

High-Impact-Strength Poly(ethylene terephthalate) (PET) from Virgin and Recycled Resins

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SYNOPSIS

Poly(ethylene terephthalate) (PET) is a useful high-temperature plastic. Its shortcoming is that it has poor impact-strength properties. The impact strength of this polymer was dramatically improved by blending with a copolyester thermoplastic elastomer, or an acrylate core/shell elastomer. The addition of triphenyl phosphite (TPP) to the polyester elastomer/PET blends encouraged molecular weight buildup and resulted in improved impact strength and tensile properties. It was suspected that the phosphite interacts chemically with the components of the blend during processing and produces the improvements. Phosphorus-31 (^{31}P)-NMR techniques have provided a direct spectroscopic probe of the chemical nature of the phosphite additive after the processing steps. Solution and solid-state spectra have revealed the presence of products in which the polymer chains are grafted and crosslinked through the phosphorus additive. Up to a 60-fold increase in impact strength of PET was obtained by blending with elastomers in the presence of TPP. Amorphous PET is susceptible to environmental stress cracking by many solvents, whereas crystalline PET or PET elastomer blends exhibit high resistance to solvent cracking. Similar improvements in properties were also realized when PET obtained from recycled soft drink bottles was used. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The high cost of the development, synthesis, and commercialization of new polymers, and the interest in postconsumer recycling of polymers, has shifted much of the research emphasis for new materials into the areas of reinforcing, alloying, and blending of existing polymers. This research has the added advantage that materials can be tailor-made to meet specific end-use requirements.

Poly(ethylene terephthalate) (PET) is a low cost, high-performance thermoplastic. Its major uses are in fabrics and soft drink bottles. In its crystalline form, the plastic has a very high flex modulus and a high heat deflection temperature. Being a thermoplastic, it is processable by injection molding, and, hence, it can have an excellent surface appearance suitable for painted part applications. The polymer has a high heat

deflection temperature, which assures that parts made of this polymer will be able to go through a paint oven cycle without warpage. The most serious shortcoming of this material is its very low impact strength.

PET regrinds from soft drink bottles are now available at a reduced price from many sources. The regrinds have only slightly reduced molecular weight and mechanical properties as compared to virgin polymer. Either form of the polymer will be usable in automotive engineering applications, only if the impact strength is improved. In this paper, we will discuss a new compatibilization technology employing aromatic phosphites for blends of PET and elastomeric polyesters that result in high-impact-strength compositions.^{1,2}

EXPERIMENTAL

Materials

The PET used is a condensation polymer produced from dimethyl terephthalate and ethylene glycol. It

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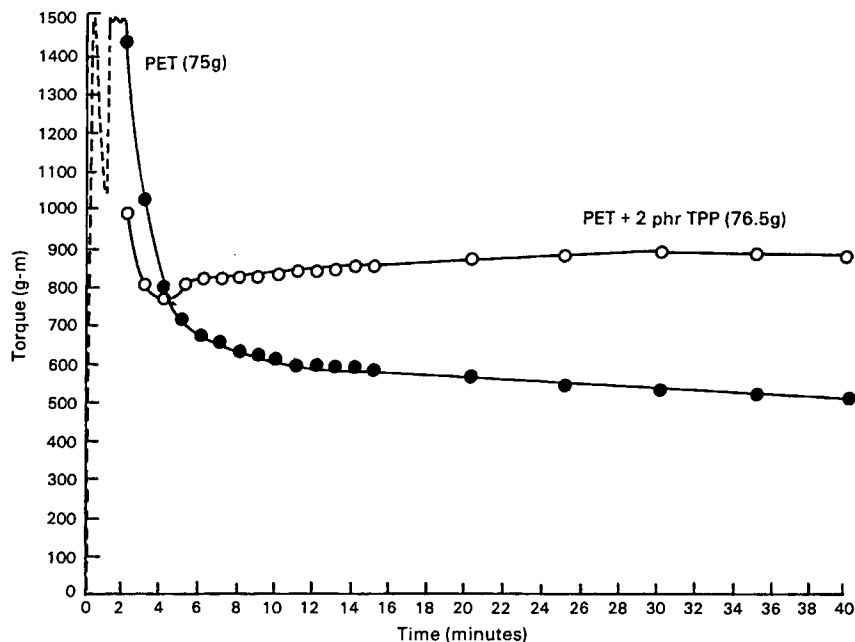


Figure 1 Torque versus time of PET, and PET containing TPP during mixing in a Brabender Plasticorder at 271°C and 75 r/min blade speed.

was obtained from the Eastman Kodak Company under the name Kodapak PET 7352. It has a bulk density of 1.40 g/cm³ and an intrinsic viscosity of 0.76 dL/g. The number average molecular weight is 24,000, and the weight-average molecular weight is 48,000. Two grades of PET soft drink bottle regrinds were obtained from wTe Recycling/Star company in form of flakes. The designation of these grades were D-717-AF-Green and D-716-AF-Clear.

To improve the impact strength of the PET, blends of the polymer were prepared containing polyester and polyether elastomers. These include a block copolymer of *n*-butyl terephthalate hard segment and ethylene oxide/propylene oxide soft segment (Hytrel 4074, DuPont), and butyl acrylate-methyl methacrylate core shell polymer (EXL3330, Rohm and Haas).

