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Thermal and dynamic mechanical analysis on metallocene ULDPE/PP blends to optimize impact properties

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Abstract

Metallocene polymerized ultralow density polyethylenes (ULDPE) were found to be effective impact modifiers for rigid matrices such as polypropylene (PP). This is mainly due to the very high level of comonomer incorporation with homogeneous short chain branching distributions (SCBD) brought about by the single site metallocene catalysts. However, a very heterogeneous Ziegler Natta copolymer of 0.88 specific gravity was found to be surprisingly effective in impact modification efficiency.

A variety of thermal and morphological techniques were used in this study including differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and low voltage scanning electron microscopy (LVSEM). It was found that the modulus difference between the two phases, degree of coupling as evidenced by morphology at the phase boundaries, and crystallizable fraction of the rubber phase all played an important role in impact modification. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Short chain branching distribution; Ultralow density polyethylenes; Polypropylene

1. Introduction

One of the consequences of metallocene catalysts' ability to homogeneously incorporate high levels of co-monomers is the significantly depressed beta relaxation, which at high contents, resembles a glass transition, Tg. These very low Tg's lead to superior subambient impact performance compared to conventional low density polyethylenes (LDPE) and linear low density PE's from Ziegler–Natta catalysts. Additionally, these metallocene copolymers, despite their exceptionally low crystallinity, remain free flowing due to their narrow composition distribution. These two properties combined allowing them to be used as efficient impact modifiers for rigid matrices such as polypropylene [1–3]. However, in one of our earlier studies [1], a very heterogeneous Ziegler–Natta (ZN) ULDPE, although very difficult to process by itself, was found to have surprisingly good low temperature impact efficiency in polypropylene. It was proposed that the extremely broad compositional distributions led to enhanced coupling between the rigid matrix and the elastomeric domains. It is the goal of this study to determine if this interface can be 'tuned' through deliberate broadening of the short chain branching distribution (SCBD). Perhaps, through this under-

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standing, we can further optimize the impact modification efficiency of metallocene ULDPEs.

Available literature on impact modification indicate that the morphology plays an important role on effectiveness, hence in this study we characterized these blends by thermal analysis and dynamic mechanical analysis to determine the likely origin for the performance difference and attempt to construct a plausible model that fits most observations. It was hoped, through studies like this, additional insights can lead to further performance improvements.

2. Experimental

2.1. Materials

2.1.1. Binary blends

1. Matrix polypropylene (PP w/0.91 specific gravity, MFR=2)[1];
2. dispersed phase ZN ultra-low density polyethylene-A (0.88 specific gravity, ULDPE, MI=0.8; see Footnote 1) and
3. dispersed phase homogeneous ULDPE -B (0.87 specific gravity ULDPE, MI=5).

2.1.2. Interface modifier in ternary systems

1. High density polyethylene; (HDPE 0.96 specific gravity, 20 MI), modifier A.
2. Homogeneous medium density polyethylene (MDPE 0.935 specific gravity, 2.5 MI), modifier B.
3. Homogeneous very low density polyethylene (VLDPE, 0.902 specific gravity, 1 MI); modifier C.

Polyethylene modifier blends were first compounded and pelletized with the 0.87 specific gravity base modifier B in a 1:4 ratio of PE to ULDPE. The resultant modified ULDPE pellets as well as base ULDPE resins were blended with the PP material and compounded on a 38 mm Davis Standard extruder with a two-stage screw and a Maddox mixing section at a melt temperature of 230°C and extrusion casted into 200 μm film. The target composition was 75% PP and 25% modified ULDPE or 100% ULDPE. The base blend for interface modification was made from ULDPE B. The modified composition was targeted to contain 5% interface modifiers.

