Sulfonyl Azides—An Alternative Route to Polyolefin Modification

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ABSTRACT: Low-density polyethylene was modified to incorporate aniline moieties by reactive processing with 4-aminobenzenesulfonyl azide. Under melt-processing conditions, the loss of nitrogen produces a sulfonyl nitrene which, in the singlet state, interacts with the substrate primarily by C–H insertion. Polymeric blends prepared from aniline-grafted polyethylene and nylon-66 showed improved tensile and impact properties over and above nylon blended with virgin polyethylene. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 1395–1402, 2002; DOI 10.1002/app.10302

Key words: polyethylene; nitrene; reactive processing; blend; nylon-66

INTRODUCTION

Polyolefins, such as polyethylene and polypropylene, share a large portion of the plastics market because of their low cost and versatile properties. However, a lack of chemical functionality creates several problems, including reduced paintability tensile modulus and limited compatibility with other polymers.[1,2]

Modification of the polyolefin during melt processing by employing a free-radical initiator and functional monomer, such as maleic anhydride, acrylic acid, or glycidyl methacrylate, is a common method employed to overcome these limitations.[1,2] Thermal decomposition of the initiator during processing provides a source of free radicals that leads to grafting of the monomer, as well as undesirable reactions such as homopolymerization of the functional monomer, and chain scission and/or crosslinking of the base polymer. The relative degree of monomer grafting is dependent on the chemical nature of the polymer, the processing conditions, and the type of free-radical initiator/monomer combination employed.[1,3,4]

An alternative approach to the reactive processing strategy described above involves the use of sulfonyl azides. This class of compound was investigated previously as a means of incorporating functional groups onto the backbone of elastomers and as a crosslinker for the vulcanization of rubbers.[5–7] Thermal decomposition of the sulfonyl azide at appropriate processing temperatures generates reactive nitrenes that, in the singlet state, are known to undergo carbon–hydrogen (C–H) insertion to form sulfonylamido linkages.[8–10]

It was envisaged that polyolefins such as low-density polyethylene[11] (LDPE) may also be modified with the use of functionalized sulfonyl azides. Decomposition of the sulfonyl azide during melt processing should lead to modification of the polyolefin through C–H insertion reactions along the polymer backbone. Such a strategy has the potential to limit the number of crosslinking and/or chain scission reactions usually associated with polyolefin modification if the sulfonyl nitrene reacts in the singlet state, instead of the triplet state, because triplet state nitrenes are known to

react primarily by H-abstraction pathways.[8,9] As a further benefit, the use of such a reagent to modify polyolefins avoids employing both a free-radical initiator and a functional monomer to effect grafting.[8,9]

In this article, LDPE was modified with a sulfonyl azide to incorporate aniline functional groups. The resulting polymer was processed with nylon-66 to assess how the incorporation of polar aniline groups affects the mechanical performance of the resultant blend. It is well known that the incorporation of low-modulus polymers into engineering plastics results in an overall toughening of the material at the expense of tensile properties.[12] However, incorporation of functional groups onto the elastomer that can chemically interact with functional groups associated with the engineering plastic improves the performance of such materials because of the formation of chemical interactions between the respective polymer domains.[2,10] Such interactions allow stress to be effectively transferred across the polymer–elastomer interface. In the case of nylon-66 modified with LDPE, the incorporation of aniline groups should also act to compatibilize such blends through H—bond and acid–base interactions between the respective polymer domains.

EXPERIMENTAL

Materials

Film-grade LDPE was obtained from Kemcor Australia (LD4200) and nylon-66 was obtained from DSM. All other chemicals were of analytical reagent purity and were obtained from the Aldrich Chemical Co.

Synthesis

4-Acetamidobenzenesulfonyl Azide (2)

4-Acetamidobenzenesulfonyl chloride (1) (48.6 g, 208 mmol) was dissolved in 500 mL acetone and the solution was cooled to a temperature of 0°C. Over a period of 60 min, a chilled aqueous solution of sodium azide (14.2 g, 218 mmol, 150 mL) was added dropwise and the resultant solution allowed to stir for a further 60 min at that temperature. The solution was then poured onto an ice/water slurry (1.5 L) and the white precipitate was collected at the pump, washed with ice-cold water, and dried under vacuum. 4-Aminobenzenesulfonyl azide could be used in the next step directly or recrystallized from a solution of acetone and water for analysis (yield 48.4 g, 97%).