Compatibilizers investigated include the following organic phosphites obtained from GE Specialty Chemicals: triphenyl phosphate, bis(2,4-di-*tert*-butylphenyl)pentaerythritol diphosphite (Ultranox 626), distearyl pentaerythritol diphosphite (Weston 618), trisnonylphenyl phosphite (Weston TNPP), and poly(dipropylene glycol)phenyl phosphite (Weston DHOP). Two antioxidants were used in our study, namely, dilaurylthiodipropionate (DLTDP, ICI Chemicals) and tetrakis[methylene 3-(3',5'-di-*t*-butyl-4'-hydroxyphenyl)propionate]-methane (Irganox 1010, Ciba Geigy), and two fillers, talc (Mistron Vapor, Talc International Company)

and 3-mm chopped glass (Owens Corning). All materials were used as received.

Processing Procedure

Processing characteristics of PET and its blends with elastomers, stabilizers, and processing aids were conducted using the Plasticorder viscometer made by the Brabender Company. The torque required for mixing the blends in a temperature controlled bowl, having twin blades designed for mixing of plastics, was recorded with time. The temperature was kept at 271°C, and the blades were rotated at 75 rpm. Because of the sensitivity of PET toward degradation by moisture, the resin was dried 4 to 12 h in a vacuum oven set at temperatures between 105 and 150°C. Other resins and additives capable of absorbing moisture were also dried under the same conditions. Two of the samples were mixed in the Brabender Plasticorder for 15 min at 271°C, compression molded into 3.2 × 102 × 102-mm plaques in a press at 249°C for 1 min. Tensile properties, molecular weight characterization, and nuclear magnetic resonance studies were conducted on these samples. One of the samples (7030) contained only PET and Hytrel 4074, while the other (7033) contained triphenyl phosphite in addition to the two polymeric ingredients.

Blending of PET with the other ingredients was done using the plasticorder extruder barrel. The

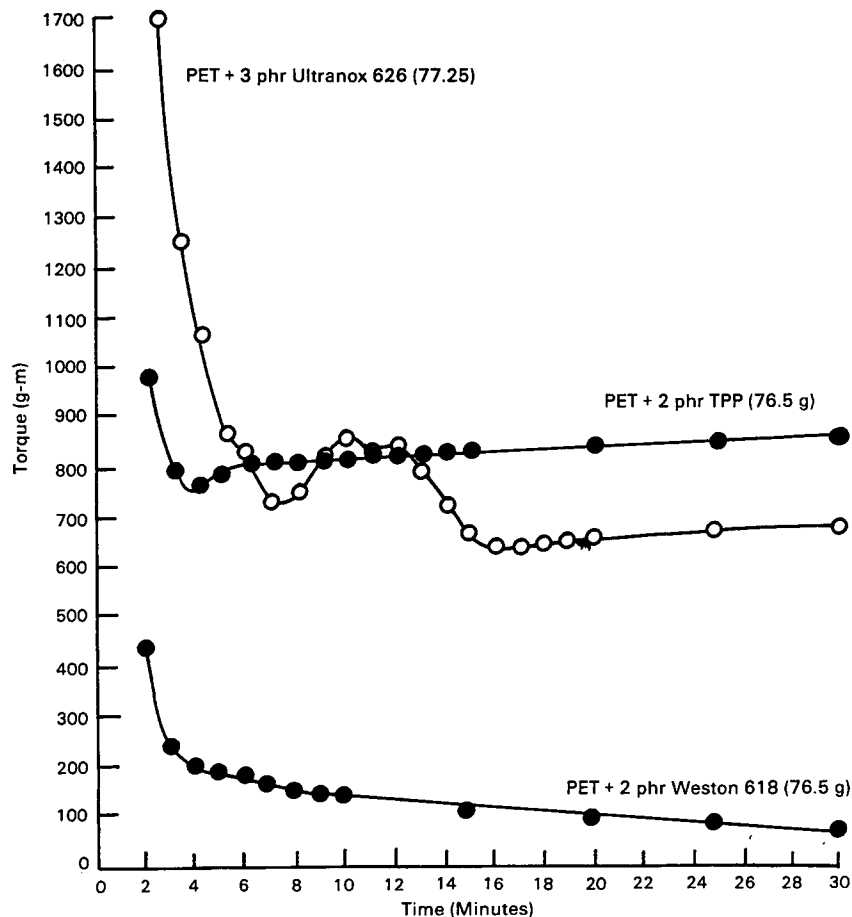


Figure 2 Torque versus time during Brabender Plasticorder mixing at 271°C and 75 r/min blade speed of PET containing different phosphites.

barrel had an L/D ratio of 25 : 1. The compression ratio of the extruder screw was 4 : 1. All ingredients of the blends were first dry blended in a beaker. They were then gradually fed into the extruder barrel. The screw speed of the extruder was maintained at 75 rpm. Four temperature zones were adjusted and controlled for each extrusion. The rear of the extruder was controlled at a constant temperature whose value was selected for easy feeding of the blends into the extruder screw. The temperature range used for the various blends was 232–284°C. The middle and the front zones of the extruder were controlled at 271°C, and the nozzle temperature was maintained at 230°C for all of the blends. The extrudates were air cooled, chopped, and stored in a desiccator until they were molded. However, if the samples were stored in the desiccator over 24 h, redrying in a vacuum oven at 150°C for a minimum of 4 h was carried out prior to molding.

The injection molding of the extruded and chopped samples of PET blends was performed us-

ing two machines. A New Britain 75TP injection molder was used to prepare plaques 76 × 152 × 3.2 mm in dimensions. The L/D ratio of the screw in this machine is 20 : 1. The temperatures of the front zone of the injection barrel and of the injection nozzle were maintained at 271°C, while the temperature of the rear zone of the barrel was kept at 250°C for all materials molded. Adjustments in mold fill time, shot size, molding cycle time, and injection pressure were made to obtain the best molded part appearance for each of the PET blends. In all cases, the mold temperature was maintained at 150°C using electric heaters.

