

# Peroxide Modification of a Multicomponent Polymer Blend with Potential Applications in Recycling\*

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## SYNOPSIS

A mixture of seven immiscible "virgin" plastics, namely low and high density polyethylene (LDPE and HDPE), polypropylene (PP), polyvinyl chloride (PVC), crystal and high impact polystyrene (PS and HIPS), and polyethylene terephthalate (PET), in proportions representative of those currently found in post-consumer plastics containers, was compounded in a corotating twin-screw extruder. The mechanical properties of the blend were improved through the addition of relatively high concentrations of a dialkyl peroxide which was also found to drastically affect the blend morphology. The results are interpreted in terms of improved dispersive mixing favored by the similarity in the rheological behavior of the modified blend components, improved physical properties of certain blend components upon peroxide modification, and, possibly, enhanced interfacial adhesion. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Recycling of commingled plastic wastes is often limited to the production of low value or specialized products (e.g., timber replacement). This can be related to the immiscibility and incompatibility of the majority of the polymers found in those wastes. The mechanical properties of immiscible blends are known to depend on blend morphology and composition (including the presence of fillers and fibers), the properties of their components, and the interfacial adhesion at phase boundaries. As a result, the production of value-added compounds from recycled commingled plastic wastes could be accomplished through control of at least one of the above factors.

Although chemical modification of mixed plastic wastes has not been investigated until recently, it seems already to offer some opportunities. Fellahi

et al.<sup>1</sup> have improved the stress at break and the impact strength of mixed plastics waste by simply processing it in the presence of a dialkyl peroxide. These improvements could be due to the formation, by recombination of macroradicals, of copolymers acting as compatibilizing agents which reduce the interfacial adhesion at phase boundaries. But they could also be related to the modified rheological behavior of the components in the peroxide-reacted blend. As reported by Yu et al.,<sup>2,3</sup> a peroxide can alter the blend morphology of a virgin LDPE/PP blend in a beneficial manner by minimizing the rheological disparity of the blend components and enhancing dispersive mixing. More experimental work seems necessary to clarify the exact effect of peroxides on mixed-waste plastics. Such information could be useful in other investigations where a peroxide is used in the presence of a monomer in order to functionalize polyolefin backbones,<sup>4-7</sup> and, hence, improve interfacial adhesion.

In this article, a mixture of seven virgin plastics, in proportions representative of those currently found in post-consumer plastic containers collected in France, are modified through the incorporation of a dialkyl peroxide. Special attention is paid to the blend morphology and mechanical properties, before and after modification, as related to changes in the

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rheological behavior of the individual blend components through the action of peroxide. It should be realized that the multicomponent blend used in this work is a model system which includes limitations as a realistic representation of materials collected as waste. Typical commingled resin waste streams may contain, in addition to impurities, a variety of process stabilizers and anti-aging additives (often depleted); in such systems, one would expect differences in the reactivity of the peroxide.

## EXPERIMENTAL

### Materials

The components of the blend and its composition are listed in Table I. Each resin has been chosen so that its melt flow rate (MFR) and/or grade match those encountered in collected post-consumer rigid containers. A PVC resin was preferred to a PVC compound, in order to limit interfering reactions from potentially reactive additives. The only extra PVC additive used was the heat stabilizer butyltin mercaptide (T137, Atochem North America) at 1.5 wt % as recommended by the PVC manufacturer. The selected peroxide was a solid version of 2,5-dimethyl-2,5-di(*t*-butylperoxy)hexane (Lupersol 101XL, 45–48% active, Atochem North America); it is widely used in reactive extrusion,<sup>5</sup> due to its thermal stability, and its ability to generate sufficiently reactive radicals to complete the process within the short residence time allowed in an extruder. Manufacturer's reported half-lives range from 68 s at 180°C to only 2.4 s at 220°C. In the following text, peroxide concentrations always refer to weight percentages of the free-flowing powder Lupersol 101XL and not of active peroxide.

