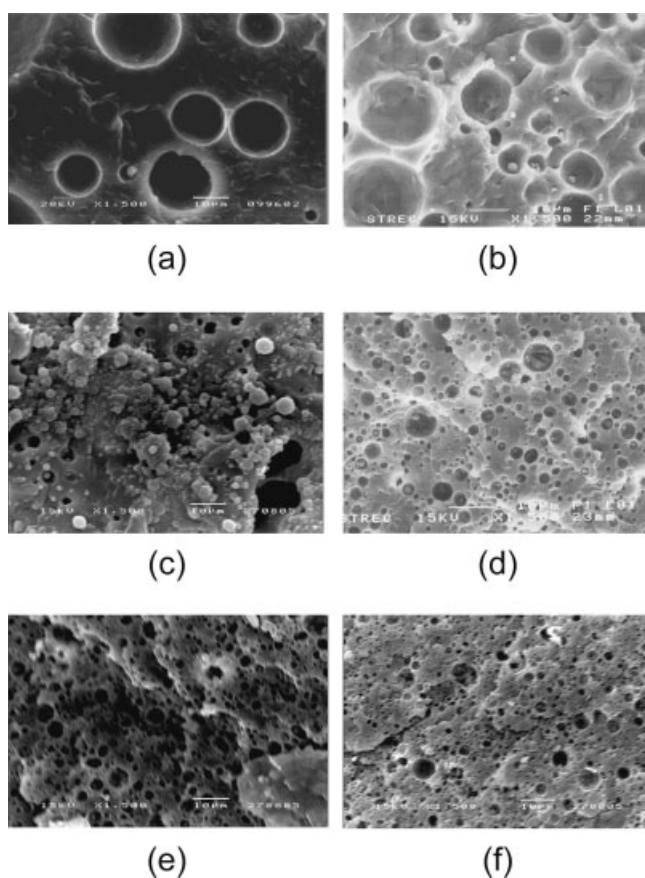


Figure 1 Scanning electron micrographs of 20/80 HDPE/PA6 blends with added HDPE-g-MAH compatibilizer (no zinc oxide) at the following weight percentages : (a) 0, (b) 0.1, (c) 1.0, (d) 2.5, (e) 5.0, and (f) 10.0 phr.

a rate of 10°C/min. A TA Instruments Q1000 differential scanning calorimeter with liquid nitrogen cooling was used for this study, and was routinely calibrated with four different standards (cyclopentane, biphenyl, indium, and tin) at a 10°C/min heating rate. The melting characteristics of the two components were determined during this initial scan, while the glass-transition temperature was determined during a second scan after the material was held at 250°C for 5 min and rapidly cooled to -100°C to assure good sample-pan contact and eliminate complicating enthalpy relaxation effects. The fractional crystallinity was determined by integrating the area under the respective melting exotherms, and converting these enthalpies to fractional crystallinities using a melting enthalpy of 293 J/g for polyethylene and 190 J/g for polyamide.³⁶ Crystallinities were calculated on a component basis, i.e., a polyethylene fraction crystallinity of 0.5 means that half of the polyethylene (including the polyethylene in the grafted copolymer) in the given blend is crystalline. Nonisothermal crystallization kinetics were performed on different samples using a PerkinElmer DSC 7 at a cooling rate of 10°C/min after heating

the sample to 250°C and holding for 5 min. Crystallization temperatures represent temperatures corresponding to the onset of crystallization.

RESULTS AND DISCUSSION

Scanning electron micrographs of fracture surfaces after dissolution of the minor component are shown in Figures 1 and 2. Examinations of these micrographs, as well as dispersed phase sizes determined from these micrographs (Table II), indicate that, based on this measure of blend compatibility, at least 2.5% of the compatibilizing agent is required to achieve maximum compatibilization efficiency. The amount of compatibilizer required for maximum efficiency is substantially higher than that found previously for HDPE/PA66 with HDPE-g-MAH compatibilizer,²⁸ as well as ethylene-acid copolymer and copolymer ionomer compatibilizers for blends between PA6 and LDPE.^{35,37} Table II also indicates that the addition of zinc oxide causes slightly larger dispersed phase size at a given compatibilizer concentration.