For the preparation of standard tensile, flex, and heat deflection temperature specimens, the Newburg Industries Imperial Injection Molder 30 ton machine was used (Model H130RS). The L/D ratio of the screw used in this machine is 20 : 1. As in the case of the New Britain, the temperatures of the nozzle and the front end of the barrel were maintained at 271°C, while the barrel rear zone temperature was

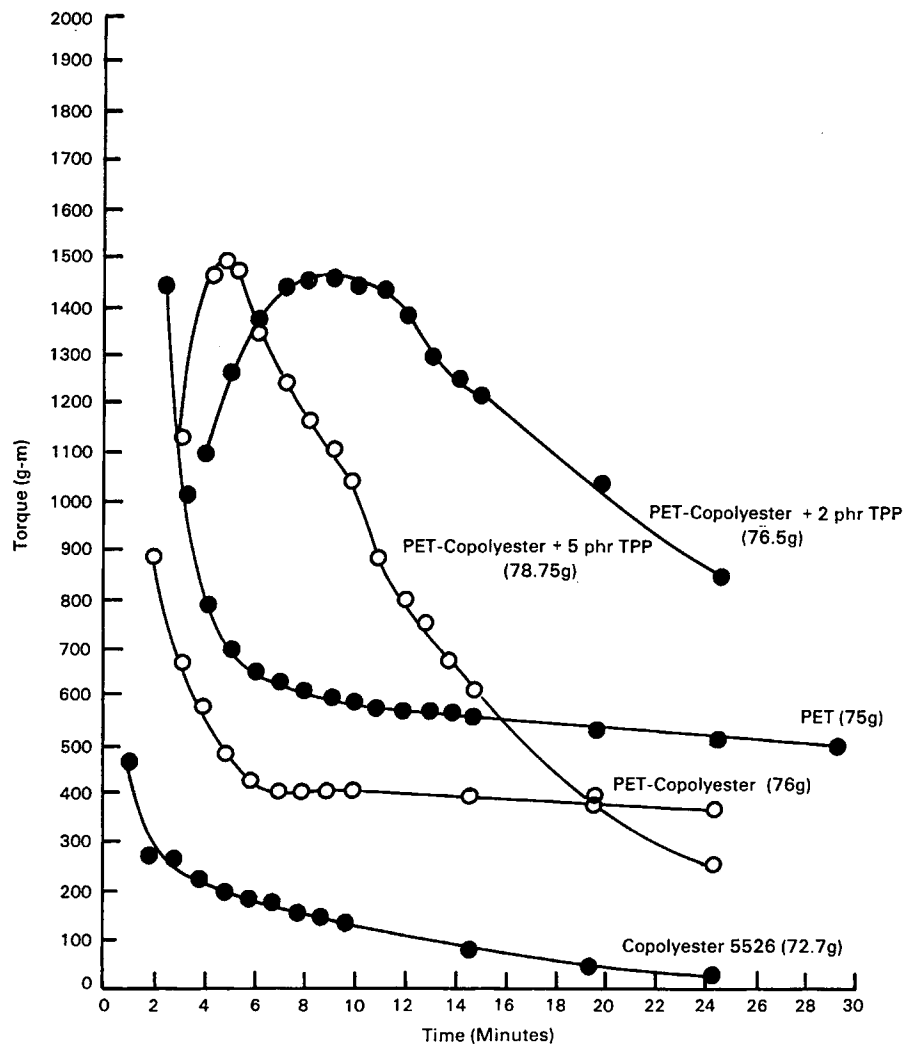


Figure 3 Torque versus time of PET-copolyester blends during mixing in a Brabender Plasticorder at 271°C and 75 r/min blade speed.

kept at 232°C. Again, to obtain the best molded surface and part appearance, adjustments were made in injection pressure (1.4 to 10 MPa), mold temperature (65–99°C), and total injection cycle time (45–180 s) for each of the PET blends.

Property Measurements

The property of the PET that was of most interest to us was the impact strength. We measured this property by two methods. In the first method, the Izod pendulum equipment was used per the ASTM D256 test procedure to measure the notched and, in some cases, the unnotched impact strength of the PET blends at room temperature. For some samples, the notched Izod impact strength values were also measured at 0°, –15°, and –30°C. The second

method employed an instrumented constant velocity dart apparatus manufactured by the Rheometrics Company. The sample used in this method was the 87 × 152 × 3.2-mm plaque. It was positioned in front of the dart and clamped tightly in a ring fixture located inside an environmental chamber. Dart speeds of 6.7, 0.67, and 0.067 m/s were used for characterizing the impact strength of the PET blends. The advantage of this method over the Izod method is that it is not a single value test method but instead it describes the failure process quite completely. For example, using this method, the entire load-versus-deflection and energy-versus-deflection curves were measured for each sample. From these curves, modulus values, as well as energy-to-yield, energy-to-failure, strain-to-yield, and strain-to-failure values, were obtained.