### Processing

Prior to extrusion, all blend components, including the peroxide, were always first premixed in a batch mixer. All compounding and reactive modification operations related to the blend of the seven plastics were conducted in a 30 mm fully intermeshing corotating twin-screw extruder (TSE) (ZSK-30, Werner & Pfeleiderer) with a screw configuration designed for high dispersive mixing. The extrudates were cooled in a water trough and then pelletized. In spite of the multistaging capabilities of the twin-screw extruder, compounding and reactive extrusion operations were run separately to ensure a high efficiency for each step.

First, PVC as a thermally sensitive thermoplastic was compounded separately with 1.5 wt % butyltin mercaptide. In spite of this stabilization, PVC was not expected to survive typical PET processing temperatures (appr. 265–285°C) when processed together with PET. Although recycled household packaging polyolefin-based chips containing 5% PET may be processed in industrial-scale extruders at temperatures as low as 200°C, it was found that the virgin PET pellets used in this study could not be processed at 200°C in the smaller diameter 30mm TSE. As a result, predried PET pellets were first compounded at 265°C with HDPE at a 1 : 3 weight ratio in order to obtain a dispersed phase of PET which could then be processed at a lower temperature. Thus the blend of the seven plastics, identified as B7, was prepared by compounding in the TSE a premix of a blend of HDPE/PET, the stabilized PVC, LDPE, PS, HIPS, and PP in appropriate ratios. A screw speed of 150 rpm, a feed rate of 120 g/min and a temperature profile of 130–170°C were used. During this step, a melt temperature of 210°C at the die was observed.

**Table I** Materials Used in the Seven-component Plastics Blend

	Grade	Manufacturer	Wt % in the Blend	Melt Flow Rate*
LDPE	PE 1412	Chevron Chemical	45	35.0
HDPE	PAXON AD60-007	Allied Signal	15	0.7
PVC	PVC-1070	Georgia Gulf	15	0.71**
PS	Amoco G1	Amoco	7.5	8.5
HIPS	Styron (r) 484	Dow Chemical	7.5	3.0
PP	Pro-fax 7523	Himont	5	4.0
PET	Kodapak 9921W	Eastman Kodak	5	1.2

\* Manufacturers data obtained from Plaspec<sup>®</sup> data base.

\*\* Inherent viscosity of PVC.

After drying, the pelletized B7 was extruded at various temperature profiles in the presence of different wt. percentages of peroxide: 0% as reference, 0.5%, 1%, 1.5%, and 2%. The residence time was estimated to be around 2 min.

In order to evaluate the effect of peroxide on each individual resin, 1% of peroxide was added to each in a 15 mm fully intermeshing co-rotating TSE (AVP, chemical machinery). For the majority of the polymers, the set conditions were chosen in order to have a melt temperature around 200°C and a residence time of 2 min. HDPE was run at a lower temperature and within a shorter residence time in order to prevent extensive crosslinking which would generate an unprocessable material. In this particular case, the reaction was completed during subsequent sample preparation by compression molding for rheological characterization. PET was run, of course, above its melting point.

B7 test specimens were prepared from the pre-dried pellets in a 40-ton Van Dorn injection molding machine equipped with a two-cavity ASTM test specimen mold, at a 110–160°C barrel temperature profile, 2.2 MPa injection pressure, and 25 s overall cycle. Mold temperature was set at 38°C.

### Characterization

Injection molded samples were tested for tensile properties and Izod impact strength according to ASTM standards.

For morphological characterization, injection-molded parts were first cooled in liquid nitrogen and then immediately microtome-sectioned. Non-polyolefinic phases were extracted from the sectioned surfaces by using room temperature solvents: benzene for PS and HIPS, tetrahydrofuran for PVC, and a 70% hexafluoroisopropanol/30% dichloromethane mixture for PET. Extracted and non-extracted surfaces were then sputtered with gold-palladium before examination by scanning electron microscopy (SEM).

A Rheometrics mechanical spectrometer (RMS-800) in a 25-mm-diameter parallel plate arrangement at 190°C was used in order to study the rheological behavior of the blends and their components.

