Dual Phase, Co-Continuous Morphology from Mixtures of Recycled Polystyrene/Curbside Tailings Materials

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Introduction

Virtually all studies of polymer mixtures made by the processing of virgin polyethylene and polystyrene show that the blends possess poor mechanical properties when compared to the individual components. This is generally attributed to the lack of good interfacial adhesion between the blend components with the result that an applied stress cannot be efficiently transferred between the phases.[1,2]

Recent research, however, has shown that it is possible to fabricate objects which possess strength and utility by the mixing of certain recycled polymeric materials previously thought to be incompatible.[3] By the blending together of polystyrene with the "mixed plastics" component of the recycling stream it has been found to be possible to produce materials which behave mechanically and appear morphologically like fiber reinforced composites. Moreover, there exists a unique composition range where the mechanical properties are optimal, and the morphology as determined by scanning electron microscopy is interlocked and co-continuous, forming a three dimensional interpenetrating network.

A simple, semi-empirical relationship, which relates the composition region where dual phase co-continuity can be expected to occur to the viscosity ratio and volume ratio of the blend components has been evaluated with respect to these systems and good agreement has been found.

Dual Phase Co-Continuity

If two polymers are processed under the proper conditions of composition and viscosity, it may be possible to cause the two components to form continuous interlocking phases regardless of miscibility.[4] In this type of dual phase co- continuous structure, the two phases intertwine in such away that both phases remain continuous throughout the material. This morphology is analogous to that of a sponge soaked in water where both sponge and water form continuous systems.[5] The resulting microstructure in this type of system enables each phase to share in the load bearing capability of the material. This reduces somewhat the need for efficient stress transfer between the phases required for dispersed phase blends.[6] This type of morphology has been observed in many polymer blend systems under the proper conditions.[7]

Based on experimental observations that the phase with the lower viscosity or the higher volume fraction tended to form the continuous phase, Jordhamo, Manson, and Sperling[8] suggested a semi-empirical expression relating the region where dual phase co-continuity can be expected to occur to the viscosity ratio and the volume ratio of the blend components. Their paper asserts that the condition for dual phase co-continuity is the application of shear to a polymer blend system close to the phase inversion region. The model predicts that phase inversion should occur when the viscosity ratio and the volume ratio are about equal, i.e. when (1)

$$\frac{\eta_1}{\eta_2} = \frac{\phi_1}{\phi_2}$$

η_i is the viscosity of phase i and ϕ_i is the volume fraction of phase i.

Figure 1 is an idealized plot of viscosity ratio versus composition ratio. The dashed line in this figure represents the equality in Equation 1 and indicates the midpoint of the phase inversion region. Dual phase co-continuity can be expected in a region of viscosity ratio/composition ratio space around the phase inversion line. This region is arbitrarily indicated in Figure 1 by the solid lines enclosing the phase inversion line. The exact width and shape of this region will depend upon the system under consideration and will have to be determined experimentally. If a system has properties such that it lies below the dual phase region, then phase 1 will be the continuous phase and vice versa. In general, for a fixed set of processing conditions, the viscosity ratio will be a constant and phase continuity is most easily obtained by altering the volume fraction of the components. It should also be possible to predict the composition ratio required if the viscosities of the components are known.

Materials And Processing

The base material used throughout this study is known as New Jersey Curbside Tailings (NJCT). NJCT is defined as the rigid plastic containers (mainly bottles) which remain in the post-consumer plastic waste stream after the more valuable PET soda bottles and the natural HDPE milk and water containers are mined out. These materials are obtained from recycling programs in New Jersey which request only PET soda and natural HDPE from their households.

The post-consumer plastics employed in this study which were collected from New Jersey communities, are brought to a pilot plant facility located at Rutgers University in Piscataway, New Jersey, where the PET soda and natural HDPE are mined from the waste stream and processed. The remaining materials, the NJCT, are then shredded and granulated into approximately 3/8-inch flakes without any other separations having been performed. The base NJCT are therefore an unwashed, unseparated mixture of post-consumer waste plastics. Included in the NJCT are any materials normally found on plastic containers such as metal caps or closures, paper labels, and product residues.