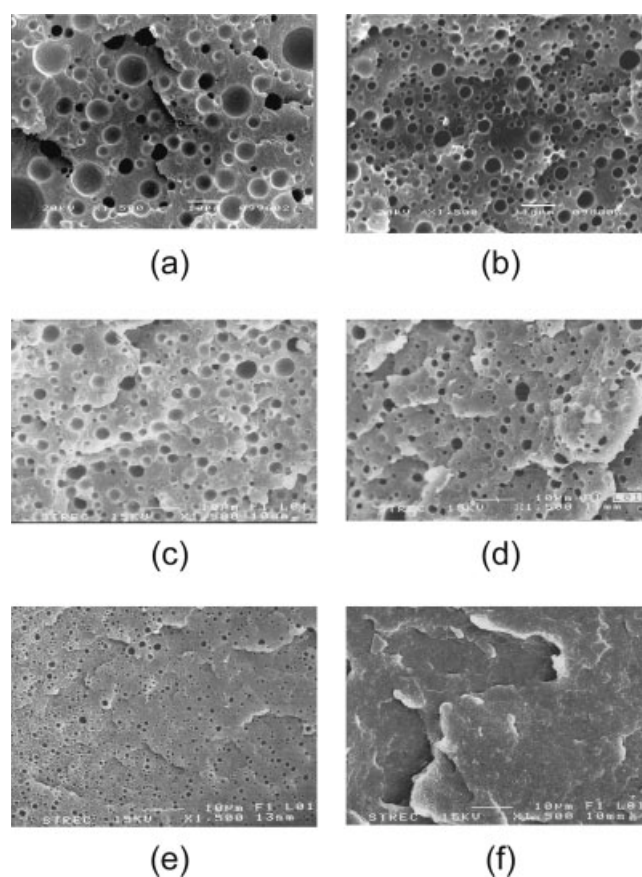


Figure 2 Scanning electron micrographs of 80/20 HDPE/PA6 blends with added HDPE-g-MAH compatibilizer (no zinc oxide) at the following percentages : (a) 0, (b) 0.1, (c) 1.0, (d) 2.5, (e) 5.0, and (f) 10.0 phr.

TABLE II
Dispersed Phase Sizes for Blends

	Compatibilizer amount (phr)	Dispersed phase size without zinc oxide (μm)	Dispersed phase size with zinc oxide (μm)
HDPE/ PA6 80/20	0	4.9	4.9
	0.1	2.6	3
	1	2.4	2.9
	2.5	1.7	1.7
	5	0.7	1.2
	10	0.2	0.5
HDPE/ PA6 20/80	0	14	14
	0.1	13.8	10.4
	1	3.9	5.7
	2.5	3.3	4.5
	5	2.8	3.4
	10	2.3	2.4

Ideally, the substantial reduction in dispersed phase size morphology is an evidence of improvements in interfacial adhesion, and hence will translate into improvements in mechanical properties.

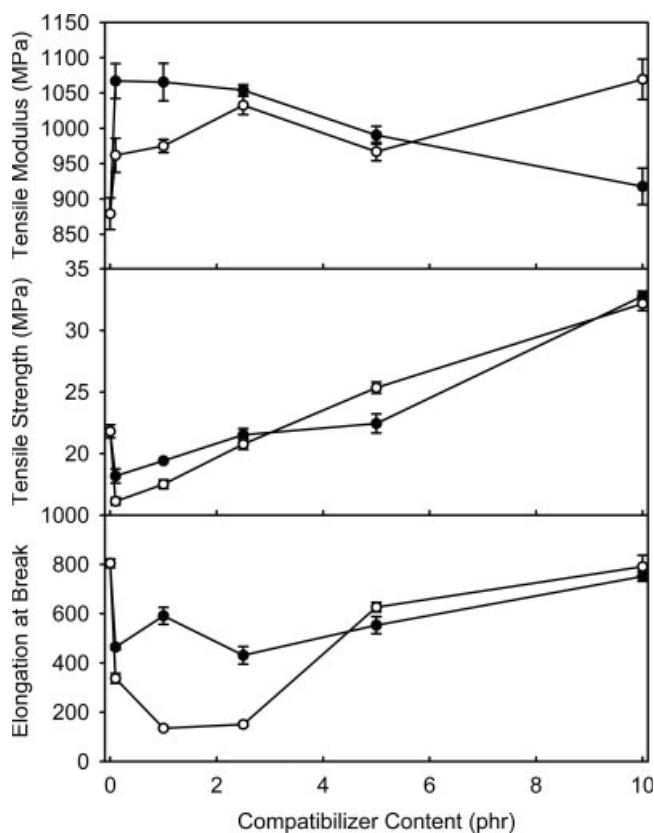


Figure 3 Tensile results for HDPE/PA6 80/20 blends made using compatibilizer with zinc oxide addition (open symbols) and compatibilizer without zinc oxide addition (filled symbols). The values for pure HDPE were: modulus = 1120 MPa, tensile strength = 39.5 MPa, and elongation at break = 1140%. The values for PA6 were: modulus = 2110 MPa, tensile strength = 74.5 MPa, and elongation at break = 205%.

Tensile properties of the blends are displayed in Figures 3 and 4; inconsistency in the results as a function of compatibilizer fraction is much larger than the error bars would suggest. Error bars were calculated by running multiple samples cut from the same sheet; hence, it is likely that molding inconsistencies are the cause of the disagreement.

The effect of compatibilizer is much different than expected, except for the ultimate properties of the HDPE/PA6 20/80 blends. The tensile strength and elongation shown in Figure 4 for the HDPE/PA6 20/80 blends have the expected curve shape: a rapidly increasing plot that reaches a plateau roughly at a compatibilizer content corresponding to the content that shows the maximum compatibilization efficiency in scanning electron micrographs, i.e., $\sim 2.5\%$ compatibilizer. The percentage increase in tensile strength versus the uncompatibilized material is $\sim 25\%$, which is significantly higher than the approximate 15% found for the HDPE-g-MAH compatibilizer in HDPE/PA 66 blends at a 25/75 weight fraction.²⁸ However, this value is substantially smaller than the $\sim 50\%$ found in HDPE/PA 6 blends for compatibilizers such as ethylene-vinyl acetate²⁴ or an ethylene-methacrylic acid-isobutyl acrylate terpoly-