## RESULTS AND DISCUSSION

### Processing

In preliminary experiments, the reactive extrusion process parameters were the same as those selected

for the compounding of the seven plastics in the absence of peroxide. But the melt temperature and the amount of peroxide drastically influenced the appearance of the extrudate in the following manner: at 215°C without peroxide, white; at 225°C with 1% peroxide, blue-black; at 230°C with 2% peroxide, green and porous; at 235°C with 3% peroxide, yellow and porous.

Since the change in color was presumably due to degradation, in order to obtain white material the temperature profile along the barrel was suitably modified (110–160°C) so that, when possible, the melt temperature was kept below 215°C. With this new profile, the melt temperature was 198°C with 0.5% peroxide, 200°C with 1%, 210°C with 1.5%, and 220°C with 2%. With 1.5% peroxide the extrudate was still white but included a few green spots; it became green with 2% peroxide. The latter two extrudates were very brittle, and on-line pelletizing was impossible.

The more peroxide was added, the yellower were the injection molded samples; in fact, samples reacted with 2% peroxide were definitely yellow. Yellowing was attributed to the degradation of the PVC phase, since samples with 1% peroxide became white after extraction with tetrahydrofuran.

### Mechanical Properties and Morphology

Mechanical properties of injection molded B7 samples are summarized in Table II. With respect to Izod impact strength, higher values were always observed for unnotched samples versus the notched ones. SEM micrographs, parallel and perpendicular to flow, revealed morphological differences between the core and skin regions of those injection molded samples; for example, dispersed phase particles were spherical in the core (Fig. 3), whereas some were elongated in the flow direction in the skin (Fig. 1). Those elongated particles could behave like reinforcing fibers, although of low aspect ratio. Skin/core structures having different morphology and/or composition have been suggested as possible reasons for differences between notched and unnotched impact strength of injection molded commingled post-consumer plastics.<sup>13,14</sup> In these systems the choice of molding conditions and the presence of compatibilizers seem to promote skin/core morphologies with different domain size in the core region.

Almost no change was observed in the notched impact strength upon the addition of the peroxide; this is not surprising, since only small-scale yielding would be encountered, leading to values one might

**Table II** Effect of Peroxide on the Mechanical Properties of B7

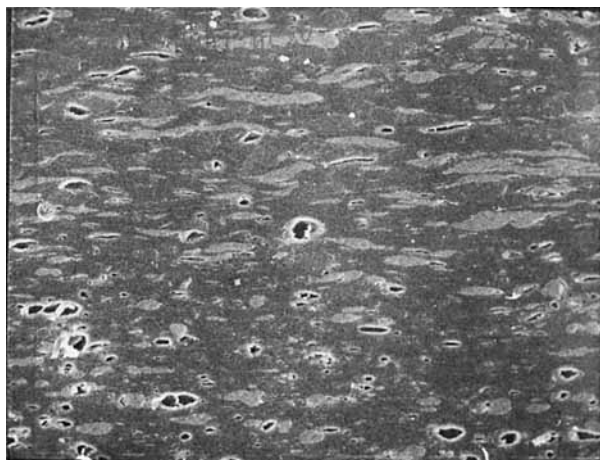
Amount of Peroxide Added in B7, %	0	0.5	1	1.5	2
<b>Izod impact strength</b>					
-Notched, J/m	59	67	55	55	45
(Standard deviation)	(23)	(17)	(6)	(6)	(2)
-Unnotched, J/m	133	216	465	385	180
(Standard deviation)	(17)	(20)	(35)	(31)	(14)
<b>Tensile Properties</b>					
-Stress at Yield, MPa	10.9	13.2	16.9	—	—
(Standard deviation)	(0.2)	(0.1)	(0.4)	—	—
-Stress at Break, MPa	10.2	12.5	16.9	20.6	19.3
(Standard deviation)	(0.3)	(0.1)	(0.4)	(0.3)	(0.8)
-Elongation at Yield, %	3.9	5.4	6.8	—	—
(Standard deviation)	(0.4)	(0.5)	(0.7)	—	—
-Elongation at Break, %	13.1	10.6	12.5	9.8	7.8
(Standard deviation)	(0.7)	(0.7)	(0.8)	(0.9)	(0.2)