The polymeric composition of NJCT was estimated by analyzing a representative batch of containers delivered to the Center for Plastics Recycling Research (CPRR) at Rutgers University. NJCT are primarily polyolefinic in nature, containing approximately 80% HDPE (non-milk and non-water jug), 4% low-density polyethylene (LDPE) and 4% polypropylene. Other polymers included in NJCT are polystyrene (3%), polyvinyl chloride (4%) and PET (5%). These estimates were confirmed by an independent study carried out at Rensselaer Polytechnic Institute utilizing a selective dissolution technique.[9] The results are presented in Table 1. The exact polymeric composition of NJCT could be expected to vary slightly depending upon time of year and geographic location of the collection program.

Two basic forms of NJCT are utilized in this study. The first being a "bulk" form of NJCT as described above. From these materials, large cross- section, "lumber like" profiles which are approximately eight feet long are extruded from the raw NJCT utilizing an ET/1 extrusion molding machine.[10] The second form of NJCT used in this study is an upgraded form in which the raw NJCT were run through the resin recovery pilot plant facility at Rutgers University's Center for Plastic Recycling Research and then melt-filtered and repelletized utilizing a Welding Engineers counter rotating, non- intermeshing twin screw extruder. The result of this process is a clean, mainly polyolefinic mixture (NJCT as above minus PVC, PS, and PET) of plastic material which can be processed on conventional equipment. This material is referred to as NJCT "Floats".

The NJCT, being mainly polyolefins, produces products, which are relatively flexible and have a low modulus. In order to improve upon the mechanical properties of these materials, polystyrene was blended with both forms of NJCT. Two different polystyrene materials were used to mix with the "raw" NJCT materials. The first polystyrene, which was blended with the NJCT was obtained from Mobil Chemical Company's expanded polystyrene regrind operation. This polystyrene will be referred to as "MPS". This particular source of polystyrene was chosen to represent a densified expanded polystyrene which was processed with care to avoid degradation in the densification stage. This post-industrial polystyrene was plant scrap, which was initially used to make foamed products and was densified and pelletized prior to being mixed with the NJCT. The second polystyrene utilized for this research was obtained from Plastics Again Inc., one of the pioneers in the recovery of post-consumer polystyrene, which includes foamed products. This polystyrene will be referred to as "PPS". The Plastics Again polystyrene was chosen to represent a typical, post-consumer, mixed polystyrene recycling feedstock. Only the MPS polystyrene was blended with the NJCT Floats.

The specific polystyrene/NJCT compositions (percent by weight), which were fabricated for these experiments are as follows: 0/100, 10/90, 20/80, 30/70, 35/65, 40/60 and 50/50 for the MPS. The formulations for the PPS are the same with the inclusion of a 45/55 mixture.

These mixtures of plastics were blended in 400-500 pound batches and physically premixed in the feed hoppers of the ET/1 for the raw NJCT. To produce samples from the NJCT Floats, the materials were premixed and injection molded into ASTM type "dogbones" utilizing a Newbury 30 ton injection molding machine.

Mechanical Testing

All mechanical tests were performed on a MTS model 810 universal tester. Compressive measurements were performed on the ET/1 samples while tensile measurements were performed on the injection molded samples. Actuator rate for both tensile and compressive measurements was 0.254 cm/minute (.1 inch/minute).

Scanning Electron Microscopy

Scanning electron microscopy (SEM) was performed on representative samples of the NJCT/PS materials. The samples were notched and then fractured at the temperature of liquid nitrogen. The polystyrene phase was extracted by solvent leaching the samples in toluene.

Samples were then mounted on aluminum SEM studs and gold coated. The SEM micrographs were taken on a International Scientific Instruments 151-40 microscope set to 15 Kev.