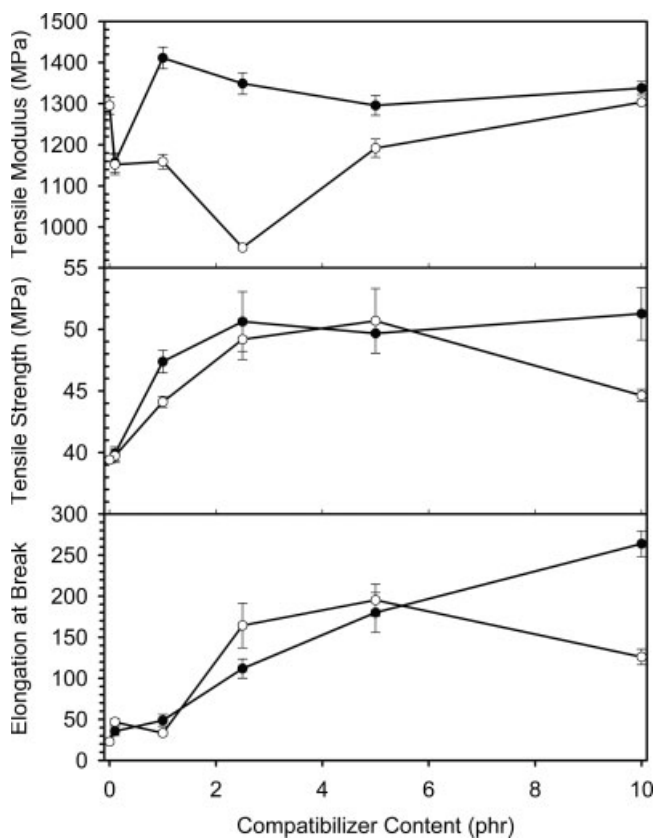


Figure 4 Tensile results for HDPE/PA6 20/80 blends made using compatibilizer with zinc oxide addition (open symbols) and compatibilizer without zinc oxide addition (filled symbols).

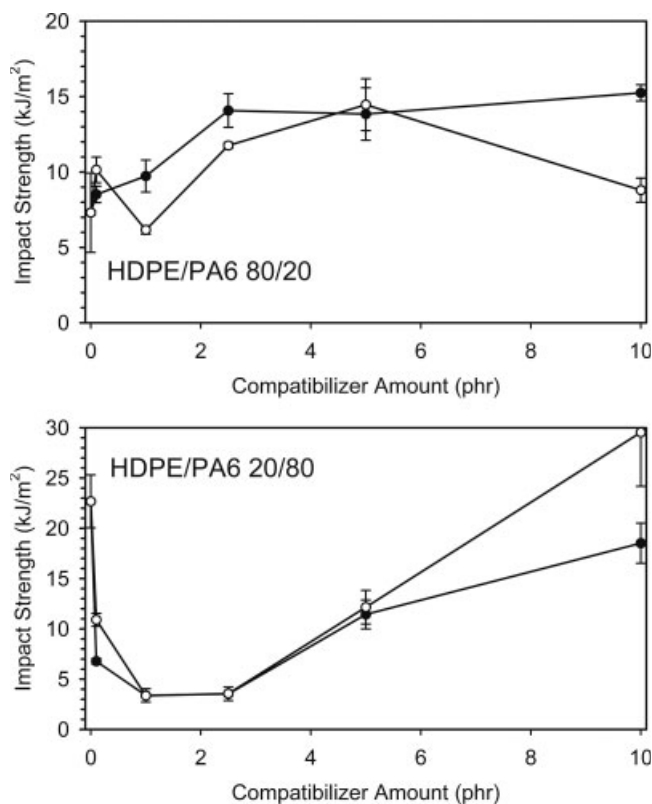


Figure 5 Impact strength of HDPE/PA6 blends. The values for pure PA6 and pure HDPE were 5.7 ± 1.4 kJ/m² and 15.0 ± 0.5 kJ/m², respectively.

mer zinc ionomer.¹² The tensile strength in the HDPE/PA6 20/80 blend is only 20% lower than a simple mixing rule prediction using pure material properties. The modulus for the materials without zinc is, in general, higher than the modulus for the zinc-neutralized materials in the HDPE/PA6 20/80 blends as shown in Figure 4. This difference in modulus between the two types of samples is not explained by crystallinity, since the fraction of nylon crystallinities are within experimental error of one another. Given the overall inconsistency of the results, whether this result is real or not cannot be determined with absolute confidence.

The behavior of the HDPE-rich materials in tensile tests should be more complicated, since the addition of compatibilizer will not only strengthen interfacial interactions, but also affect the continuous phase. The tensile strength and elongation at break drop with the addition of compatibilizer at first and then increase, eventually to values above the uncompatibilized blend. We do not understand the reason for the initial decrease, although the behavior occurs in materials with and without zinc. Overall, the modulus seems to be constant with compatibilizer content and there is no consistent, statistically significant difference between materials with and without zinc in the HDPE/PA6 80/20 blends.