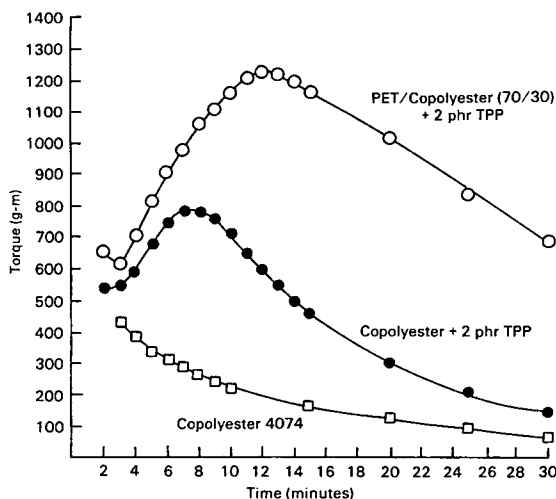


Figure 4 Torque versus time for copolyester (4074) and for a PET-copolyester blend during mixing in a Brabender Plasticorder at 271°C and 75 r/min blade speed.

Other properties of the PET investigated include tensile and flexural properties. Both of these properties were measured at room temperature using the Instron testing machine per the ASTM D-638 and D-790 procedures, respectively. For some of the samples, the susceptibility to environmental stress cracking was determined during exposure to toluene, acetone, methanol, ethylene glycol, monoethanol amine, and *n*-heptane. An elliptical form was used to apply gradually increasing stress on the sample during exposure.³

Molecular weights of all blends were measured by gel permeation chromatography using samples taken from the molded parts dissolved in *m*-cresol. Solid-state ³¹P spectra were obtained at 81 MHz on an IBM WP200SY spectrometer equipped with a multinuclear probe manufactured by Doty Scientific, Inc. Spectra were obtained using both a Bloch decay pulse sequence and a cross-polarization (CP) pulse sequence. High-power proton decoupling was used during accumulation. A 4–5 μs 90° pulse was used for all experiments. The recycle times were generally 15–30 s for Bloch decay experiments and 5 s for CP experiments. Spectra were collected with and without magic-angle-spinning (MAS) of 3.5–5 kHz.

Solution-state ³¹P-NMR spectra were obtained at 109 MHz on an IBM NR270AF spectrometer. All samples were prepared in *m*-cresol. Although heating was necessary to dissolve these samples, it was minimized as much as possible due to concerns that the solvent may interact with the phosphorus species and alter the structures. All samples did not form clear solutions; however, the materials were suffi-

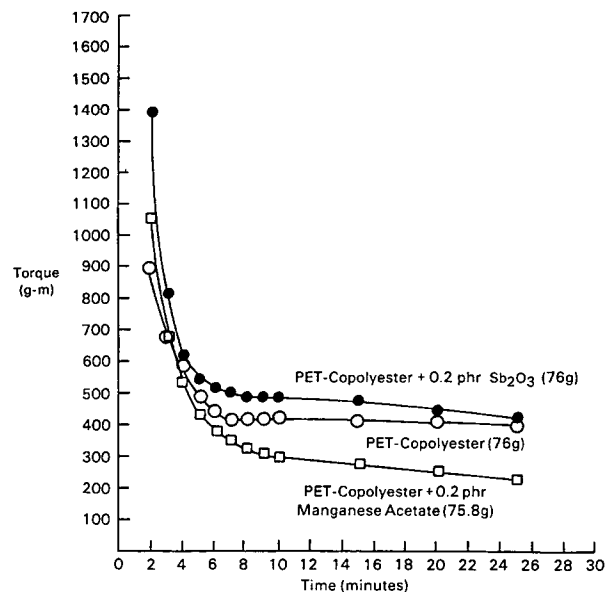


Figure 5 Torque versus time for (80/20) PET-copolyester blends with and without transesterification catalysts antimony oxide and manganese acetate. The mixing temperature is 271°C and blade speed is 75 r/min.

ciently swollen by the solvent so that high-resolution spectra could be obtained. Proton-decoupled spectra were obtained in the unlocked mode using a 45° pulse of 6 μs, a spectral width of 33333 Hz, 8K time domain data points, and a recycle time of 1 s. These spectra were generated using the Bruker pulse program, POWGATE, which allows fast data acquisition at the expense of quantitative information. Proton-coupled spectra were obtained under the same experimental conditions using the Bruker pulse program, GATEDEC.

All ³¹P chemical shifts are referenced with respect to external 85% phosphoric acid (H₃PO₄) at 0 ppm and are reported taking downfield shifts as positive. All NMR experiments were performed at room temperature.

Table I GPC Determined Molecular Weights of as Received PET and Copolyester Elastomer Pellets and Molded Samples of the Blends^a

Sample	M_w	M_n	M_w/M_n	M_z
Copolyester elastomer	162,000	59,000	2.75	340,000
PET	78,000	33,000	2.36	134,700
7030	74,500	33,600	2.22	131,000
7033	97,800	40,400	2.42	186,500

^a All samples were dissolved in *m*-cresol.