Rheological Measurements

Viscosity measurements were performed on a Rheometrics Inc. RMS-800 mechanical spectrometer at the Rheometrics facility in Piscataway, NJ. The spectrometer was configured in the parallel plate mode. Viscosity as a function of frequency was determined at 220 °C (the processing temperature used in the ET/1) for all three materials as well as viscosity as a function of temperature. Prior to the viscosity measurements, it was determined that strain was in the linear region.

Results

The addition of PS into the NJCT materials improves the modulus, yield stress, and the ultimate strength. Figures 2a and 2b are plots of the modulus and yield stress versus composition for the three systems tested. Up to the 30% PS composition range, all materials tested show a "law of mixtures" (additive) type of response in which the property in question is some weighted average of the component properties. In the 30 to 40 percent PS composition range however, the three systems show a positive deviation from the additive response and a relative maximum in the properties.

SEM micrographs indicate that as the polystyrene is incorporated into the NJCT materials that it is drawn into long rods and plates in the direction of flow (Figure 3). The material may therefore be thought of as being similar to a fibrous composite. As the law of mixtures is considered the upper bound for the mechanical properties of a fiber composite, it is not surprising that these materials follow a similar relationship.

In the composition range where the mechanical properties are optimal, SEM micrographs indicate that the polystyrene and NJCT (mainly polyethylene) form co-continuous phases which are intermingled or intertwined in such a fashion as to produce an interpenetrating or interlocking of the phases (Figure 4).

Prediction Of Dual Phase Composition Region

If one desires to study the co-continuous structure in mixtures of recycled or virgin polymers, it would be valuable to be able to utilize the relationship (discussed earlier) proposed by Jordhamo, Manson, and Sperling to estimate the composition range where this could be expected to occur. If this relationship can be shown to apply to systems such as those studied in this work, then it may be possible to save time and effort in the study of new systems by being able to focus in on the composition range of interest. In order to determine if this is a feasible approach to take in the future, this relationship was applied to the three systems reported on in this study.

To be able to apply this relationship to a polymer system, the viscosity and the volume fraction of each component at the particular processing temperature must be known. For the analysis of the materials used in this study, all samples are considered to consist of two components, a polyolefinic component and a polystyrene component. The nature of the different polymers, which are inherently contained in the NJCT floats is going to be ignored and this material will be considered to be a single material. This simplifies the analysis and allows the "bulk" viscosity determined for the floats to be used in the calculations instead of worrying about the individual viscosities of the components.

In order to estimate the volume fraction of each material contained in the various mixtures, only the polyolefinic portion of the NJCT was considered. This was estimated to be 90% of the bulk NJCT material. To convert from weight percent of the mixtures at room temperature to volume percent at the processing temperature, the densities of the materials at the processing temperature must be known.

The densities of all three materials were determined utilizing a Kayeness brand extrusion plastometer with the barrel temperature set at 220 °C. It is known that one inch of piston travel in the extrusion plastometer displaces 1.804 cubic centimeters of volume. The material extruded after one inch piston travel was collected for all samples and weighed. From this information the densities of the materials was determined. The density of the NJCT floats was found to be .75 gms/cm3 at 220 °C and the densities of the MPS and the PPS at 220 °C were found to be .95 and .94 gms/cm3 respectively.

Once the densities are determined, the volume percent of each material at the processing temperature may be determined from

$$VOL\%_{PS} = \frac{V_{PS}}{V_{PS} + V_{NJCT}} = \frac{M_{PS} / \rho_{PS}}{M_{PS} / \rho_{PS} + M_{NJCT} / \rho_{NJCT}} x100 \qquad (2)$$

where M is the mass of the material and p is the density at the processing temperature.

In order to estimate the viscosities of the materials under the processing conditions, simple model flow calculations were performed using the particular machine geometries to obtain an estimate of the shear rates involved. Once the shear rate is known, it is possible to determine the angular frequency required in a parallel plate rheometer to obtain the particular rate. The viscosity may then be determined from an experimental plot of viscosity versus shear rate (at the processing temperature) for the various materials.