2.2. Characterization

Thermal analysis was carried out on a TA Instruments 2100/2910 Differential Scanning Calorimeter (DSC) at cooling rates of 10°C/min to −30°C after equilibration at 200°C to erase the previous thermal history. The 2nd melt was carried out at a heating rate of 10°C/min. Dynamic Mechanical Analysis (DMA) was conducted on a Seiko DMS-110 Dynamic Mechanical Analyzer over a temperature range of −150 to 150°C. over a frequency range of 0.5–100 Hz. Rheological measurements were done on a Rheometrics Fluids Rheometer at 200°C with a parallel plate geometry over a frequency range of 0.1–200 rad/s.

Impact studies were performed on a Dynatup (Model 8200) Instrumented Impact Tester with a 2 cm semi-spherical tup interfaced with personal computer with LabView automation software. A 14 cm circular film holder was used for sample mounting. Samples were conditioned and tested in a computer controlled, liquid N_2 cooled, environmental chamber [1].

Electron microscopy was carried out on the film samples microtomed at −100°C in a Reichert FC4E cryo-ultramicrotome and stained in RuO_4 vapor for 60 min or etched in *n*-heptane at ambient temperature in a sonic bath for 30 min. The film samples were first relaxed at 180–200°C for 5 min before microtoming. Imaging was carried out on a JEOL 6300 LVSEM or a JEOL 35CF SEM (Fig. 1).

3. Results and discussions

Fig. 1a through c indicate the cystallization curves of ternary metallocene ULDPE/PP blends with 5% of modifier A, B and C. It is immediately apparent that the HDPE modifier crystallized near the PP main peak in Fig. 1a. The MDPE's crystallization was clearly visible as a distinct shoulder on the low temperature

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[1] MI and MFR refer to melt index and melt flow rate in °C/min according to ASTM D-1238 at 190 and 230°C, respectively.

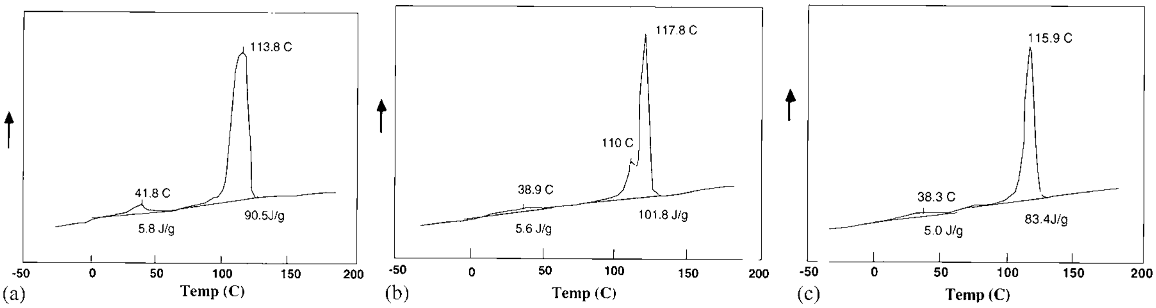

Fig. 1. The cystallization curves of ternary metallocene ULDPE/PP blends with 5% of modifier A, B and C.

slope, while the VLDPE became indistinct, located in-between the crystallization peaks of PP and the ULDPE.

Instrumented impact data are shown in Figs. 2–5.

The reference blend with the metallocene modifier has a very low brittle/ductile transition of about −35°C. After rising steeply with temperature after the B/D transition, the impact energy moderated somewhat before rising again at about −15°C to a very strong plateau at ambient temperature. In comparison, the Ziegler–Natta heterogeneous modifier gives a surprisingly low B/D transition of −35°C. After steady increases at a slightly lower rate than the reference, it begins to decrease at about −15°C and ending at room temperature at a significantly lower value than the reference. As discussed in the previous paper, this was probably caused by the larger particle size of the dispersed phase.

The modifier A with 5% of a highly crystallizable high-density polyethylene achieved a B/D transition at −35°C, equaling that of the reference blend. However, between −40°C and −20°C, the impact performance was slightly but detectably lower than that of the

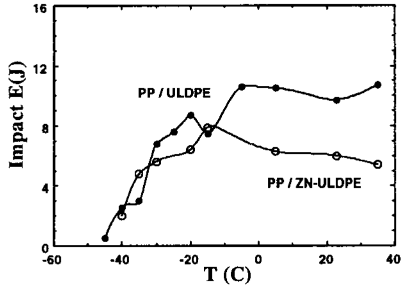

Fig. 2. Impact comparison.