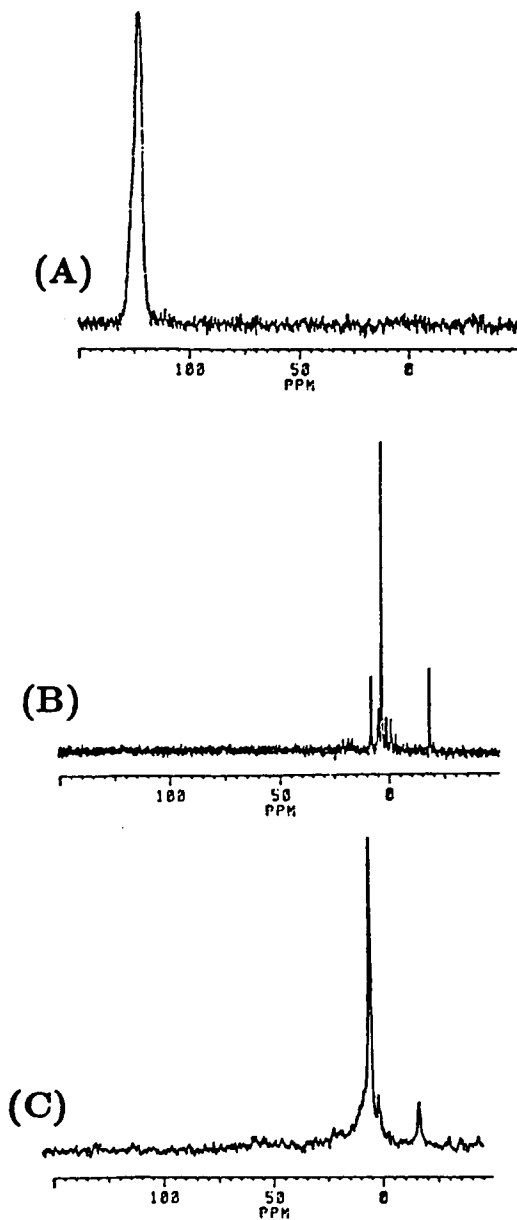


Figure 6 ^{31}P -NMR spectra. (A) Neat aromatic phosphite, (B) solution-state of 7033 material in *m*-cresol, (C) solid-state Bloch decay spectra of 7033 obtained with MAS and high-power decoupling.

Samples from the molded parts that were subjected to an extraction procedure with hot chloroform in a refluxing extraction apparatus were also analyzed. The materials were shaved to a thickness of 5 μm using a microtome. Approximately 500 mg of material were placed in platinum baskets and extracted for 48 h. The extracted residue was analyzed by proton NMR techniques in deuteriochloroform.

Proton NMR solution experiments in deuteriochloroform determined the chemical structure of the

copolyester elastomer. This analysis revealed a mixture of 29 wt % propylene oxide, 13 wt % ethylene oxide, 49 wt % butylene terephthalate, and 9 wt % butylene isophthalate units.

RESULTS AND DISCUSSION

Our approach for developing high-impact-strength PET from virgin or recycled resins was to blend the PET with polyester elastomers and to investigate the use of stabilizers and transesterification catalysts to compatibilize the blends. This section of the paper will deal with the processing, characterization, and properties of the PET and its blends.

Processing Characteristics

The investigation of processing characteristics of PET and its blends was conducted using the Bra-

Table II ^{31}P Chemical Shift and Coupling Constant Assignments for Phosphorus Compounds with Structures Similar to Possible Reaction Products^a

	Chemical Shift (ppm)	Coupling Constant (Hz)
Phosphites		
$\text{P}(\text{C}_6\text{H}_5)(\text{OC}_4\text{H}_9)_2$	+178	
$\text{P}(\text{OC}_2\text{H}_5)_3$	+138	
$\text{P}(p\text{-OC}_6\text{H}_4\text{CH}_3)_3$	+127.6	
$\text{P}(\text{OC}_6\text{H}_5)_3$	+127.3	
Phosphates		
$\text{OP}(\text{C}_2\text{H}_5)(\text{OC}_2\text{H}_5)_2$	+32.5	PCH = 19.2
$\text{OPH}(\text{C}_4\text{H}_9)_2$	+29	PH = 308
$\text{OPH}(\text{C}_6\text{H}_5)_2$	+22.9	PH = 490
$\text{OP}(\text{CH}_3)(\text{OC}_6\text{H}_5)_2$	+22.8	
$\text{OP}(\text{C}_6\text{H}_5)(\text{OC}_2\text{H}_5)_2$	+16.9	
$\text{OPH}_2(\text{OC}_4\text{H}_9)$	+15.6	PH = 570
$\text{OPH}_2(\text{OC}_2\text{H}_5)$	+15	PH = 567
$\text{OP}(\text{C}_6\text{H}_5)(\text{OC}_6\text{H}_5)_2$	+11.8	
$\text{OPH}(\text{OC}_2\text{H}_5)_2$	+7.4	PH = 690
$\text{OPH}(\text{OC}_3\text{H}_7)_2$	+7	PH = 685
$\text{OPH}(\text{OC}_4\text{H}_9)_2$	+6.7	PH = 670
$\text{OPH}(\text{OC}_4\text{H}_9)(\text{OC}_6\text{H}_5)$	+4.2	PH = 716
$\text{OPH}(\text{OC}_6\text{H}_5)_2$	+0.1	PH = 740
$\text{OP}(\text{OC}_4\text{H}_9)_3$	-0.8	
$\text{OP}(\text{OC}_4\text{H}_9)_2(\text{OC}_6\text{H}_5)$	-5.1	
$\text{OP}(\text{OC}_4\text{H}_9)(\text{OC}_6\text{H}_5)_2$	-12	
$\text{OP}(\text{OC}_6\text{H}_5)_3$	-18	

^a All chemical shifts are referenced with respect to 85% phosphoric acid at 0 ppm and are reported taking downfield shifts as positive.