Figure 5 shows an increase in impact strength for the HDPE/PA6 80/20 blend with compatibilizer content that reaches a plateau at 2.5%, similar to the tensile strength and elongation of the 20/80 blend. For the HDPE/PA6 20/80 blend, the impact strength decreases with compatibilizer content, and then rises again, similar to the tensile strength and elongation of the 80/20 blend. In other words, the behavior of the impact strength with respect to compatibilizer content is exactly opposite as to what was seen in the tensile properties. Again, there is no difference between materials with and without zinc.

As shown in Figures 6 and 7, compatibilizer does not affect the fractional crystallinity and melting point of the polyamide, except for, perhaps, a slight increase in the fractional crystallinity when polyamide is the continuous phase. This result differs versus what was reported earlier, where a drop in melting point was found with the addition of compatibilizer.¹⁷ The melting temperature of the polyamide is $\sim 1^\circ\text{C}$ higher for the high polyamide-content blend than for the low polyamide-content blend; less than the $\sim 2^\circ\text{C}$ difference found previously.¹⁷ Figure 8 shows that the peak at around 208°C , which is attributed to the γ phase, does not change consistently,

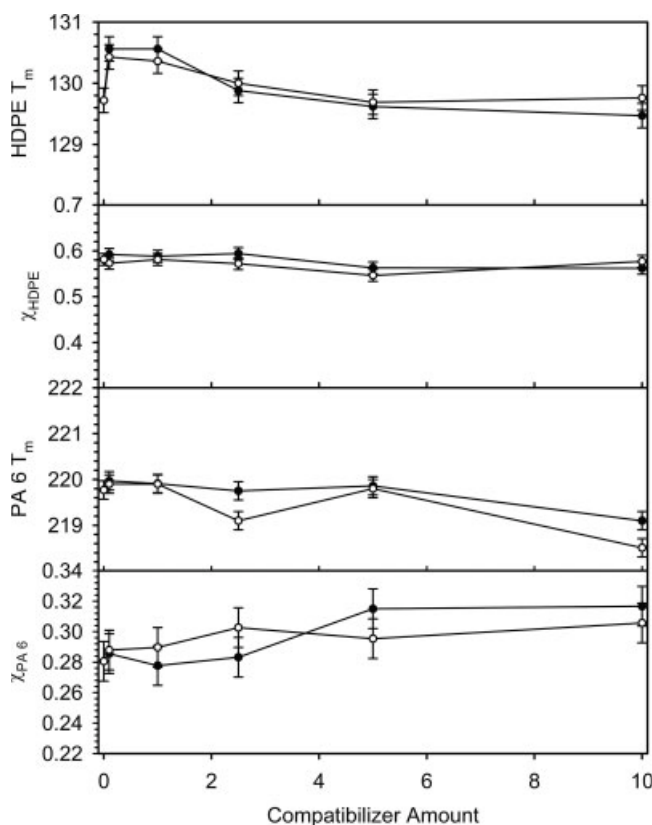


Figure 6 Comparison of melting temperatures and fractional crystallinities for PA6 and HDPE in HDPE/PA 6 80/20 blends. Filled symbols represent no zinc oxide addition, while open symbols represent the zinc-neutralized form.

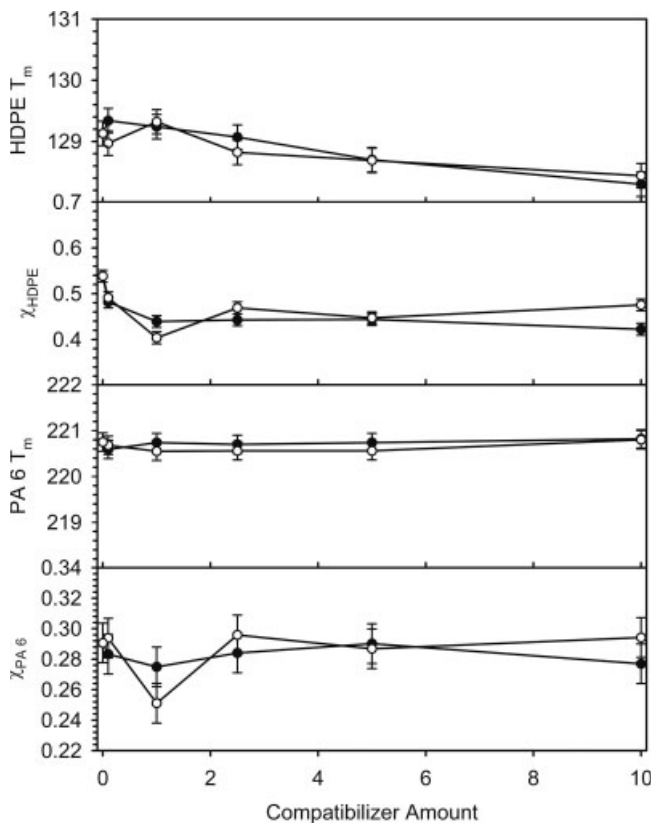


Figure 7 Comparison of melting temperatures and fractional crystallinities for PA6 and HDPE in HDPE/PA 6 20/80 blends. Filled symbols represent acid form, while open symbols represent the zinc-neutralized form.

indicating that compatibilizer does not alter the γ versus α polymorph balance, at least within the ability of DSC data to discern.

