TA Instruments
Thermal Analysis & Rheology

CALORIMETRIC & RHEOLOGY INVESTIGATION OF MODIFIED POLYPROPYLENES

By

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ABSTRACT

Polyolefins are by far the most widely used plastics in the world. The pursuit of better material properties and more intricate part shapes have led to rapid changes in the compositions of these materials. Unfortunately, testing has not kept pace with material changes. For example, materials which may pass simple tests such as melt flow index (MFI) may not perform properly, either in the molding process or as finished parts.

In this study, a series of calorimetric and rheological tests (on both solid materials and melts) are performed on a series of modified polypropylenes and the results of the tests compared against the material modifications. The results indicate that DMA (solids rheology) and DSC are both quite sensitive to the subtle differences in the materials. While similar trends can be observed in the low shear rheological properties of the polymer melts, there is less correlation of these properties to the MFI values than would be anticipated. The thermal and rheological properties observed can be related to material characteristics such as composition, molecular weight, and molecular weight distribution.

EXPERIMENTAL

Four polypropylene homopolymer samples were used in this study. The material specifications supplied by the manufacturer are listed in Table 1. The samples differ mostly by melt flow index, though sample C is synthesized by peroxide degradation of low melt flow material.

Table 1: Material Characteristics

Sample	Polypropylene Material Characteristics
A	Base homopolymer, MFI 1.5-2.2g/10min at 230°C
B	Homopolymer, MFI 8-13g/10min
C	Base homopolymer degraded to MFI 18-26g/10min
D	Homopolymer, MFI 26-34g/10min

Differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and controlled stress rheometry (CSR) experiments were performed on the samples. DSC experiments were performed at heating and cooling rates of 10ºC/min and DMA was performed in the bending mode (~0.2% strain) at 1Hz while heating at 3°C/min. Two sets of CSR experiments were performed using 4 cm, high temperature parallel plates held isothermally at 180ºC. These were oscillatory measurements with a frequency sweep from 0.1 to 100 rad/s at a constant strain amplitude (0.25% strain), and 5 minute creep/recovery experiments over applied shear stresses from 1 Pa to over 3 kPa.

RESULTS AND DISCUSSION

To fully understand the properties and processing of materials, experiments must be performed in the solid and liquid states and during the transitions from solid to liquid and vice-versa. Thermal analysis yields information about properties in the solid state and during transitions, while rheometry completes the picture by describing the properties of the fluid state.

DSC experiments are usually the first thermal analysis technique utilized, due to the ease of use and wealth of information available. Figures 1-3 show the thermal curves for the first and second heats and cooling, respectively, and Table 2 summarizes the analyses. The thermal curves for the first heating show the effects of the original processing on the transitions, while the second heating shows quite different behavior induced by the relatively slow 10°C/min cooling rate (including formation of new crystal states). There is general correlation between the MFI of the polymers and both melting temperature and enthalpy (measured during first heat), though material C (the degraded sample) does not follow the general trend. The cooling curves are more indicative of the inherent material properties than are the heating curves. (1,2) There is even stronger correlation between MFI values and the crystallization temperatures and enthalpies. The shape of the curve for material C (degraded sample) shows that the degradation process creates a material quite different from the native homopolymer.