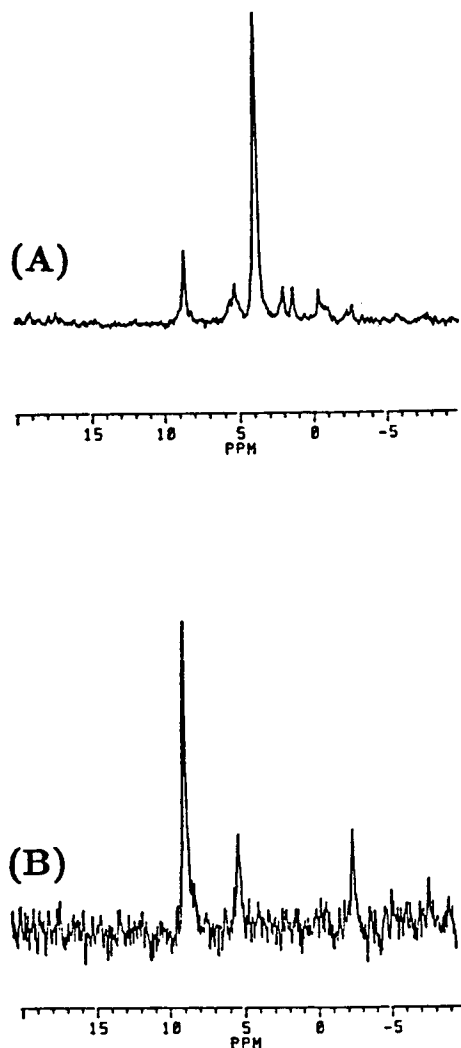


Figure 7 ^{31}P -NMR solution-state spectra of (A) 7033 before extraction with chloroform, (B) 7033 after extraction.

bender plasticorder. Torque measurements using this instrument were conducted at constant temperature, 271°C , and constant shear rate, namely, blade speed of 75 rpm. Generally between 70 and 80 g of PET pellets or PET dry blend with the other ingredients was placed in the Brabender chamber, which, at that time, had already been maintained at 271°C and 75 rpm. The material was compacted into the chamber using a hammer arm, which consisted of a cover for the mixing chamber inlet attached to a long arm, which maintained a constant weight on the cover during mixing. Compaction was carried out for a minute or two. The torque generated during the melt mixing of ingredients was recorded versus time on a chart recorder.

As seen in Figure 1, in the case of pure PET, a sharp decrease in torque is observed in the first 6

min of mixing. This period includes the time spent in compacting the sample into the mixing chamber and the time needed for the sample to reach the chamber temperature. After that, a slow decrease in torque is observed with time, and it is attributed to the breakdown in the molecular weight of the PET as a result of the continued mixing at the high melt temperature of 271°C . Lower molecular weight gives rise to lower melt viscosity and, hence, lower torque. The addition of triphenyl phosphite (TPP) to PET reverses this trend of torque decrease. After the initial equilibration period, a marked increase in torque occurs after 4 min of mixing as seen in Figure 1. This is followed by a more gradual increase in torque with time. Not all organic phosphites lead to torque buildup. As seen in Figure 2, the addition of an aliphatic phosphite, distearyl pentaerythritol diphosphite (Weston 618), leads to fast degradation in torque to very low values in a relatively short period of time. For example, the torque value of PET containing this phosphite is only 150 g m after 10 min of mixing as compared to 800 g m for the PET containing the TPP. On the other hand, the addition of aromatic phosphites, such as trisnonylphenyl phosphite (TNPP), poly(dipropylene glycol)phenyl phosphite (DHOP), or bis(2,4-di-*tert*-butylphenyl)pentaerythritol diphosphite (Ultranox 626, also shown in Fig. 2) gives rise to a torque versus time curve similar to that of TPP.

The mixing characteristics of blends of PET with copolyesters were also investigated. The copolyesters are block copolymers consisting of *n*-butyl terephthalate hard segments and either poly(ethylene oxide)-poly(propylene oxide) (Hytrel 4074) or polytetramethylene glycol (Hytrel 5526) soft segments. The torque versus mixing time at 271° for copolyester 5526 is shown in Figure 3. The curve looks like that of PET, also shown in Figure 3, except that the torque values are very much reduced at all mixing times. A blend of 80/20 (w/w) PET/copolyester has a torque-time curve similar in shape to those of the pure components, and, as expected, the torque values are in between those of the pure components (Fig. 3).

The addition of TPP to the PET/copolyester blends gives rise to a new phenomenon. As seen in Figure 3, addition of 2 phr TPP to an 80/20 PET/copolyester (5526) blend results in much higher torque values. For example, after 4 min of mixing, the torque value of the blend containing the TPP is 1100 g m, as compared to 600 g m for the blend without the TPP. And whereas a decrease in torque with time is observed thereafter for the blend without the TPP, the torque increases markedly for the

Table III Notched Izod Impact Strength of PET Formulations

Formulation	Major Ingredients	Notched Izod Impact Strength (J/m)
PET (Kodapak 7352)	PET	16
1	PET + Mistron Vapor talc (3%) ^a	25
2	PET + glass fiber (23.3%)	68
3	PET + glass fiber (22.3%) + TPP (2.2%)	66
4	PET + copolyester 5526 (18.8%)	27
5	PET + copolyester 5526 (22.4%) + TPP (2.2%) + glass fiber (22.4%)	157
6	PET + copolyester 4074 (22.4%) + TPP (2.2%) + glass fiber (22.4%)	206
7	PET + core/shell polyester (19.5%) + TPP (1.6%)	47
8	PET + core/shell polyester (33.7%) + TPP (2.9%)	973
9	PET + core/shell polyester (25.7%) + TPP (1.5%) + glass fiber (22.1%)	124
10	PET + copolyester 4074 (30%)	26
11	PET + copolyester 4074 (29.1%) + TPP (2.9%)	97
12	PET + copolyester 4074 (23.1%) + glass fiber (23.1%)	177

^a All percentages are on weight basis.

blend containing the TPP, reaching a maximum value of 1470 g m after 9 min of mixing. A sharp decrease in torque follows this maximum. However, even after 25 min of mixing, the torque of the blend containing the TPP is 870 g m, which is much higher in value than the 400 g m torque for the blend without the TPP (Fig. 3). Addition of 5 phr TPP to the blend gives results similar to the addition of 2 phr, except that the maximum in torque is reached at lower mixing time (6 min), and the viscosity is reduced to a value of only 290 g m after 25 min of mixing. Hence, it is beneficial to add 2 phr rather than 5 phr TPP to the blend (Fig. 3).