The results for the estimated volume percents of the different compositions as well as the volume ratios and viscosity ratios are presented in Table 2.

Figure 5 shows the plots of viscosity ratio versus composition ratio for the three systems studied. As the viscosity ratio for each system is assumed to be constant throughout the composition range, the plot for each system is therefore parallel to the composition ratio axis of the graph. The darkened symbols represent compositions for which SEM micrographs indicate a dual phase co-continuous morphology is present. The dashed lines in the figure indicate the dual phase region. The width of the dual phase region was determined experimentally from the known dual phase compositions. The shape of the region was chosen arbitrarily since more experiments would have to be carried out in order to define the actual shape of the region. Sample compositions, which plot above this region would be expected to have the NJCT as the continuous phase while compositions which plot below this region would be expected to have polystyrene as the continuous phase.

Conclusions

The data presented here tends to confirm the usefulness of utilizing the semi-empirical relationship presented in Equation I, and applying it to mixtures of recycled plastics to estimate the region where dual phase co-continuity may be expected. This may prove to be a useful tool in future work on the mixing of waste plastics to produce "new" materials formulations for processing into finished products. As the dual phase co-continuous morphology corresponds to compositions in which the mechanical properties are optimal, it will be of use to be able to predict where this effect will occur. All that will be required is knowledge of the different materials viscosity at the particular processing conditions.

A note of caution is in order for attempting to utilize the co-continuous phase structure for producing finished goods. As mentioned in[11], this morphology can be expected to be unstable to processing at strain rates, which are different from those at which the co-continuous structure was produced. For example, if pellets were produced by an extrusion process under the conditions necessary to form a co-continuous or interpenetrating polymer blend and then injection molded into the finished article at a different strain rate, there is no guarantee that the structure will be maintained. This problem will be most severe when the viscosity of one or both of the components in the blend has a strong dependence on the shear rate.

Acknowledgments

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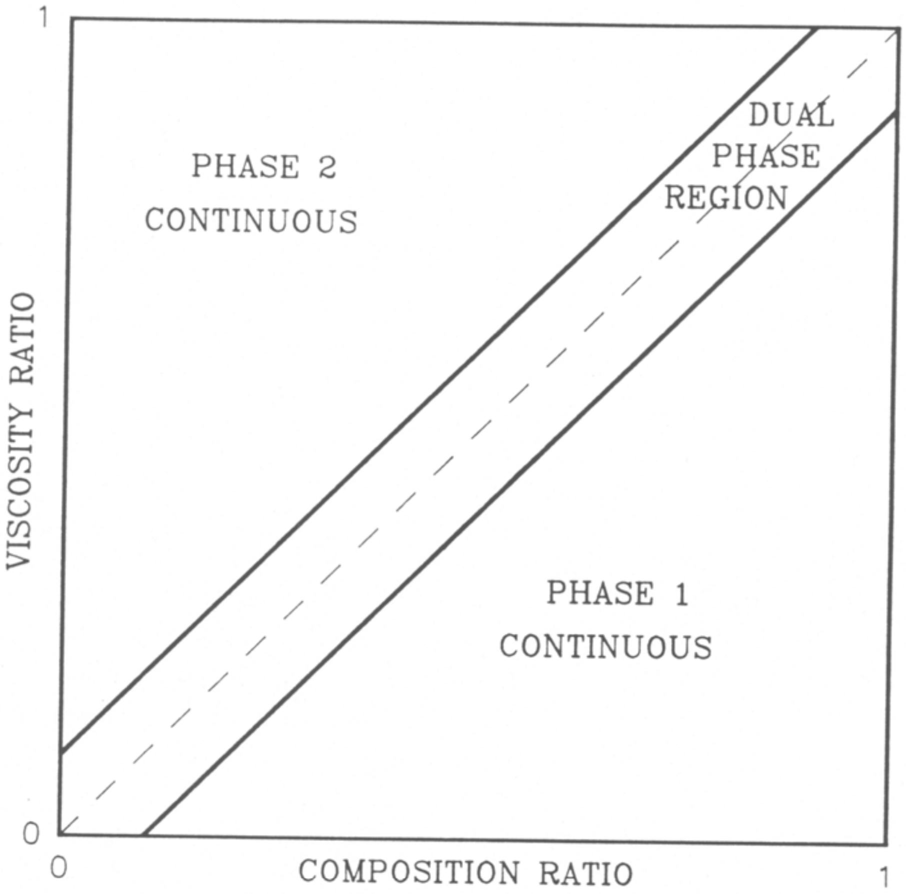