Figure 1: DSC Thermal Curves for First Heat at 10ºC/min

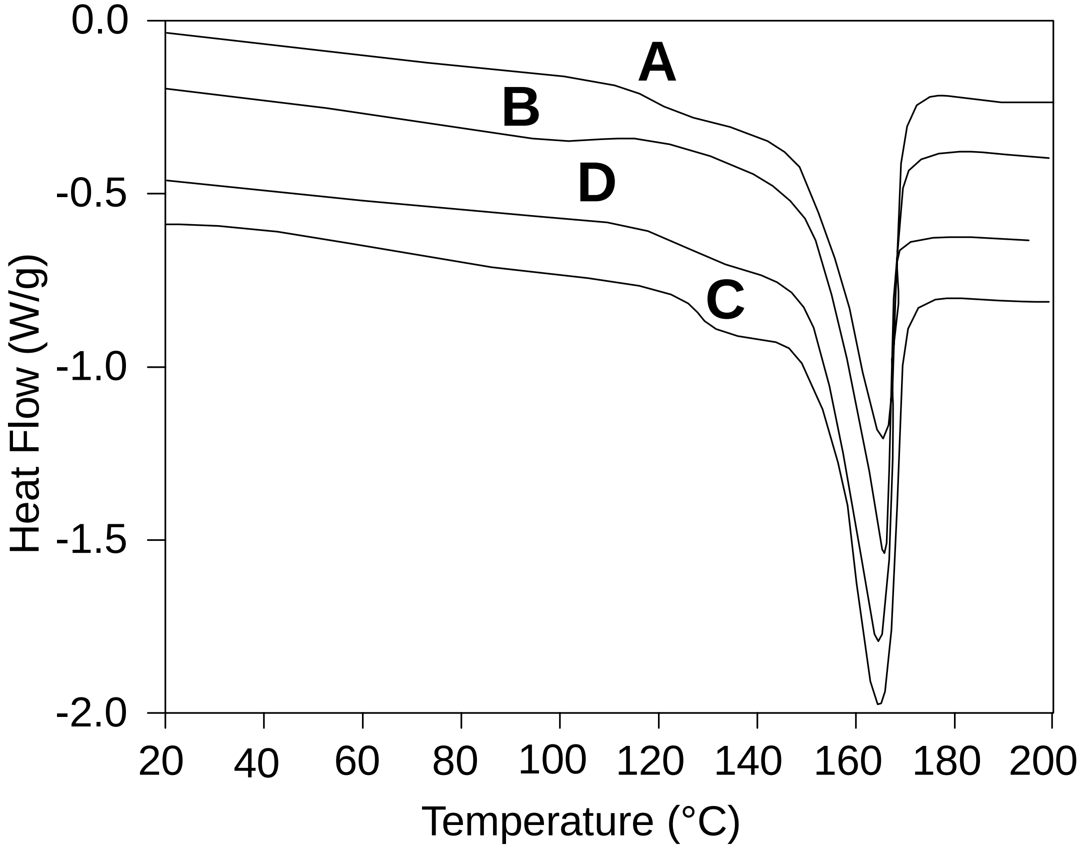


Figure 2: DSC Thermal Curves for Second Heat at 10ºC/min

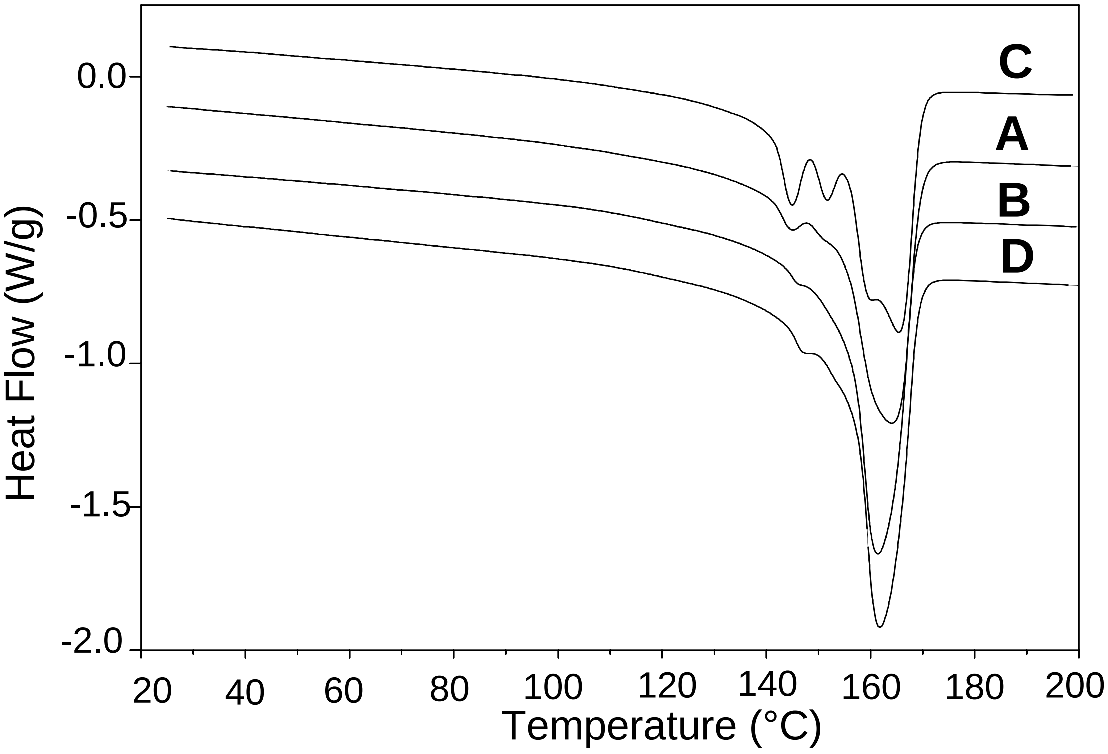


Figure 3: DSC Thermal Curves for Cooling at 10ºC/min

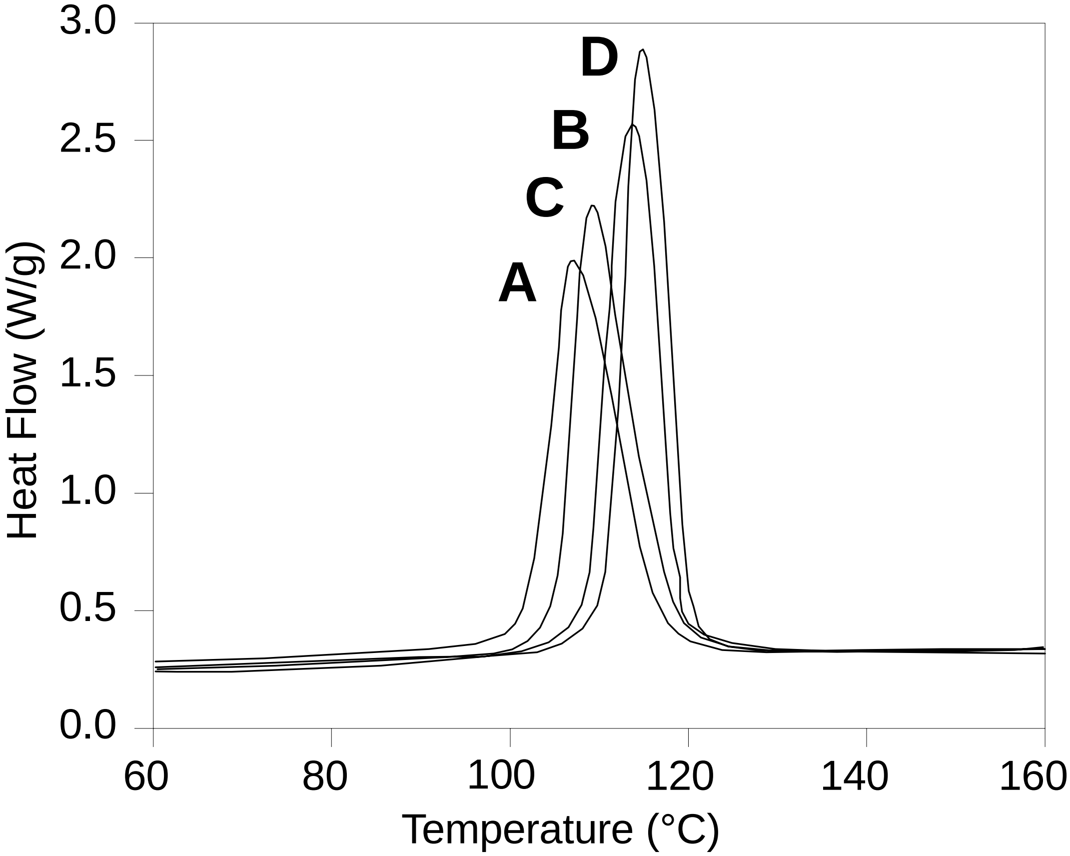


Table 2: Thermal Results

Sample	Tg (°C)	Tan δ @ Tg	Tm (°C)	T_f (°C)	Tc (°C)	ΔHm (J/g)	ΔHc (J/g)
A	10.0	0.072	165.2	116.4	107.6	95.4	89.5
B	10.4	0.061	165.5	119.0	114.2	96.7	92.2
C	10.4	0.063	164.9	117.5	109.7	94.0	90.7
D	8.6	0.053	166.0	119.9	115.6	99.5	93.8

Tg = DMA tan delta peak temp., Tm = DSC melt peak temp., T_f and Tc = DSC crystallization onset and peak temperature respectively, ΔHm = DSC enthalpy of melting, ΔHc = DSC enthalpy of crystallization.

DMA measures the viscoelastic properties of the solid state. DMA is most sensitive to molecular motions in the amorphous portion of the semi-crystalline polypropylene. Figure 4 shows the tan delta (damping) curves. Two transitions are seen: the glass transition around 10ºC, and a transition in the 75-100ºC range associated with motions of the crystallites. The heights of the glass transition peaks of samples A-D decrease roughly in order of increasing MFI, indicating correlation between mobility of the amorphous fraction and molecular weight. Since Tan δ peak heights also decrease roughly in order of the increase in melting and crystallization temperatures, the decreasing mobility is probably caused by decreasing amorphous content. (3)