The effect of TPP on the copolyester alone is shown in Figure 4. The addition of TPP to copolyester 4074 increases the torque values and gives rise to a maximum in the torque versus time curve at about 8 min of mixing. The increase in torque is, however, much lower than the increase observed when TPP is added to a blend of PET and copolyester. The maximum torque, in the case of the poly-

ester, is 790 g m, whereas the maximum torque for the blend is 1230 g m.

In an attempt to explore the mechanism of polyester-phosphite interactions, we investigated the interactions between the polyesters and known transesterification catalysts. As seen in Figure 5, the addition of either antimony oxide or manganese acetate to an 80/20 PET/copolyester blend results in the same shape for the torque versus melt mixing time curve as the pure PET-copolyester blend. The torque values were slightly higher in the case of the blend containing the antimony oxide and significantly lower for the blend containing the manganese acetate. Hence, neither of these two compounds causes the viscosity buildup observed in the case of the aromatic phosphites.

Molecular Weight Determination

The molecular weights of the resins and the blends were determined to find out if the increase in melt

Table IV Notched Izod Impact Strength of Select PET Formulations at Low Temperatures

Formulations	Notched Izod Impact Strength (J/m) at			
	RT (23°C)	0°C	-15°C	-30°C
PET (Kodapak 7352)	16	21	21	26
PET + glass fiber (Formulation 2, Table III)	68	77	72	79
PET (Rynite SST)	160	154	139	103
PET + copolyester 4074 + TPP + glass fiber (Formulation 6, Table III)	206	166	116	100
PET + core/shell polyester + TPP (Formulation 8, Table III)	973	887	89	58

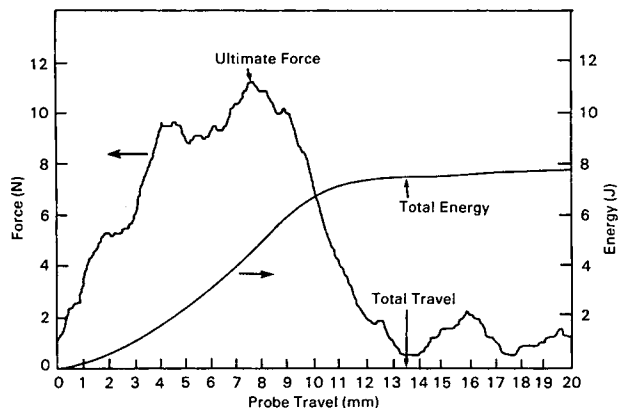


Figure 8 Force and energy curves versus probe travel for PET containing copolyester obtained using the rheometrics constant velocity dart method at probe speed of 6.7 m/s.

viscosity, in the presence of phosphite, is caused by molecular-weight buildup. The results are shown in Table I for a copolyester sample (pellet), a PET sample (pellet), and for blends 7030, without phosphite, and 7033 containing 3 phr triphenyl phosphite. The 70/30 PET copolyester blends were prepared by mixing in a Brabender Plasticorder bowl and compression molding, as described in the experimental section. Examination of the results shows that the molecular weight of the 7030 blend is about that of the virgin PET. The expected increase in molecular weight due to the incorporation

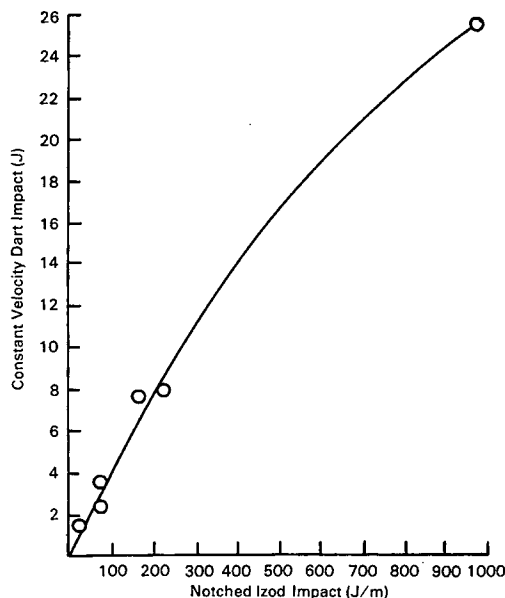


Figure 9 Comparison of the notched Izod impact strength and constant velocity dart impact strength of select PET formulations.

of copolyester is perhaps nullified by the degradation in molecular weight due to processing. However, the presence of 3 phr phosphite in the 7033 blend leads to markedly increased molecular weight. It is reasonable, then, to relate the increase in melt viscosity in the presence of phosphite to molecular-weight

Table V The Impact Strength of Select PET Formulations Obtained by the Constant Velocity Dart Method