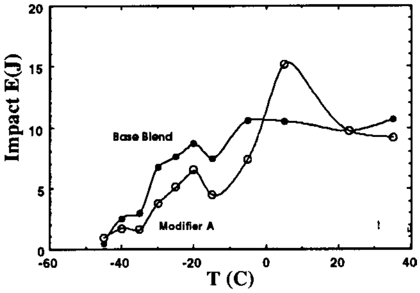

Fig. 3. Modifier A (HDPE) impact.

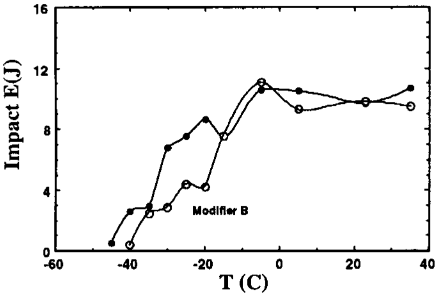

Fig. 4. Modifier B (0.935 density).

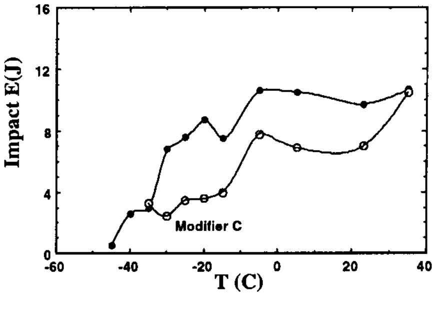

Fig. 5. Modifier C (0.902 density).

reference, presumably from the slightly lower ULDPE content (20% versus 25%). However, at about −20°C, after the beta relaxation of the ULDPE, the impact energy rises sharply, significantly surpassing that of the reference blend before settling down to near equality at room temperature. This strong rise and high ambient impact clearly indicated the effectiveness of the interface coupling the modifier was designed for, validating the hypothesis set forth in the previous paper.

For modifier B, a 0.935 medium density homogeneous polyethylene, the B/D transition was slightly elevated to about −30°C and the rise at about −20°C was still evident. However, the impact performance above −20°C pretty much matched that of the base reference. This indicated a moderate level of the modification of the interface.

For modifier C, it appears an anti-synergism was at work: the modifier was too high of a crystallinity to improve deep subambient impact, and yet too low of a crystallinity to modify the domain interface. As a result, the impact performance stayed significantly below the reference material throughout the temperature range.

Dynamic mechanical analysis (DMA) uses low amplitude sinusoidal stresses to probe various molecular relaxation processes in the polymer at various temperatures. The gamma relaxation at about −120°C for polyethylenes was assigned the so-called 'crankshaft' motion [4] of more than four methylene sequences. In addition, there is a strong inverse relationship between the crystallinity and the intensity of the relaxation. Evidently, at higher crystallinities, the crystalline matrix constrains and restricts the crankshaft motion at these temperatures. In addition, earlier DMA studies [5] correlated the intensity of the gamma transition with subambient impact performance of PP/EPR blends of varying rubber content and processing conditions (Fig. 6). In this case, the rigid matrix is the crystalline PP phase, while the rubber domains is the dispersed phase. An analogy may also exist where the freedom of motion for the rubbery phase is modulated by the surrounding rigid matrix. Here, the coupling at the domain interface must be the source of the modulation.

For pure ULDPE's the gamma relaxation is quite active and as a result the brittle–ductile transition is located at temperatures far below the beta relaxation, the main relaxation for the rubber phase. For example, the base metallocene modifier with a beta maximum of −44°C exhibits a B/D transition at −75°C.