expect under near-plane conditions. However, the peroxide was found to drastically modify the impact strength of unnotched samples. The best result was obtained when 1% of peroxide was added: the impact strength was increased by 250%. This improvement may be due to at least two factors. On one hand, SEM micrographs shown in Figures 1 and 2 seem to reveal that the number of elongated particles in the skin is higher in the peroxide-modified sample and that those fibrils have a lower diameter (also confirmed by micrographs perpendicular to the flow), and, perhaps, a higher aspect ratio. On the other hand, the peroxide could have drastically modified the mechanical properties of certain components: for instance, it has already been observed

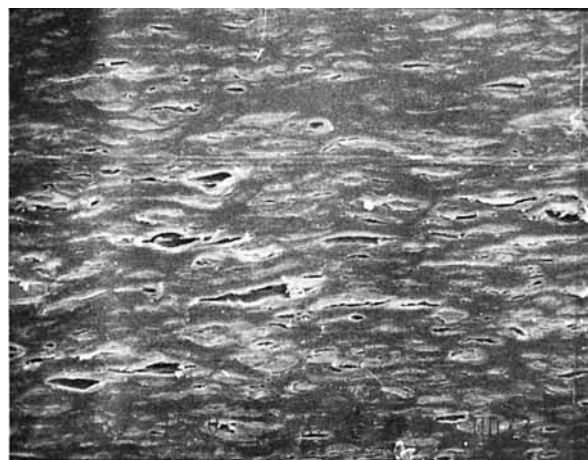
that HDPE can have much higher Izod impact strength when it is crosslinked by peroxide.<sup>8</sup> In summary, the peroxide-modified B7 may be considered as a composite structure containing more efficient reinforcing elements.

The tensile properties of B7 are also modified by the addition of peroxide. At 1.5% and higher peroxide concentrations, the stress at break was the highest; but at the same time the samples did not yield and the elongation at break was reduced. This could explain the difficulties encountered in pelletizing those samples on-line after extrusion.

At 1% peroxide, the elongation at break was very slightly reduced, and the stress at yield and break were increased respectively by 55% and 65%. This



**Figure 1** SEM microphotograph of B7 showing a section parallel to the flow direction near the mold surface;  $\times 250$ .



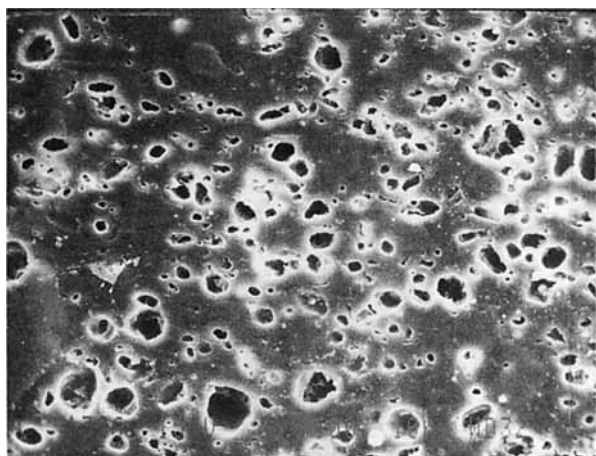
**Figure 2** SEM microphotograph of the 1% peroxide modified B7 showing a section parallel to the flow direction near the mold surface;  $\times 250$ .

may be attributed to the factors discussed earlier (fibrous skin, property modification of blend components), and also to a finer dispersed morphology in the core region, as shown in Figures 3 and 4.