^{1}H-NMR (200 MHz, CDCl$_3$) δ 8.4 (1H, s, NH), 7.86 (d, 2H, J = 9 Hz), 7.79 (d, 2H, J = 9 Hz), 2.23 (s, 3H, CH$_3$).
^{13}C-NMR (50 MHz, CDCl$_3$) δ 169.5 (CO), 144.1 (C4), 132.3 (C1), 128.9 (C2, 6), 119.6 (C3, 5), 24.7 (CH$_3$).
FTIR (KBr) v_{max} 2126 (N$_3$), 1676 (CO), 1160 (SO$_2$N).
MS (EI, 70 eV) 240 (M$^+$), 198.
Elemental anal. calcd. for C$_8$H$_8$N$_4$O$_3$S$_1$: C, 40.00%; H, 3.36%; N, 23.32%; O, 19.98%; S, 13.35%. Found: C, 40.04%; H, 3.27%; N, 23.33%; O, 20.25%; S, 13.11%.

4-Aminobenzenesulfonyl Azide (3)

Twelve grams of *p*-acetamidobenzenesulfonyl azide (5.1 mmol) and 45 mL concentrated HCl was heated at reflux for 35 min. Upon cooling to approximately 5°C, the solution was neutralized with saturated sodium bicarbonate solution and solid sodium bicarbonate until a pH of approximately 6 was reached. The light brown mixture was extracted with diethyl ether, washed, dried (MgSO$_4$), and then filtered through celite. Evaporation of the diethyl ether solution provided a brown solid which could be recrystallized from a small portion of diethyl ether at −20°C to provide light brown crystals (yield 7.52 g, 76%).

^{1}H-NMR (200 MHz, CDCl$_3$) δ 7.69 (d, 2H, J = 8 Hz, H2, 4), 6.71 (d, 2H, J = 8 Hz, H3, 5), 4.37 (broad s, 2H, NH$_2$).
^{13}C-NMR (50 MHz, CDCl$_3$) δ 152.6 (C4), 129.9 (C2, 6), 125.3 (C1), 114.0 (C3, 5).

Table I   Extrusion and Injection Molding Temperature Profiles

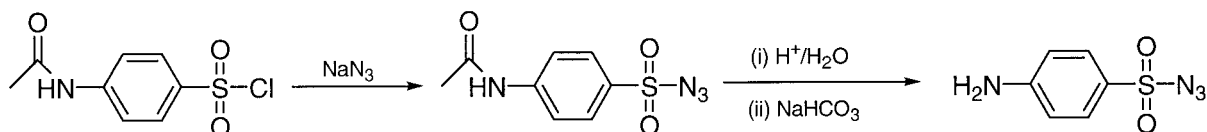| Method	Hopper	2	3	4	5	Die
Temperature (°C) extruder LDPE samples	170	185	190	190	190	180
Temperature (°C) extruder LDPE–nylon-66 blends	240	265	265	265	265	240
Temperature (°C) injection-molded LDPE samples	175	180	185	185	—	70
Temperature (°C) injection-molded LDPE–nylon-66 blends	260	265	265	270	—	110

Figure 1 Synthesis of sulfonyl azide (3).

FTIR (KBr) v_{max} 3480 (NH), 2126 (N$_3$), 1160 (SO$_2$N). MS (EI, 70 eV) 198 (M$^+$), 156.

Elemental anal. calcd. for C$_8$H$_8$N$_4$O$_3$S$_1$: C, 36.36%; H, 3.05%; N, 28.27%; O, 16.14%; S, 16.18%. Found: C. 36.57%; H, 3.11%; N, 28.36%; O, 15.96%; S, 16.00%.

4-Aminobenzenesulfonyl Azide Modified LDPE

LDPE was modified with sulfonyl azide (3) by using a Brabender Plasticorder fitted with roller rotors. The LDPE pellets were spray coated with a solution of sulfonyl azide (3) dissolved in ethanol/toluene. Most of the solvent was evaporated by means of a nitrogen stream, with the remainder removed at reduced pressure. The coated pellets were transferred to the Plasticorder and melt mixed at 190°C at a rotor speed of 30 rpm for 10 min. Samples were prepared for analysis by first removing low-molecular-weight impurities by repeated methanol precipitation of a hot (100°C) toluene solution of the polymer before drying to constant weight at reduced pressure.