FIGURE 1: Idealized Viscosity/Composition Space

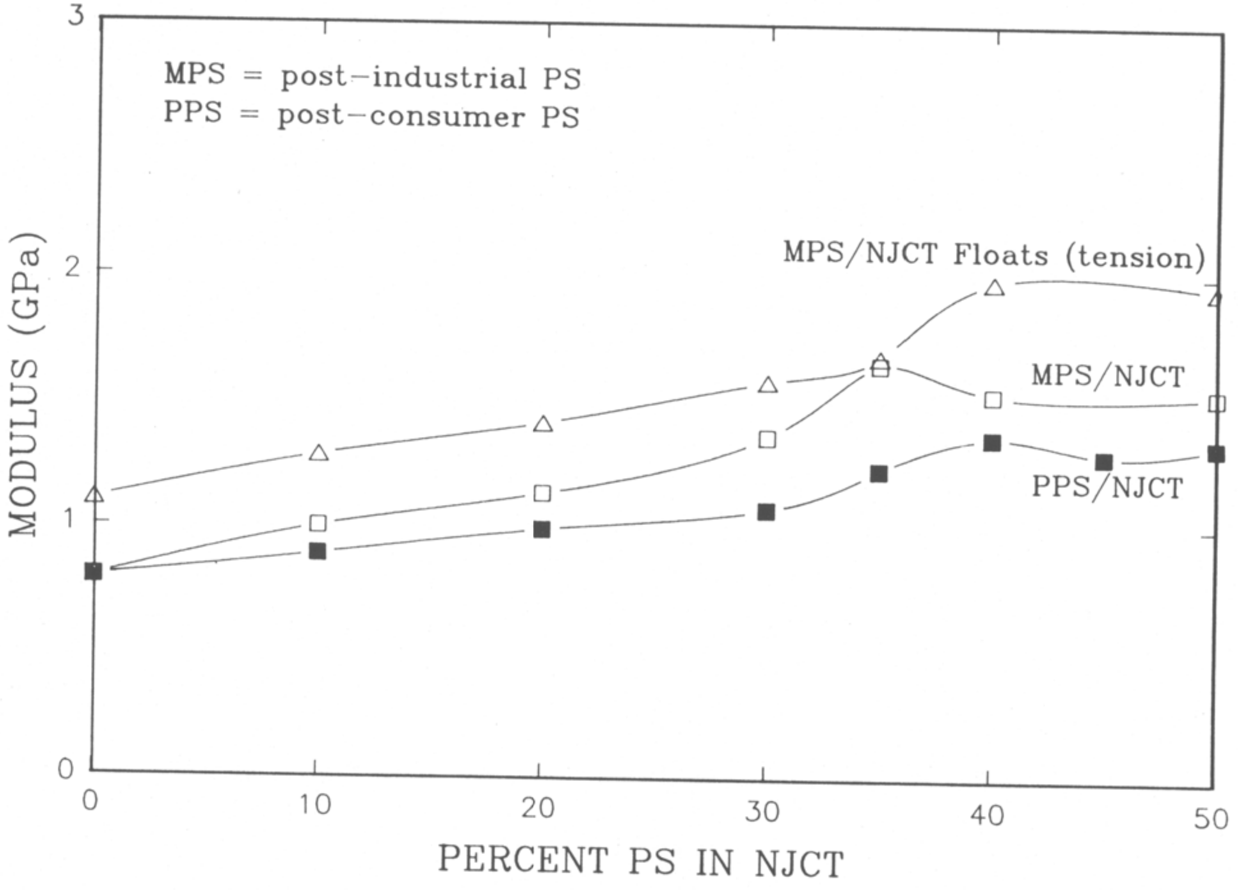

Figure 2a: Modulus versus Composition for PS/NJCT