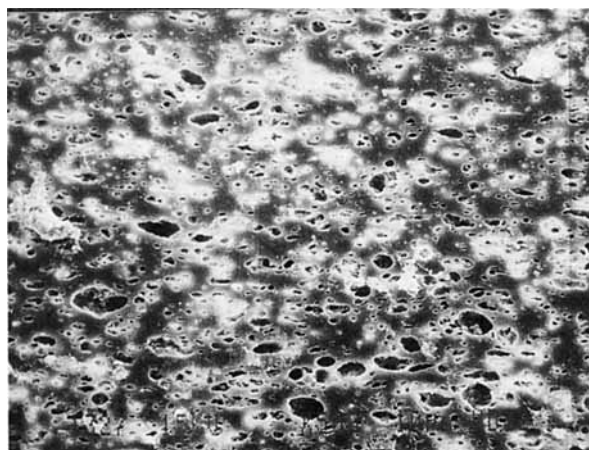
Finer morphologies and improved mechanical properties could also be the result of improved interfacial adhesion due to the creation of amphiphilic species by macroradical recombination. The present investigation conducted no experiments to verify this hypothesis, although recent work by Lambla and coworkers<sup>9-11</sup> has demonstrated the importance of interfacial free-radical reactions. By using low peroxide concentrations, these authors created *in situ* during processing of immiscible blends a high level of grafted species, resulting in morphology stabilization and improvement of mechanical properties. The reactivity of the peroxide was believed to be localized at the blend interface through the use of a monomer that would simultaneously play the roles of peroxide carrier at the interface and co-reagent for the "compatibilizing" reaction.

### Rheological Properties

As discussed earlier, the highest improvements in the B7 mechanical properties were obtained in the samples modified with 1% peroxide; it was found that the morphological changes in these samples were significant. Since those changes could be due to a modified rheological behavior of the B7 components through the addition of peroxide, the effects of the peroxide on the viscosity of the individual components was further investigated. It was assumed that the viscosity of each component in the peroxide-modified B7 would be approximated by the viscosity of the same component if it were to be



**Figure 3** SEM microphotograph of B7 (after extraction of the non-polyolefin phases) showing a section normal to the flow direction in the core region;  $\times 500$ .



**Figure 4** SEM microphotograph of the 1% peroxide modified B7 (after extraction of the non-polyolefin phases) showing a section normal to the flow direction in the core region;  $\times 500$ .

modified separately in the extruder. This is, of course, a simplified assumption since it would imply equal partitioning of the peroxide in each phase, comparable reaction rates within each component, and, perhaps, low localized peroxide activity at phase boundaries.

Viscosity curves at 190°C are shown in Figures 5 and 6. It should be noted that the data obtained for the peroxide-modified PVC are not very accurate since this material was unstable during viscosity measurements; as a matter of fact, it was found that 1% peroxide promoted its degradation, both during processing and viscosity measurements. Also, it should be noted that the viscosity of PET was measured above its melting point (275°C); of course, the viscosity of the amorphous/crystalline PET during compounding of the B7 at the much lower processing temperature used should have been higher.

The direction (increase or decrease) and the magnitude of the viscosity change were found to depend on the type of resin. Significant viscosity increases were observed for the polyethylene components as a result of branching/crosslinking. A significant viscosity decrease was observed for the degraded PP component as a result of hydrogen abstraction and beta scission. The styrenics and the PVC showed a less pronounced viscosity decrease, whereas only a slight viscosity increase (at higher temperatures) was observed for the PET component. If it is assumed that the major component, LDPE, formed the continuous phase, then the morphology of any dispersed phase would be affected by the ratio of its viscosity to the LDPE viscosity. The peroxide effect on this viscosity ratio is shown in