Compounding

LDPE samples from the Plasticorder were ground into small pellets and dried at 60°C for at least 12 h in a desiccated oven prior to injection molding by using an 80 ton Battenfeld injection molder. Alternatively, LDPE–nylon-66 blends were prepared by using a compounding single-screw Axxon R40F benchtop extruder. LDPE and nylon samples were dried at 60 and 80°C, respectively, for at least 12 h and mixed thoroughly prior to extrusion. The screw speed was set at 120

rpm, which correlated to a residence time of approximately 2 min (see Table I for temperature profiles) with the blended samples again dried thoroughly prior to injection molding.

Analysis

Proton and ^{13}C-NMR analysis was completed on a Bruker 200 MHz NMR spectrometer operating at either 200 MHz for proton or 50 MHz for C-13 spectra. Samples for analysis were dissolved in deuterated chloroform and referenced to residual CHCl$_3$ (7.26 or 77.0 ppm). FTIR spectra were obtained by using a Bio-Rad spectrometer using a scan speed of 5 kHz and a resolution of 4 cm^{-1}.

Differential scanning calorimetry (DSC) was carried out by using a TA 2920 MDSC employing Advantage software. The instrument was calibrated against indium (156.6°C), distilled water (0°C), and cyclohexane (−86.7 and 6.9°C). Great care was taken to provide samples of even thickness, dimensions, and weight (10 mg), which were subsequently crimped in nonhermetic pans and analyzed at a scan rate of 10°C. Such sample preparation provided a reproducibility of ±0.3°C for the thermal transitions observed.

Physical Testing

Tensile testing was carried out by using an Instron tensile testing apparatus (5565) utilizing a 30-kN load cell according to the ASTM 638 standard. A crosshead speed of 50 mm/min was used
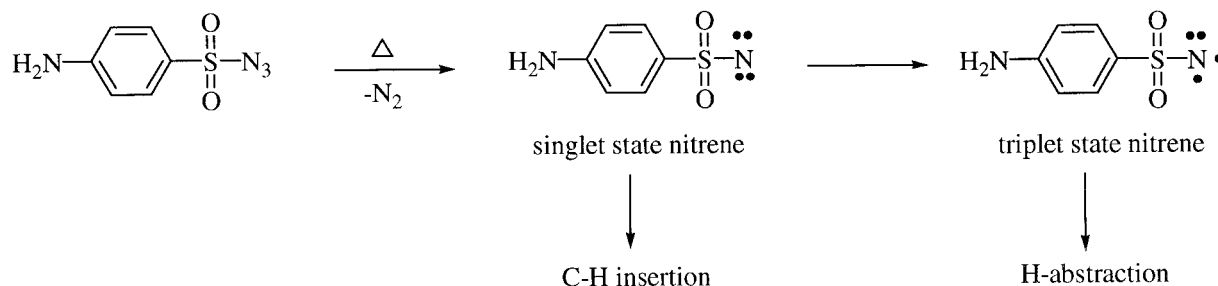

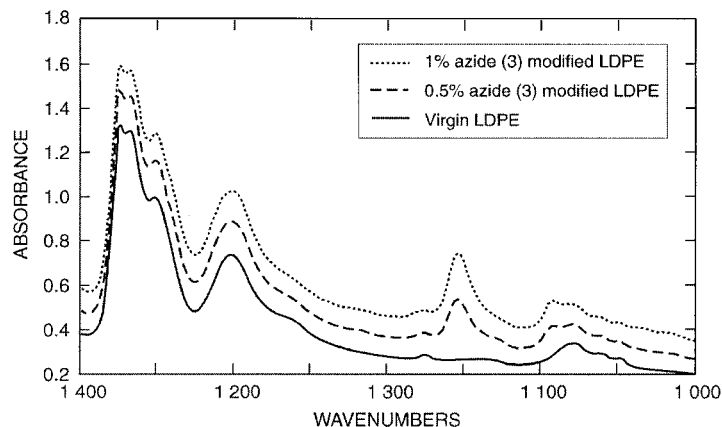**Figure 2** Simplified thermolysis/reaction pathways of sulfonyl azide (3).