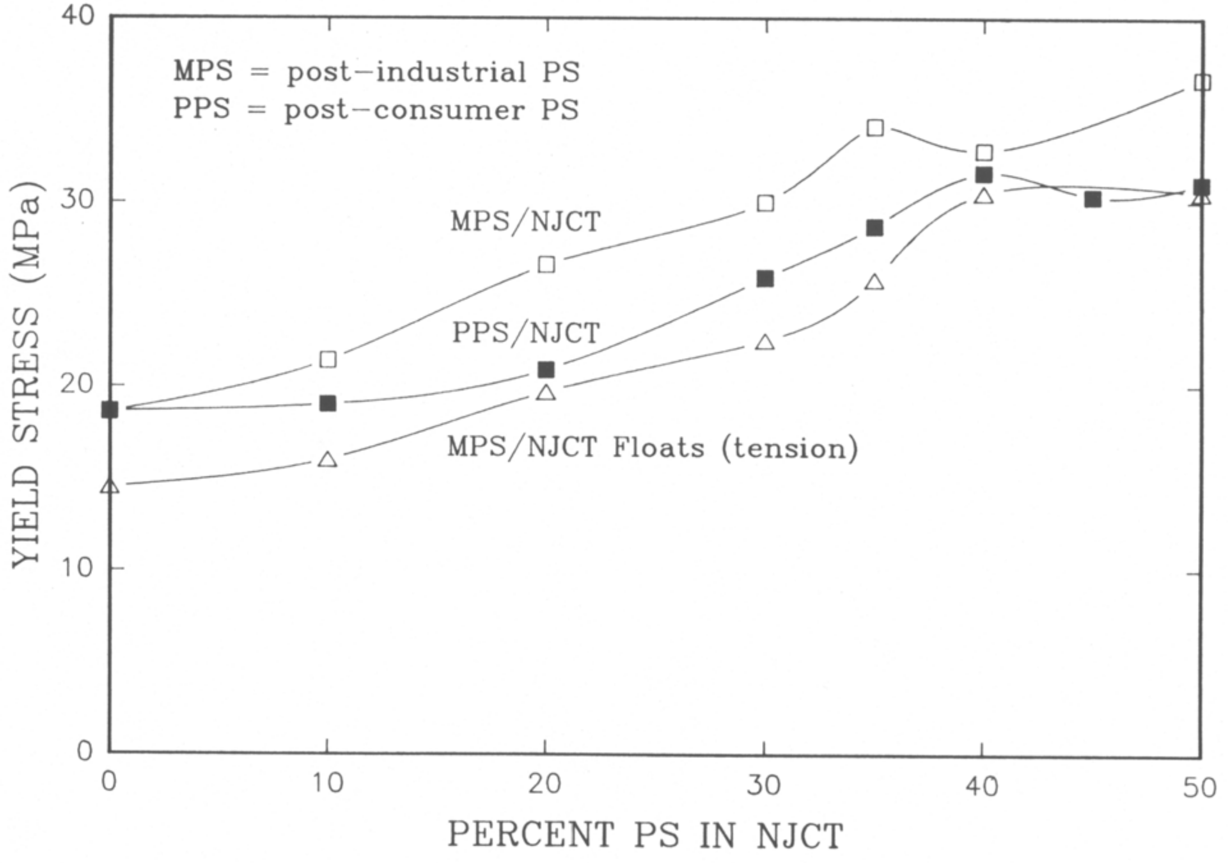

Figure 2b: Yield Stress versus Composition for PS/NJCT

Figure 3: SEM Micrograph of 35/65 MPS/NJCT Floats Parallel to Flow Direction.