Figure 4: **Comparison of DMA Tan Delta Curves**

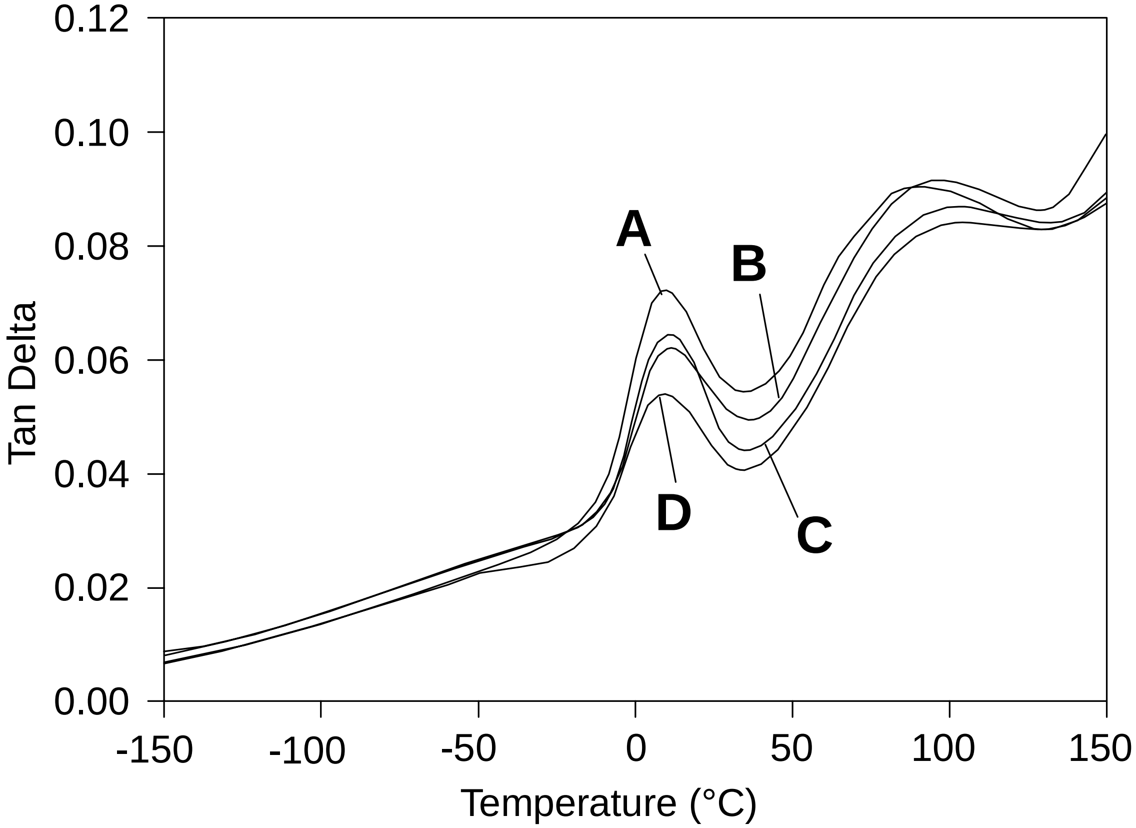
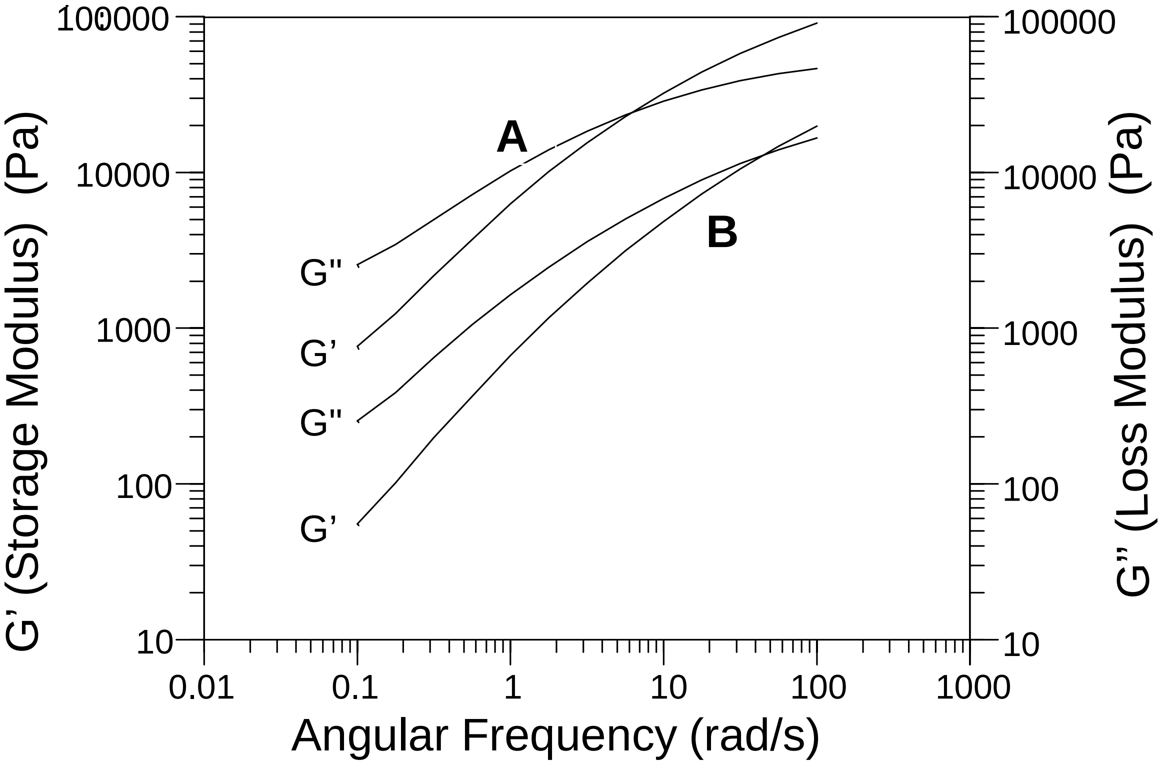