The effect of compatibilizer on the HDPE phase is quite substantial when the HDPE is in low concentration. The addition of a significant amount, relative to pure HDPE, of a presumably miscible lower crystallizing component, i.e., HDPE-g-MAH, not surprisingly lowers both the melting point and fractional crystallinity. However, the addition of HDPE-g-MAH cannot solely be responsible because at equivalent amounts of HDPE-MAH/HDPE content, i.e., 1–2.5% in the low HDPE-content blend, which corresponds to 4–10% in the high HDPE-content blend, there is a drop in χ_{PE} for the low HDPE-content blend but no drop in the high HDPE-content blend. This result is definite evidence that the stronger interaction with the polyamide in the low HDPE-content blends is disrupting the crystallinity of the HDPE blend. The only consistent explanation is that, at constant HDPE/HDPE-g-MAH ratio, a substantial drop is seen only when HDPE is the minor phase since a much larger fraction of ethylene segments are near the interface. One possible explanation why compatibilization affected the minor phase HDPE,

but not the minor phase PA6, is that having more amine endgroups involved with interfacial bonding will not disrupt crystallinity, since endgroups would not crystallize even if not bonded to the interface. In contrast, acid groups occur all along the main chain of the HDPE-g-MAH. Immobilization of random points along the chain due to bonding at the polyamide/polyethylene interface disrupts the crystallinity of the bonded chain as well as chains near the bonded chain. This reasoning presumes grafted and ungrafted materials are phase-mixed in the melt. The substantial drop in crystallinity is very likely the reason that the modulus in Figure 4 for the HDPE/PA6 20/80 blends is very far from being well-described by a simple mixing rule, much farther than either the tensile strength or elongation at break.

X-ray diffraction might be sensitive to small changes in polyamide crystal structure. Following the procedure given elsewhere,³⁸ the α -PA6 form is characterized by two peaks corresponding to the 200 and [002/202] crystalline planes with 2θ being found at 20.3° and 23.7° respectively, and the γ -crystalline form also by two peaks, one at 21.4° and the other at

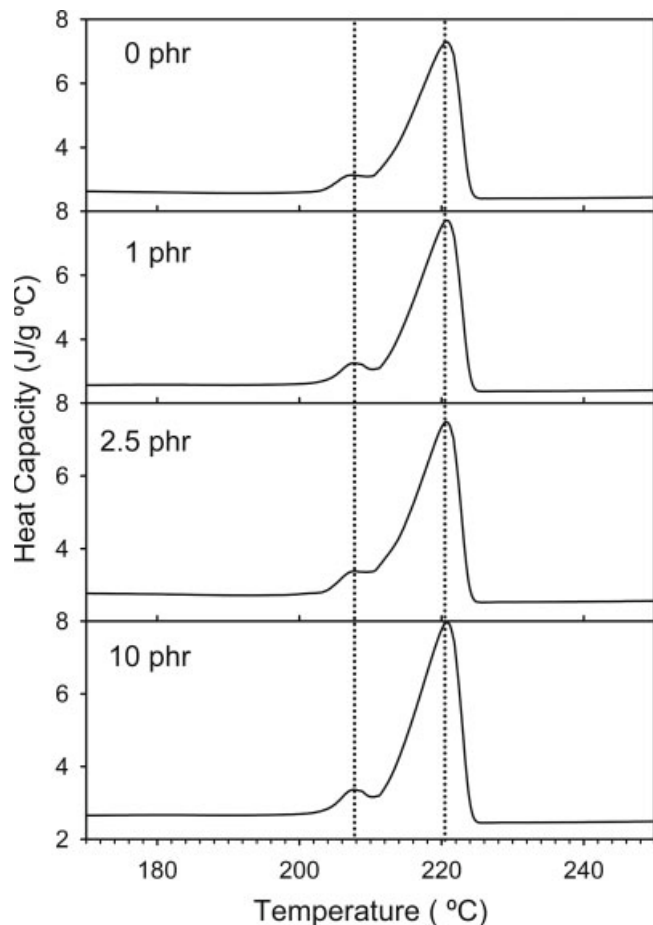


Figure 8 DSC thermogram of polyamide crystallization peak for HDPE/PA6 20/80 samples.