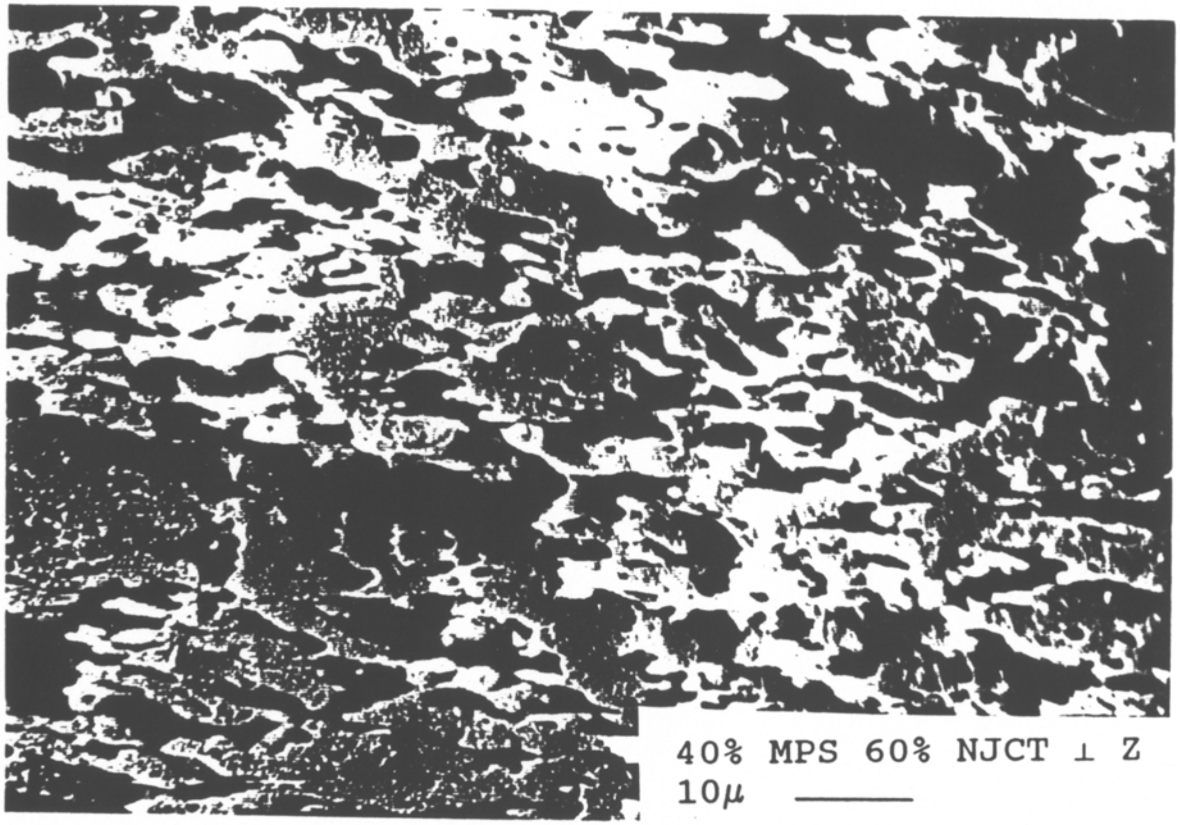

Figure 4: SEM Micrograph of 40/60 MPS/NJCT Floats Perpendicular to Flow Direction.