Figure 5: **OSCILLATORY RESULTS**
G' (Storage Modulus) and G'' (Loss Modulus) vs. Angular Frequency



Whereas DMA measures the properties of the solid state, CSR oscillatory frequency sweep experiments give insight into the viscoelastic properties of fluids. Fluid behavior ranges from ideally viscous to highly elastic. For viscoelastic fluids, the relationship between viscous and elastic behavior is frequency dependent. Figure 5 shows a typical analysis of frequency sweep data. Shear storage (elastic) modulus (G’) and shear loss (viscous) modulus (G”) are plotted versus angular frequency (all log scales) for samples A and B. The results of these analyses can be used to rank the molecular weight (MW) and molecular weight distribution (MWD) of linear polymers and can potentially indicate branching or crosslinking in a material.

Two important quantities are derived from the oscillatory data (and tabulated in Table 3): the frequency of crossover (where G’ and G” are equal) and the slopes of the G’ and G” curves in the terminal (low frequency) zone. The crossover frequency is inversely proportional to MW, while relative MWD information can be extracted from the slopes of the G’ and G” curves. (4,5) For monodisperse polymers, the values of the slopes should be 2 and 1 respectively. Deviation from those values (smaller slope values) indicate broadening of the MWD. The results indicate that sample A (MFI 1.5-2.2) has considerably higher molecular weight than sample B (MFI 8-13) as is expected from MFI values. The G’ and G” slopes imply somewhat broad MWD’s that are roughly equivalent for the standard materials. Again the degraded sample is different, most notably showing slightly higher slopes which indicate a slightly more narrow MWD (which is an expected outcome of the degradation process).

Table 3: RHEOLOGICAL RESULTS

Sample	Fc (rad/s)	G' Slope	G" Slope	η_o (Pa•s)	shear thinning (s^{-1})
A	6	0.91	0.60	41800	0.02
B	45	1.07	0.80	3990	0.2
C	89	1.19	0.85	2810	0.3
D	93	1.04	0.79	2960	0.1

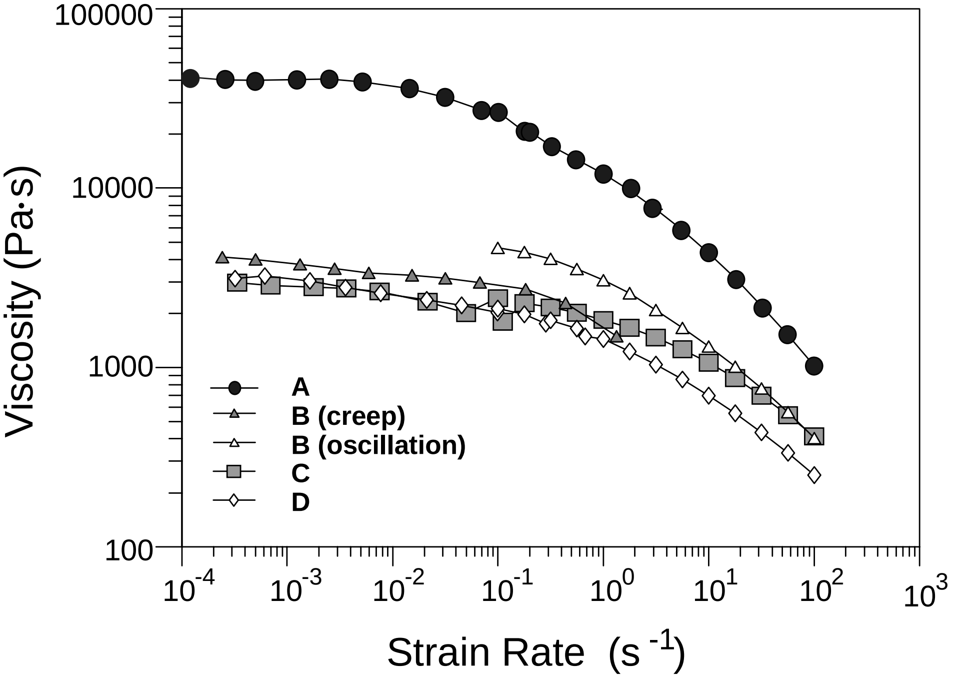
Fc = crossover frequency, η_0 = zero shear viscosity, shear thinning ($\dot{\gamma}$) = Newtonian shear rate limit (s^{-1})