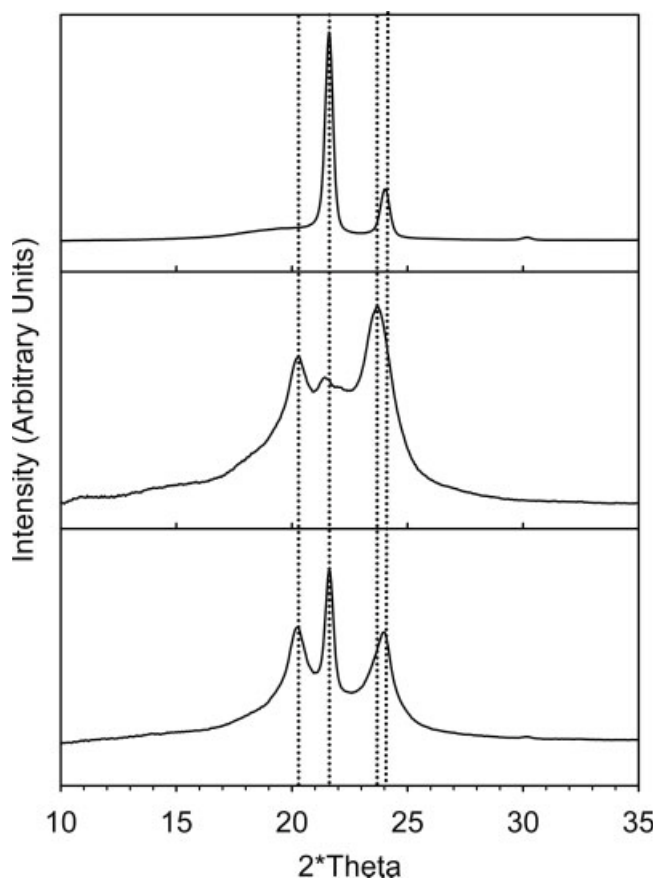


Figure 9 WAXS patterns for pure HDPE (top), pure PA6 (middle) and HDPE/PA6 80/20. The fractional crystallinity as determined by peak areas was 56.6% for pure HDPE and 40.0% for pure PA6. The fractional amount of the γ form, i.e., γ form/ $(\alpha + \gamma$ form), was calculated as 19% for the pure PA6.

22.1°. As shown in Figure 9, under the conditions used to prepare the samples used for tensile testing, the α -form predominates. Slow cooling and high crystallization temperatures leads to the preponderance of the α -form.^{39,40} It was hoped that WAXS spectra would be able to be used to quantify the amount of each crystalline structure for nylon in the blends; unfortunately, as shown in Figure 9, the polyethylene 110 and 200 reflections interfere with the 2 γ reflections, and the subsequent error in peak deconvolution was too large.

Crystallization temperatures for nonisothermal crystallization studies are shown in Figure 10. There was an extremely small exotherm for the PA6 crystallites in the HDPE/PA6 80/20 blend without compatibilizer, which disappeared entirely at 2.5% compatibilizer (spectra not shown). Disappearance of crystallization exotherms during nonisothermal crystallization experiments, e.g., fractionated crystallization, has been seen previously in polyamide blends and has been attributed to a change from heterogeneous to homogeneous nucleation as the polyamide particle

size becomes small.^{41,42} However, the drop in crystallization temperature at lower compatibilizer contents that normally is evidence of fractionated crystallization was not seen. HDPE kinetics shows no effect upon blending, with a $\sim 3^\circ\text{C}$ rise in crystallization temperature upon compatibilization. These results indicate a nucleation effect of the MAH-grafted material on the HDPE, or a nucleation effect of the PA 6 on the HDPE that occurs only after compatibilization. In the case of HDPE in the PA6 major-phase blends, there is no change in HDPE crystallization kinetics with compatibilization, but blending increases the crystallization temperature by 3–4°C. Blending leads to a $\sim 4^\circ\text{C}$ increase in polyamide crystallization temperature, which drops with compatibilization. In the case of PA6, blending causes increased nucleation; however, closer association with the HDPE segments due to compatibilization reduces this effect. Neutralization with zinc seems to have no effect, although the inconsistency in the data makes such a determination difficult.

DMA spectra are shown in Figures 11 and 12. The anomalous jump in storage modulus for the compatibilized blends immediately before the nylon melting temperature in the HDPE/PA6 20/80 blends was reproducible in the sense that the jump always occurred at certain compatibilizer amounts, but not

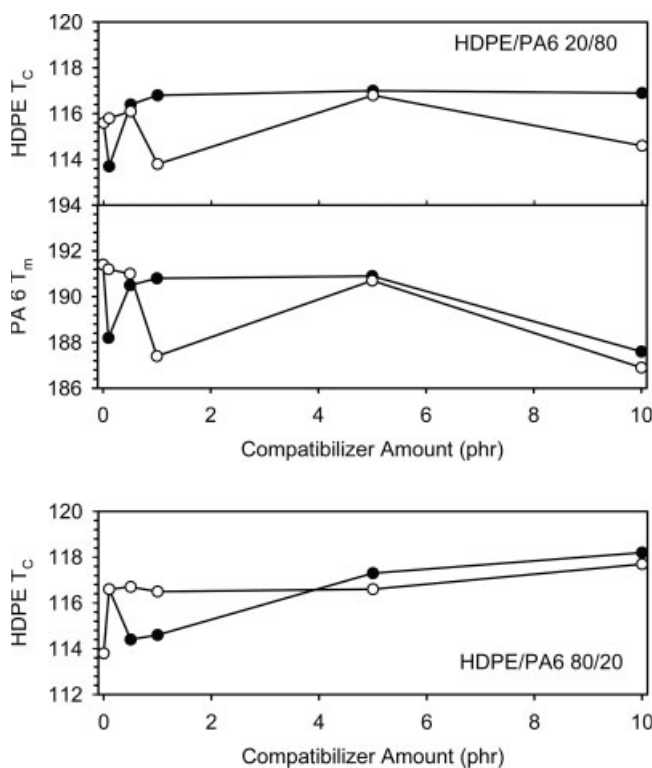


Figure 10 Temperature corresponding to maximum in crystallization exotherm for samples cooled at a rate of $10^\circ\text{C}/\text{min}$. The temperatures for pure PA6 and pure HDPE were 187.4°C and 113.8°C , respectively.