Figure 3 FTIR analysis of virgin and modified LDPE polymers.

for all specimens employing an external extensometer. Ultimate tensile strength, elongation at break, and tensile modulus values were recorded and calculated. Tensile toughness values for the composite materials, being derived from the integration of the stress versus strain curve, were also shown. Notched Izod impact testing was carried out by using a Radmana ITR 2000 instrumented impact tester in accordance with the Australian Standard AS 1146.1.

RESULTS AND DISCUSSION

The synthesis of sulfonyl azide (3) was carried out by employing a similar methodology to that previously reported (Fig. 1).[5] Treatment of sulfonylchloride (1) with a slight excess of sodium azide afforded acetamide (2) in near quantitative yield. Acid hydrolysis of the protecting group and subsequent neutralization afforded azide (3), following low-temperature recrystallization. Thermal analysis of azide (3) by DSC indicated an endotherm at approximately 37°C due to melting of the sample, and a large exotherm ($\sim$ 180 kJ mol^{-1}) with an onset temperature of approximately 154°C associated with decomposition of the azide with loss of nitrogen (not shown).

LDPE pellets coated with either 0.5 or 1.0% w/W of azide (3) were melt mixed in a Brabender internal mixer. Motor torque was analyzed during mixing and indicated that only a small increase ($<$10%) in melt viscosity occurred between samples containing the azide modifier and virgin LDPE. This result indicates that limited crosslinking took place and supports previous studies that propose that sulfonyl azides decom-

pose to form singlet state nitrenes that react primarily by C–H insertion. Intersystem crossing, which is less likely with sulfonyl compared to formal and aryl nitrenes, produces a triplet state which reacts preferably by H-abstraction pathways.[8] Such H-abstraction reactions would generate polymeric carbon-centered radicals and inevitably some degree of LDPE crosslinking (Fig. 2). Alternatively, the slight increase in torque associated with the samples incorporating azide (3) may be a result of increased intermolecular interactions and hence melt viscosity resulting from the incorporation of polar aniline groups.

Both FTIR and elemental analysis of the purified LDPE samples confirmed modification by azide (3) during melt processing. The formation of a sulfonamide group was characterized by a peak in the FTIR spectrum at 1154 cm^{-1} resulting from the sulfonamide S=O symmetric stretch which is not present in virgin LDPE (Fig. 3).[13] Elemental analysis results also confirmed the presence of nitrogen in LDPE samples modified with azide (3) but not in virgin LDPE (Table II). These results suggest a graft yield of approximately 48.1%, which compares favorably with the conversion rates achievable by free-radical grafting of basic monomers onto LDPE substrates.[14]

Thermal analysis results of the samples are provided in Table III. Increasing the level of azide

Table II   Elemental Analysis of Modified LDPE

Polymer	%C	%H	%N
LDPE	85.61	14.19	—
LDPE–0.5% azide (3)	85.77	14.55	0.04
LDPE–1.0% azide (3)	85.66	14.42	0.08

Table III DSC Transitions for LDPE Modified with Azide (3)

| Sample	α-Transition (°C)	Melt Onset (°C)	Melt Peak (°C)	Melting Enthalpy (J/g)
LDPE	40.2	99.3	108.9	86.2
LDPE–0.5% azide (3)	41.0	99.7	109.1	77.5
LDPE–1.0% azide (3)	41.9	100.4	109.5	76.5

(3) during processing provided an incremental increase in temperature of both the α-relaxation and the melting point of the LDPE samples. As indicated above, this increase in both melt and transition temperatures may result from crosslinking associated with triplet state nitrene formation or from an increased level of chain interactions associated with the grafting of polar aniline groups. Melt enthalpies were also lower for samples containing the azide modifier, suggesting a lower degree of crystallinity for the functionalized polyolefins compared with virgin LDPE.