Creep experiments also yield data on the viscoelasticity of fluids. Ideal viscous fluids deform (flow) linearly under an applied stress (retardation) and stop moving when stress is removed (relaxation). Materials with elasticity show curvature in the compliance (strain/stress) versus time curves during both retardation and relaxation (creep and recovery). Using creep experiments viscosity can be measured under very low shear rates ($<10^{-4}$ s^{-1}) up to moderate shear rates (~10 s^{-1}). Viscosity is calculated from slope of the retardation compliance curve during the steady motion. These values are identical to those measured in flow (constant rotation) experiments..

Unfortunately, polymer melt viscosity cannot be measured for shear rates over 10 s^{-1} with parallel plates (even in the flow mode) because at these rates “shear fracture” or cavitation at the edge of the sample gap reduces the shearing area (resulting in anomalous viscosities). Cox-Merz modeling can extend the range of shear rates measurable with parallel plate rheometers and often can serve as an alternative to capillary rheometry.

The Cox-Merz rule is an empirical observation which equates complex viscosity calculated from oscillatory measurements to viscosity that would be measured in shear flow; angular frequency is taken as the shear rate. Through this method the effective strain rate can be extended to over 100 s^{-1} as frequencies in excess of 100 rad/s are easily measured. Figure 6 shows the viscosity versus shear rate curves. These curves include data from both the creep (low shear rate) and the Cox-Merz modeling (oscillatory experiments). A high degree of overlap of the data sets indicates the material follows the Cox-Merz behavior, while poor overlap must be more cautiously interpreted. In this study Samples A and D follow the rule quite well, while sample C is borderline and sample B does not follow the Cox-Merz model. The viscosity values and shapes of the Cox-Merz flow curves can also yield information about molecular weight and MWD. Zero shear viscosity (η_o), for example, can be correlated to molecular weight, even with materials which do not follow the Cox-Merz rule particularly well. The shape of the curves, on the other hand, can be indicative of MWD (4), though caution must be used with samples B and C. In Table 3 the rate at which the samples shear thin (deviate from Newtonian behavior) is used as a crude measure of curve shape. Sample A has a zero-shear viscosity an

Figure 6: Flow Curves Generated Using Cox-Merz Rule



order of magnitude greater than the other materials, as is expected from the relative MFI values. MWD analysis, on the other hand, is complicated by the wide differences in molecular weight between Sample A and the other materials, and also by the poor model fit for two of the samples. Among the three lower molecular weight materials, Sample C, the degraded sample, has an extended Newtonian plateau. This is further confirmation that this material has a narrower MWD.

CONCLUSION

The three analytical techniques of this study convincingly identify the subtle differences among the modified polypropylenes. Two conclusions are drawn from this work: First, as molecular weight of the homopolymer decreases, the amorphous fraction increases, affecting both the liquid and solid state properties. Second, the degradation process alters the material composition (particularly molecular weight distribution) in ways which cannot be detected by melt flow indexing.

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