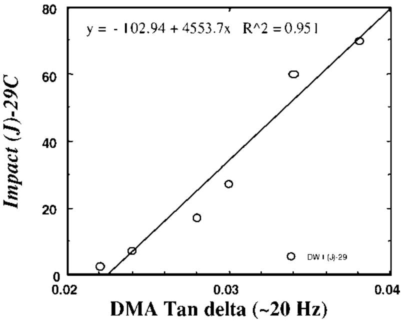

Fig. 6. Correlation of gamma intensity with impact data from reference [5].

For impact modified polymers, in the region between the gamma maximum and the beta relaxation, the mechanical coupling between the rubber phase and the rigid matrix is important in transferring stresses from the brittle matrix to the rubber domains. This coupling is reflected in the intensity of the gamma transition for similar rubber content systems.

In comparison, as shown in Fig. 7, the Ziegler–Natta modified polypropylene exhibited a significantly more active gamma relaxation compared with the metallocene ULDPE with a slightly lower crystallinity.

Thus far, based on thermal and dynamic mechanical analysis, we have inferred that the interface between the ULDPE dispersed phase and the rigid polypropylene matrix are mostly amorphous, and at cryogenic impact temperatures, remain rigid and acts as a poor

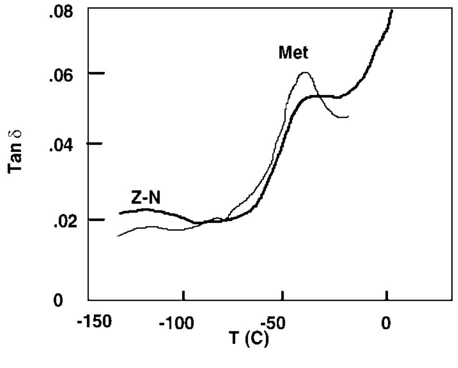

Fig. 7. DMA of ZN and metallocene modified PP.

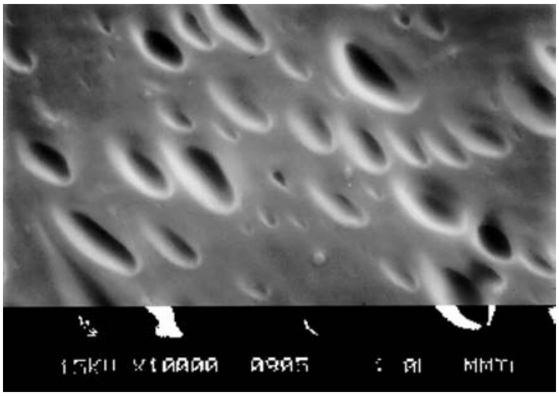

Fig. 8. *n*-Heptane etched morphology metallocene ULDPE/PP blend.

stress transfer agent between the widely different phases.

The morphology of dispersed ULDPE revealed by SEM can be used to further examine this hypothesis. In the heptane etched samples, the particles of Metallocene homogeneous ULDPE were completely extracted while the particles of Ziegler–Natta ULDPE were only slightly extracted, (Figs. 8 and 9). This leads to the conclusion that there was more extensive crystalline order at the interface with the Ziegler–Natta ULDPE making it more resistant to oxidation and less extractable.

In the binary sample A, SEM evidences pointed to a more rigid interface layer, perhaps with modulus intermediate between the polypropylene and the ULDPE rubber phase. This more 'graded' interface structure led to more efficient stress transfer and lower temperature activation of the beta relaxation process and very low D/B transitions. However, this improved coupling between the rubber phase and the matrix also came at a price: that of significantly reduced room temperature modulus and total impact energy.

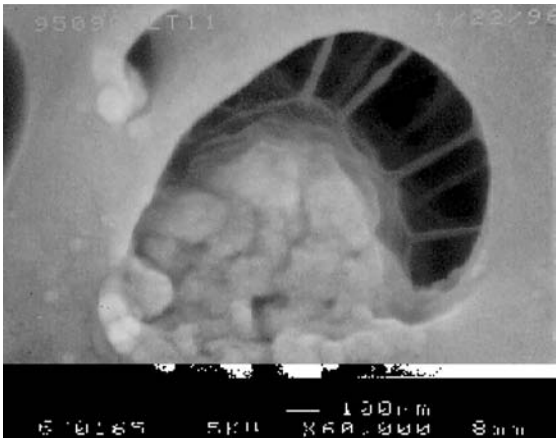

Fig. 9. Details of *n*-heptane etched morphology ZN ULDPE/PP blend.