Polyamides are often blended with polyolefins to improve certain properties such as notched impact resistance and processibility.[15] Because these two polymers are inherently incompatible, polyolefins modified with maleic anhydride or acrylates are added as compatibilizers during processing to improve the mechanical performance of these blends. The addition of such compatibilizers is known to reduce interfacial tension and increase interfacial adhesion between the respective polymer domains by providing anhydride or ester groups for chemical reaction with nylon chain ends and amido groups and regions along the compatibilizer backbone compatible with the polyolefin.[16–18]

Polyolefins modified with aniline moieties should also act as compatibilizers by increasing the interfacial adhesion when blended with polyamides, by facilitating acid–base and H–bonding interactions with the polyamide matrix. To test this assumption, the polyolefins modified with 0.5 and 1.0% w/W azide (3) discussed above were melt blended with nylon-66, and the mechanical performance and thermal properties of the blends were analyzed.

Figures 4-8 outline the change in mechanical performance for nylon-66 blends incorporating 25% LDPE modified with different amounts of azide (3). Ultimate tensile strength values were marginally improved by incorporating LDPE modified with 1% w/W of azide (3) ($\sim$ 7% improvement, Fig. 4). Samples containing the modified LDPE were also stiffer, with samples modified with 1% w/W azide (3) having a 7% improvement in tensile modulus. Elongation at break values were also improved (15%) over nylon-66 blended with virgin LDPE alone, whereas results for samples containing LDPE modified with 0.5% azide
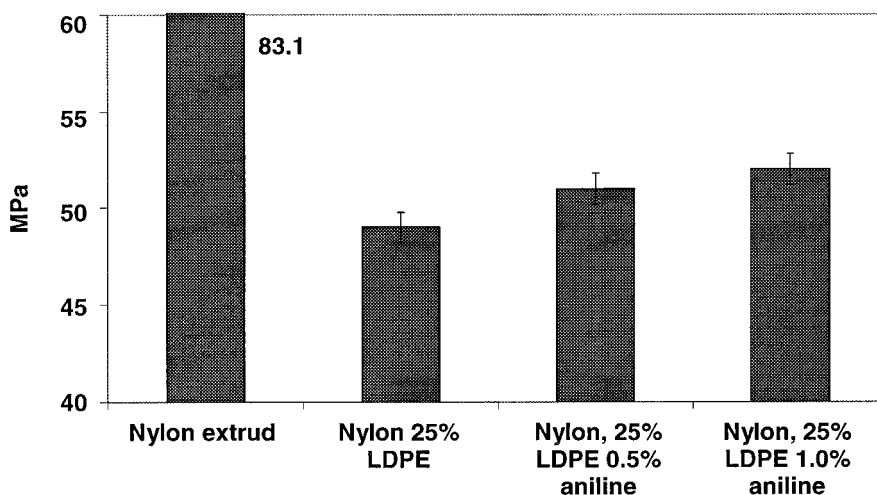
Figure 4 Ultimate tensile strength of nylon-66 blends containing 25% LDPE.
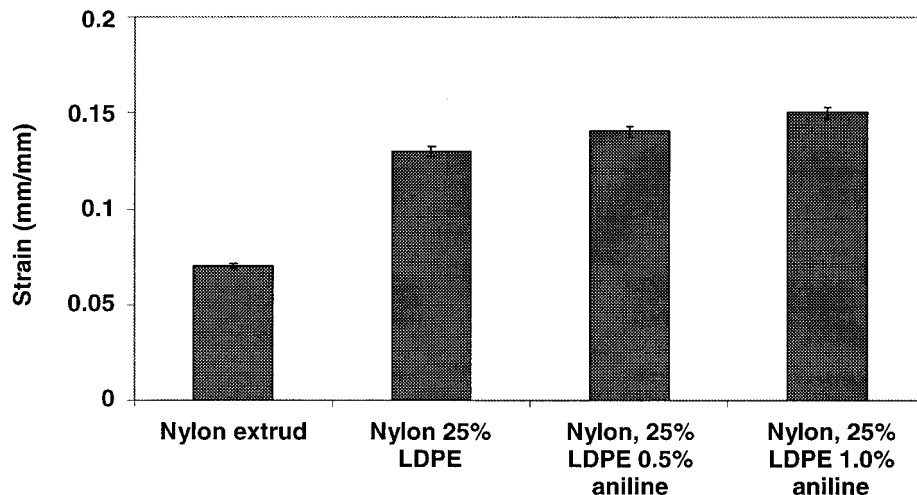
Figure 5 Elongation at break of nylon-66 blends containing 25% LDPE.