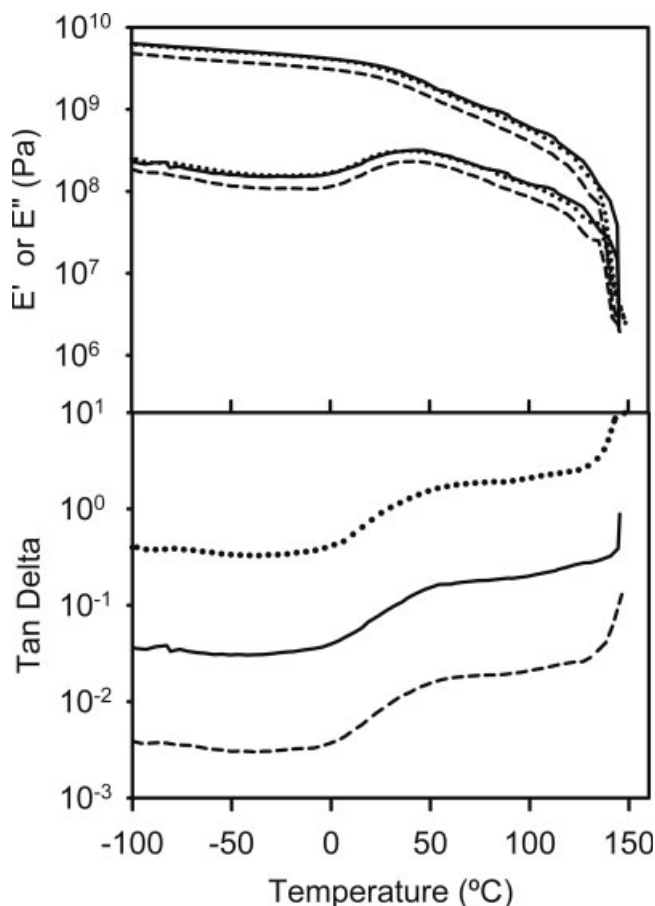


Figure 11 DMA spectra of HDPE/PA6 80/20 blend with no compatibilizer (dashed line) and blend with 1% HDPE-g-MAH compatibilizer (solid line) and with 1% HDPE-g-MAH compatibilizer after zinc oxide addition (dotted line). Tan δ for the blends without compatibilizer has been shifted downward by one decade, and tan δ for the blend made with compatibilizer partially neutralized with zinc oxide has been shifted upward by one decade to improve comparison; without shifting the three tan δ spectra overlap.

always at the same temperature. Our belief is that this jump is due to nonuniform contact of the 3-point bend fixture knife-edge(s) on the sample due to flow of the HDPE domains and the nonflow of the PA6 domains and can likely be changed by the exact characteristics of processing. However, this behavior only occurred for the blends with compatibilizer, indicating that compatibilization is relevant to this effect. The other odd behavior, which was reproducible in the sense that multiple samples cut from the same sheet were consistent, is that the storage moduli were substantially larger for the compatibilized blends. The large increases in storage moduli with compatibilization were not found in the tensile moduli displayed in Figures 3 and 4.

DMA spectra can also be used to measure the glass transition; it has been estimated that DMA is 10–100 times more sensitive to the glass transition than DSC.⁴³ Figure 12 clearly shows a peak in E'' at

36.8°C corresponding to the glass-transition temperature of nylon. However, there are other features in the DMA spectra; the hump in E'' in Figure 11 at 47.6°C is not reflected by a glass transition in DSC experiments. The two features are not separable in the blends at the frequency (1 Hz) used: that is, the peak in E'' is a convolution of the HDPE peak and PA6 peak. For the HDPE/PA6 20/80 blends, the glass transition of the PA6 is expected to dominate the behavior since the polyamide is the continuous phase and will have a much more significant impact on the mechanical properties. DSC and DMA (Fig. 13) shows that the glass transition of the polyamide decreases upon adding a small amount of compatibilizer, presumably indicating a more substantial interaction between the more mobile amorphous ethylene segments and the amorphous polyamide segments. Another possibility, that is by no means mutually