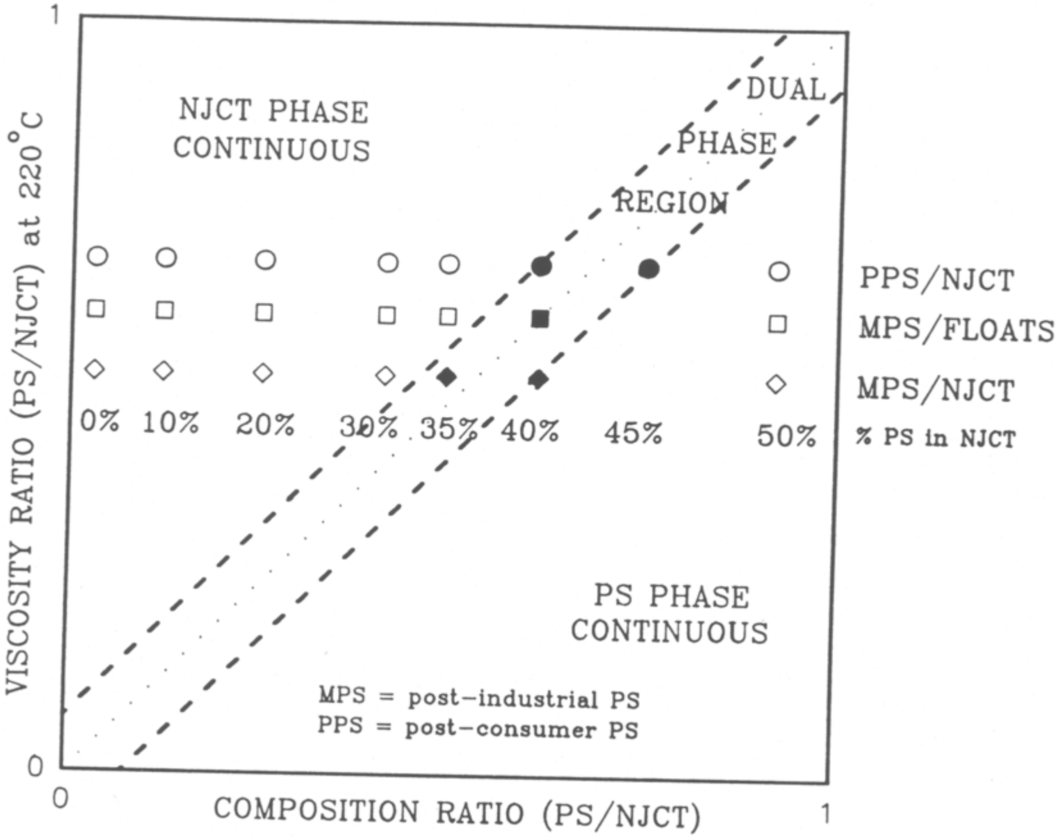

Figure 5: Plot of Viscosity Ratio Versus Composition Ratio for the Various PS/NJCT Materials Indicating the Dual Phase Compositions

POLYMER	CPRR ESTIMATES	RESULTS FROM REFERENCE 9
HDPE (non-milk jug)	80%	75.3%
LDPE	4%	3.5%
POLYPROPYLENE	4%	8.1%
POLYSTYRENE	3%	3.3%
PVC	4%	3.4%
PET (non-soda bottle) and INSOLUBLES	5%	6.4%

Table 1: Polymers Found in NJCT

SAMPLE DESIGNATION	ESTIMATED VOLUME PERCENT PS/CT FLOATS AT 220°C	$\frac{\phi_{PS}}{\phi_{NJCT}}$
100% NJCT	2.6/97.4	.03
10% PS 90% NJCT	11/89	.12
20% PS 80% NJCT	20/80	.25
30% PS 70% NJCT	29/71	.41
35% PS 65% NJCT	33/67	.49
40% PS 60% NJCT	38/62	.61
45% PS 55% NJCT	43/57	.75
50% PS 50% NJCT	48/52	.92

$$\frac{\eta_{MPS}}{\eta_{NJCT}}(220°C) = .53 \qquad \frac{\eta_{MPS}}{\eta_{NJCT}}(212°C) = .61 \qquad \frac{\eta_{PPS}}{\eta_{NJCT}}(220°C) = .68$$

Table 2: Volume and Viscosity Ratios for PS/NJCT Floats at 220°C

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