(3) were somewhat less (∼ 8%). As a result of these improvements in tensile strength and elongation, tensile toughness values were improved by 19% for samples incorporating 0.5% azide (3) and 27% for samples incorporating 1.0% azide (3).

Blends containing the modified LDPE also had improved notched impact resistance than nylon-66 blends containing virgin LDPE (Fig. 8). It is well known that polyamides have a high resistance to crack initiation but a low resistance to crack propagation, and hence, have high unnotched but low notched impact strengths.[14] This problem was addressed previously by incorporation of a second rubbery phase to form super tough nylon blends to more effectively dissipate crack energy and improve nylon toughness.[12] Samples containing the aniline-modified LDPE had superior notched impact strengths than nylon-66 or nylon-66 blended with virgin LDPE. In this case, a 55% increase in notched impact strength resulted from the use of LDPE modified with 0.5% azide (3), and almost a 100% improvement in performance using LDPE modified with 1.0% azide (3). These mechanical performance results are consistent with an increase in interfacial adhesion between the nylon-66 and LDPE phases in blends containing LDPE modified with azide (3). Hence, more effective stress transfer is possible between the nylon and polyethylene phases, which results in improved toughness of these samples.

Crystallization points and enthalpies from the DSC cooling thermographs are provided in Table
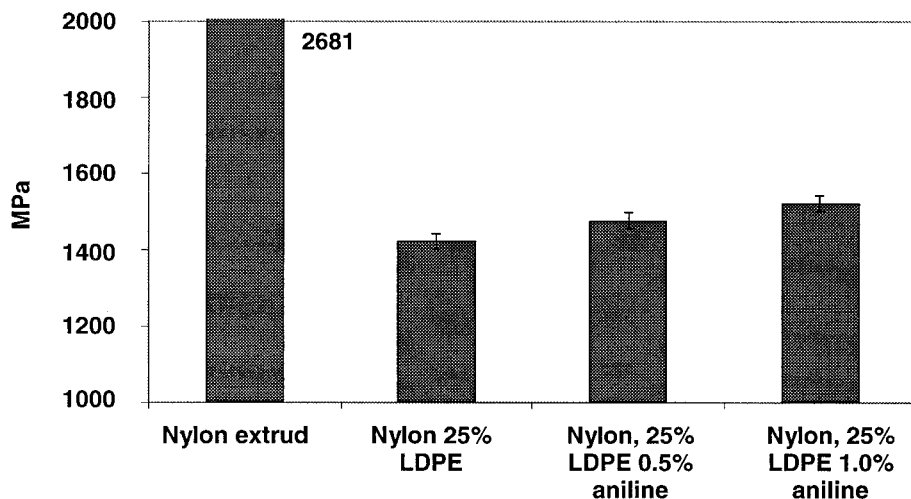

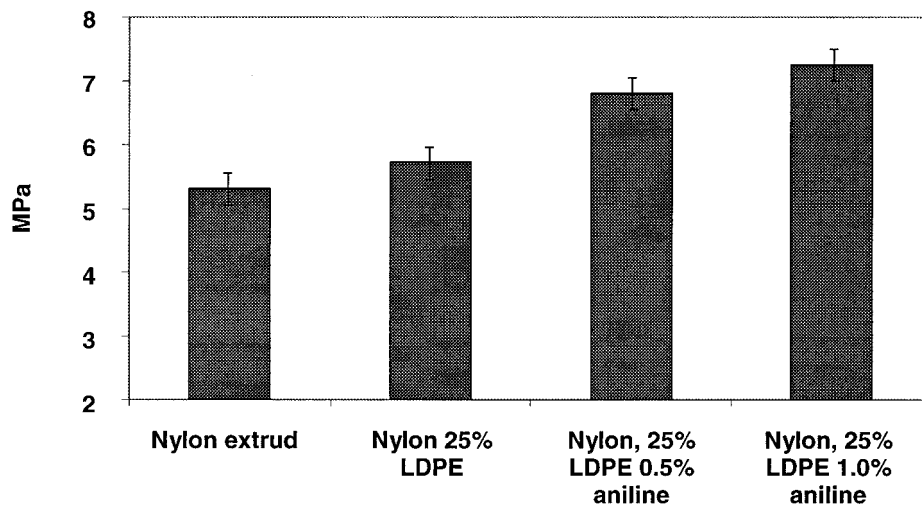**Figure 6** Tensile modulus of nylon-66 blends containing 25% LDPE.