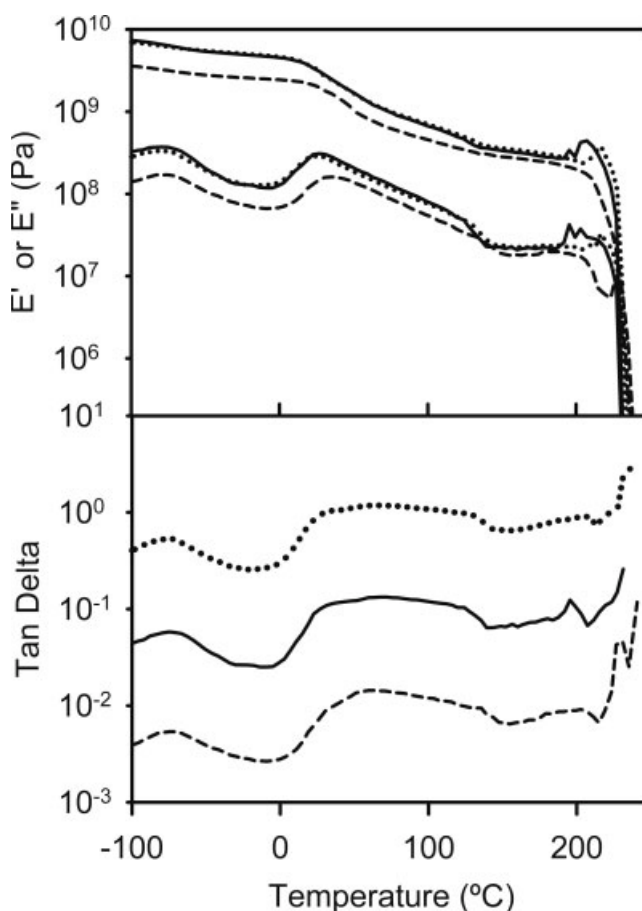


Figure 12 DMA spectra of HDPE/PA6 20/80 blend with no compatibilizer (dashed line) and blend with 1% HDPE-g-MAH compatibilizer (solid line) and with 1% HDPE-g-MAH compatibilizer after zinc oxide addition (dotted line). Tan δ for the blends without compatibilizer has been shifted downward by one decade, and tan δ for the blend made with compatibilizer partially neutralized with zinc oxide has been shifted upward by one decade to improve comparison; without shifting the three tan δ spectra overlap.

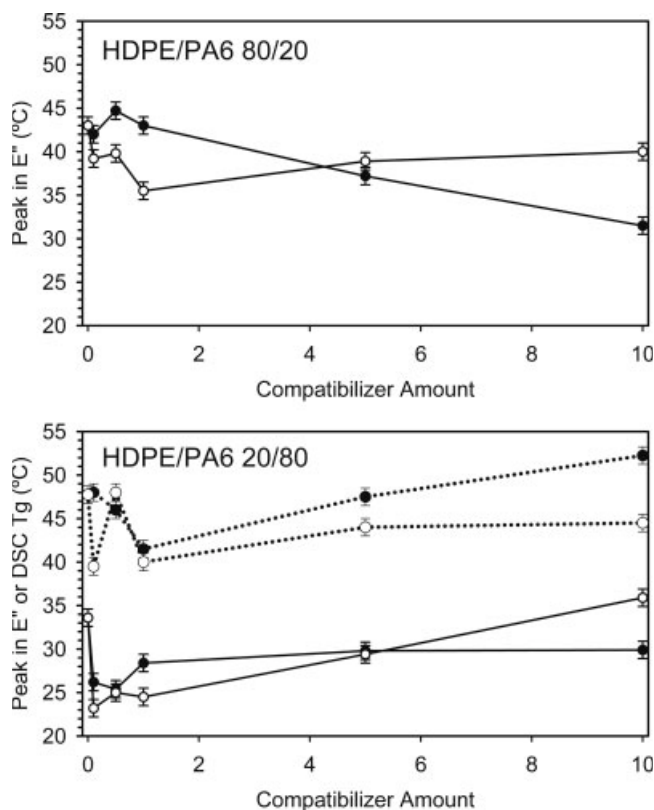


Figure 13 Location of peak in E'' for blends made with compatibilizer partially neutralized with zinc oxide (open symbols) and compatibilizer without zinc oxide (closed symbols). The values for pure HDPE and pure PA6 were 47.6°C and 36.8°C, respectively. In the bottom plot, the glass-transition temperature as measured via DSC is shown as the dotted line; the T_g was not visible in the HDPE/PA6 80/20 blends via DSC.

exclusive with the first, is that the higher concentration of amorphous ethylene segments that occur with compatibilization (Fig. 7) affects the glass-transition temperature of the PA6. Above 1 phr compatibilizer, however, the polyamide glass-transition temperature raises in both experiments spectra. Regarding the high HDPE content blends, there seems to be a slight drop in temperature and E'' peak magnitude corresponding to the $\sim 45^\circ\text{C}$ transition upon the addition of compatibilizer; perhaps due to the fact that the maleic anhydride grafted material has this transition at lower temperature.

CONCLUSIONS

HDPE with grafted maleic anhydride units has been investigated as a compatibilizer for HDPE with polyamide 6. The material acts as an effective compatibilizer, causing a marked reduction in dispersed phase size as well as an increase in tensile strength and toughness. The effect is much stronger in polyamide-rich blends than in polyethylene-rich blends. In

the former, the tensile strength is only $\sim 20\%$ less than would be predicted by a simple mixing rule. The amount of compatibilizer required for the maximum improvement is significantly higher than what was found in previous studies on similar systems. Compatibilizer affects the glass-transition temperature, crystallization kinetics, and amount of crystalline material. The addition of zinc, which is effective in increasing ethylene-acid copolymer compatibilizer performance in polyethylene-polyamide blends, has little, if any, effect in these materials. In the acid-copolymer system, the mechanism of improvement is thought to be that zinc speeds the reaction between the terminal amine and carboxylic acid; it is not clear why this would not occur in anhydride-grafted system as well. However, cases where partial neutralization with zinc has improved compatibilizer performance has occurred with materials having acid contents much greater than was used in this study.

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