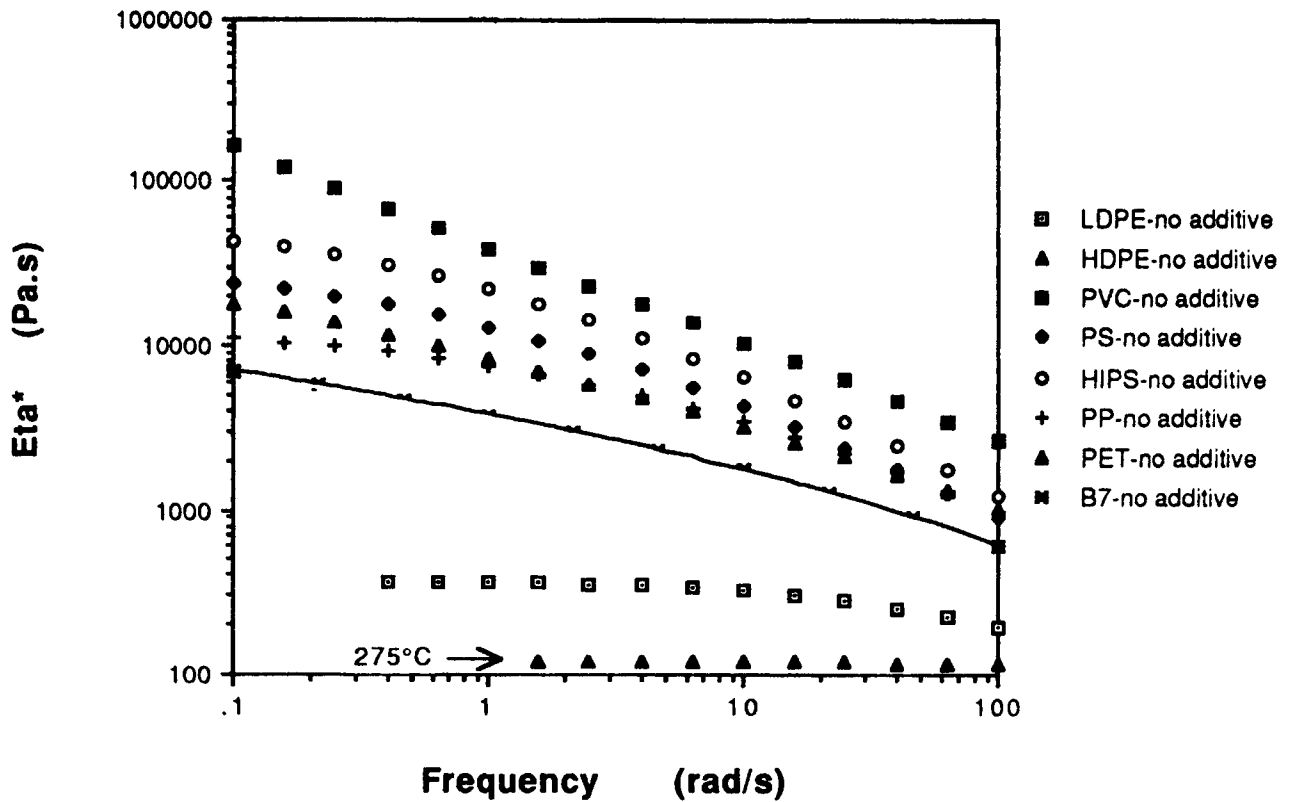


Figure 5 Viscosity curves at 190°C of B7 and its components.