Figure 7 Tensile toughness of nylon-66 blends containing 25% LDPE.

IV. LDPE modified with azide (3) had lower crystallization enthalpy than virgin LDPE. Considering the temperature reproducibility ($\pm 0.3°C$), LDPE–nylon-66 blends containing 25% virgin LDPE had similar crystallization points and enthalpies than pure LDPE and nylon-66, suggesting that the virgin LDPE and nylon-66 phases had little interfacial interaction (theoretical enthalpies calculated from the respective virgin materials are provided in parentheses in Table IV). Nylon-66 blends containing LDPE modified with azide (3), however, did show changes in both the crystallization point and the enthalpy associated with each of the domains. In general, crystallization enthalpies were reduced for the modified blends, showing that both domains were less crystalline than that expected theoretically. This suggests an improvement in interfacial interaction between the modified polymer phases, consistent with the observations from mechanical testing results for the blends.

CONCLUSION

LDPE was modified with 4-aminobenzenesulfonyl azide (3) during reactive processing of the polymer. FTIR and elemental and thermal analysis results suggest that aniline groups were grafted onto the LDPE polymer backbone because of characteristic stretches in the FTIR spectrum, the presence of nitrogen in the elemental analysis, and changes in crystallinity and melting points of
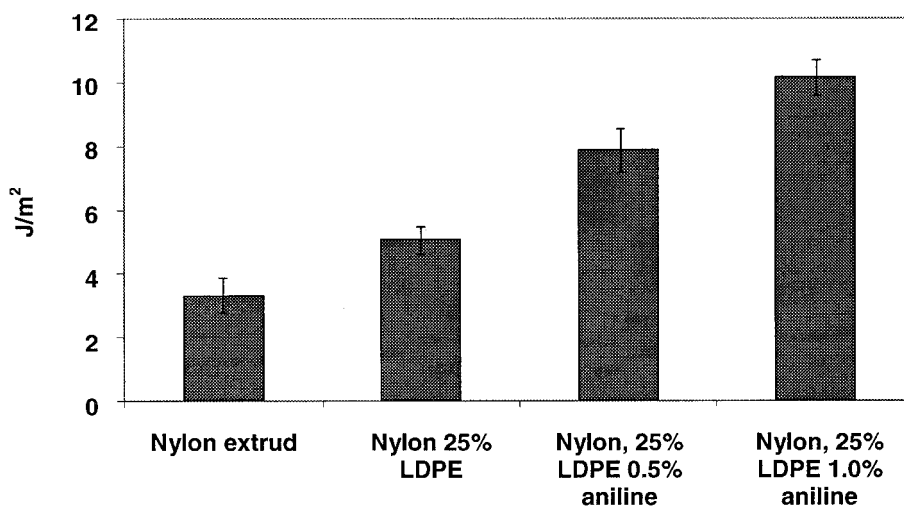

Figure 8 Notched impact resistance of nylon-66 blends containing 25% LDPE.

Table IV   DSC Cooling Transitions for LDPE–Nylon Blends

Sample	T_c (°C)		ΔH_c (J/g)	
	PE	N-66	PE	N-66
Nylon-66	—	236.9	—	55.5
LDPE	96.7	—	74.1	—
LDPE–0.5% azide (3)	96.3	—	72.1	—
LDPE–1.0% azide (3)	96.6	—	69.1	—
Nylon-66–25% LDPE	96.4	236.7	18.6 (18.5)[a]	41.4 (41.6)[a]
Nylon-66–25% LDPE [0.5% azide (3)]	95.4	234.9	17.3 (18.1)[a]	40.1 (41.6)[a]
Nylon-66–25% LDPE [1.0% azide (3)]	95.6	234.8	16.7 (17.3)[a]	37.7 (41.6)[a]

[a] Theoretical enthalpies calculated from results for virgin materials.

the polymer. Nylon-66 blends with aniline-modified LDPE have improved tensile and impact properties, consistent with an improvement in interfacial adhesion between the nylon and LDPE phases in such blends.

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