It is well known that particle size and dispersion are important factors in achieving optimal product performance and that particle size is a function of the chemical structure of the components and the differences in rheological behavior [5,6]. Rheology data indicates that the polypropylene matrix exhibits a greater shear shinning response than the dispersed phase ULDPEs. And sample A has the greatest shear sensitivity possibly due to its greater molecular weight distribution. The viscosity match at processing temperature and shear rates determines the particle size and distribution of the dispersed phases.

The homogeneous metallocene ULDPE was dispersed into approximately 1 μm particles (Fig. 8). The heterogeneous Ziegler–Natta ULDPE was dispersed into about 5 μm particles, (Fig. 9), significantly larger. It is known that the optimum particle size for the best craze initiation efficiency is approximately 0.5–1 μm [7]. This would lead one to suspect that the Ziegler–Natta ULDPE blend would be inferior. Yet the Ziegler–Natta blend exhibited a very low ductile–brittle transition and stronger response below −20°C. This behavior in low temperature performance may again be due to the stronger interfacial bond strength from the heterogeneous ULDPE. This was further supported by the more readily oxidizable and extractable shell around the homogeneous ULDPE particles. Also, the stronger interfacial coupling from the heterogeneous sample would lead to a greater reduction in modulus from a simple two phase coupling consideration.

Up to now, metallocene ULDPE Sample has proven to toughen PP most effectively. Heterogeneous ULDPE, due to its coupling effect, shows excellent toughness only at temperatures below beta relaxation. Because of reduced crystallizable fraction at the rubber phase, Heterogeneous ULDPE impact, above beta relaxation, is much less than metallocene ULDPE toughened PP. Based on this model study, further study of degree of coupling at the phase boundary, crystallizable fraction at the rubber phase, and mod-

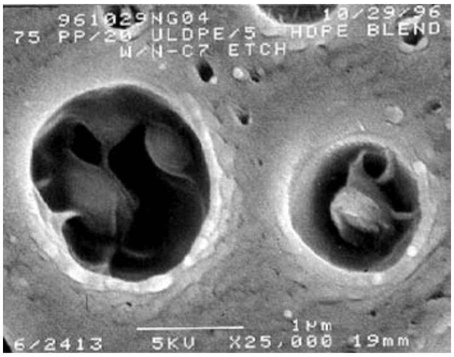

Fig. 10. *n*-Heptane etched morphology of HDPE modified ULDPE/PP blend.

ulus difference between the two phases, is conducted on how the modified ULDPE structures to toughen PP matrix.

The morphology of the polyethylene modified ULDPE is shown in Figs. 10 and 11. When HDPE (A) (0.960 density) was present within the ULDPE in Fig. 10 there was residue in the cavity after the heptane extraction, residue which was connected to the matrix with microfibrils. This did not occur at all with the VLDPE (C) modified material. When VLDPE was present within the ULDPE in Fig. 11 there was virtually nothing remaining in the cavity after the *n*-heptane extraction. These results suggest that the greater the crystallizibility of the polyethylene the greater the coupling between the matrix and the dispersed phase.

4. Summary

Fig. 11. *n*-Heptane etched morphology of VLDPE modified ULDPE/PP blend.

Previously, it was established that the ductile–brittle transition temperature of a polypropylene modified with a homogeneous ULDPE decreases linearly with the density of the ULDPE. This work has shown that the presence of a more crystallizable polyethylene within the ULDPE domains strengthens the interface between the particle and the matrix and reduces the ductile–brittle transition compared with homogeneous modifiers of equal density. The toughening occurs through the development of crystalline microfibrils of polyethylene connecting the ULDPE with the PP matrix. The extent of the coupling increases as the crystallizibility of the polyethylene increases. This work points to the direction in which impact modification can be further optimized.

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