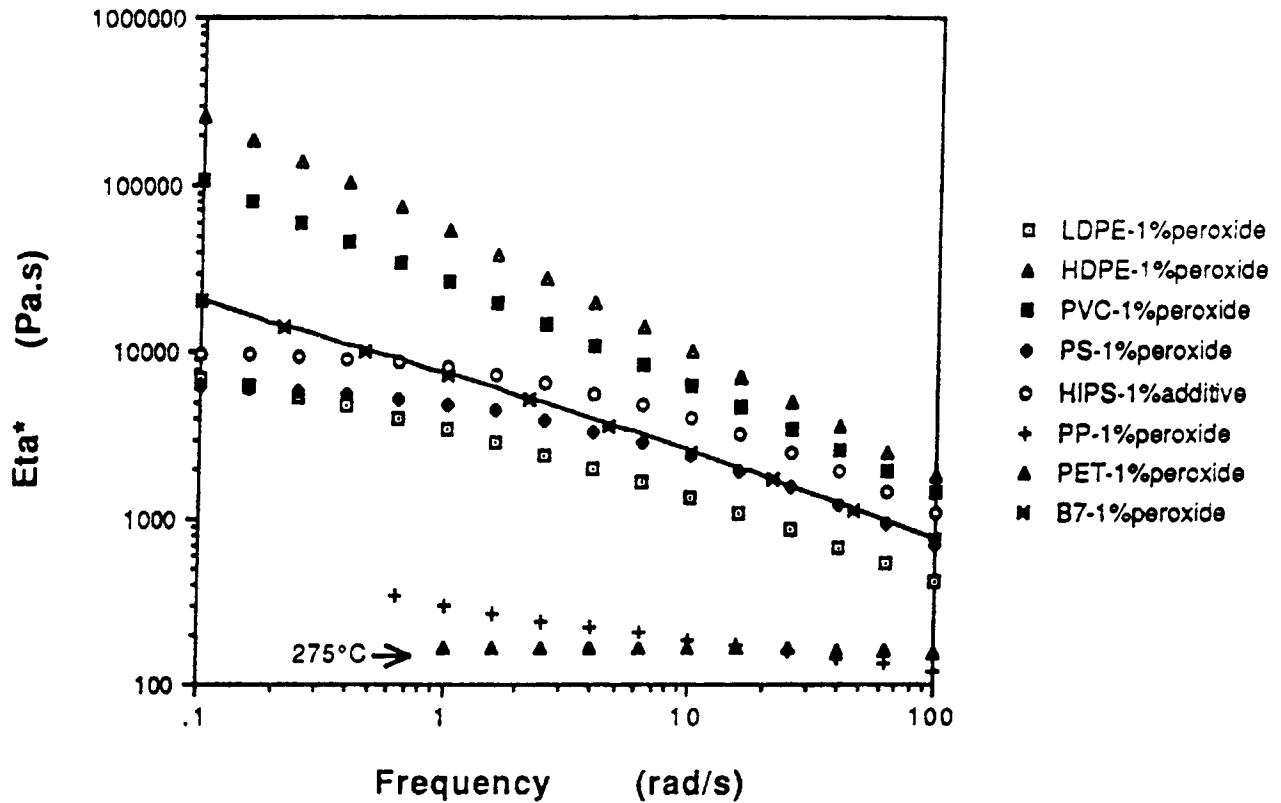


Figure 6 Viscosity curves at 190°C of the 1% peroxide modified B7 and its modified components.

**Table III** Effect of Peroxide on the Viscosity Ratio of each Dispersed Phase to the LDPE Continuous Phase at 190°C

	Frequency rad/s	Viscosity Ratio				
		HDPE/LDPE	PVC*/LDPE	PS/LDPE	HIPS/LDPE	PP/LDPE
no peroxide	0.1	50.3	452.6	66.4	119.9	30.3
	1	23.2	109.5	36.5	61.6	20.8
	100	5.2	13.2	4.7	6.3	5.0
1% peroxide	0.1	36.1	14.9	0.9	1.4	—
	1	15.2	7.5	1.4	2.3	0.1
	100	4.4	3.5	1.7	2.6	0.3

\* Peroxide data are only approximate due to PVC degradation.

Table III (PET is not included due to its complex behavior at 190°C). It can be seen that the addition of the peroxide tends to bring the ratio closer to unity for all components at all frequencies; as shown in our earlier work on the peroxide modification of LDPE/PP blends,<sup>3,12</sup> the similarities in the rheological properties of the blend components are the most favorable condition for dispersive mixing and are thus largely responsible for the finer and more uniform blend morphologies which lead to improved properties.

## CONCLUSIONS

The mechanical properties of a mixture of seven virgin plastics in proportions representative of those currently found in post-consumer plastic containers collected in France were improved through the addition of a relatively high amount of a dialkyl peroxide in a co-rotating TSE. The peroxide was found to drastically modify the blend morphology. This is due, at least partly, to the modified rheological behavior and physical properties of the blend components. Improved interfacial adhesion through the formation of "compatibilizing" copolymers could be an additional factor, although no experiments were conducted to verify its extent. Further experiments should attempt to investigate the effects of peroxide modification on an actual recyclable mixture of waste household plastics.

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