Major Ingredients	Total Energy (J) at			Total Travel (mm) at			Ultimate Force (N) at		
	6.7 m/s	0.67 m/s	0.067 m/s	6.7 m/s	0.67 m/s	0.067 m/s	6.7 m/s	0.67 m/s	0.067 m/s
PET	1.33	1.84	2.34	5.70	2.79	3.16	620	1363	1363
PET + glass fiber + impact modifiers (Rynite SST)	7.53	10.5	12.1	13.9	11.5	15.8	1037	1245	1450
PET + glass fiber (23.3%)	2.30	2.30	—	7.88	4.92	—	790	950	—
PET + glass fiber (22.3%) + TPP (2.2%)	3.40	3.60	3.60	9.96	5.34	5.00	1130	1320	1360
PET + copolyester 5526 (19.4%)	—	—	0.34	—	—	2.36	—	—	317
PET + copolyester 5526 (19.0%) + TPP (1.9%)	0.7	1.75	1.78	9.31	6.62	5.16	271	493	715
PET + copolyester 4074 (22.4%) TPP (2.2%) + glass fiber (22.4%)	7.90	9.80	9.60	13.5	12.3	12.2	1060	1130	1180
PET + core/shell polyester (25.0%)	2.31	7.12	11.8	7.28	7.32	9.05	670	2160	2543
PET + core/shell polyester (23.8%) + TPP (1.9%)	2.59	21.4	21.7	7.23	11.7	13.4	754	3544	2970
PET + core/shell polyester (33.7%) + TPP (2.9%)	25.5	27.9	25.7	17.7	17.5	18.6	2648	2670	2360

Table VI Tensile and Flexural Properties of PET Compositions

Major Ingredients	Stress (MPa)		Strain (%)		Flexural Modulus (MPa)
	Peak	Break	Peak	Break	
PET	63	63	2.9	2.8	3.5 K
PET + glass fiber	98	98	1.4	1.4	6.7 K
PET + glass fiber + TPP	106	106	2.1	1.9	6.2 K
PET + copolyester (5526)	51	51	3.4	3.5	2.4 K
PET + copolyester (5526) + glass fiber + TPP	64	63	2.0	2.0	3.6 K
PET + copolyester 4074 + glass fiber + TPP	48	42	1.9	2.2	3.7 K
PET + core/shell polyester + TPP	38	20	1.9	15.0	1.8 K

buildup. The mechanism of phosphite-polyester interaction was studied using NMR spectroscopy.

NMR Investigations

The ^{31}P nucleus has many convenient NMR properties: spin one-half, 100 natural abundance, reasonable sensitivity, moderate relaxation times, and a wide range of chemical shifts.⁴ These properties greatly simplify data acquisition and interpretation. In this investigation, two approaches are utilized: (1) solution-state NMR spectra are obtained for samples dissolved in *m*-cresol and (2) Bloch decay spectra are collected on solid samples utilizing magic-angle-spinning (MAS) and high-power proton decoupling techniques. Representative spectra for the neat phosphite additive and the 7033 blend are shown in Figure 6. There are noticeable changes throughout the spectra as one compares the various samples. Fortunately, the ^{31}P nucleus is very sensitive to small changes in its functionality. The or-

igin of the different peaks in these spectra can be determined by making comparisons to chemical shifts and coupling constants reported in the literature. A compilation of relevant ^{31}P chemical shifts and coupling constants for compounds similar to possible reaction products is shown in Table II.⁵

As shown in Figure 6(A), the neat phosphite additive exhibits a signal at +128 ppm in accord with the literature references for aryl phosphites. After the polymer compounding and processing steps, new peaks appear in the region of +10 to -18 ppm, as shown in Figure 6(B). Solid-state NMR methods provide additional information on the nature of the phosphorus species in these blends. A distinct advantage of utilizing solid-state methods is that they offer *in situ* analysis with little sample preparation. The solid-state Bloch decay spectrum, shown in Figure 6(C), does not have the resolution of the solution-state spectra, particularly in the -10 to +10 ppm region; however, the chemical shifts of the primary species are the same. A comparison with the

Table VII Optimized PET Formulations and Properties

Formulation	1	2	3	4
PET "virgin"	70	70	—	—
PET "regrind"	—	—	70	70
Copolyester elastomer	30	30	30	10
Poly(butyl acrylate-methyl methacrylate)	—	—	—	20
Trinonylphenyl phosphite (TNPP)	3	3	3	3
Antioxidant	0.3	0.3	0.3	0.3
Mistron Vapor (talc)	—	5	5	5
Chopped glass fiber ($\frac{1}{8}$ in.)	45	45	45	45
Properties				
Impact strength (J/m)	214	110	102	107
Heat deflection temperature ($^{\circ}\text{C}$)	99	158	149	167

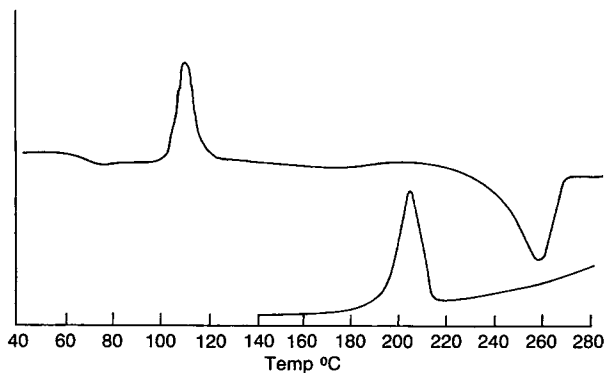
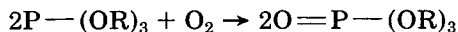


Figure 10 Differential scanning calorimetry (DSC) of high-impact strength PET material (#1 Table VII) formulated without talc.

literature reveals that signals in this region are consistent with phosphates.

The easiest assignment can be made for the signal at -18 ppm, which is in agreement with a compound of the form $(RO)_3P=O$, where R is an aryl group. This peak arises from phosphite that has acted as an antioxidant. Tertiary phosphite esters, in particular aromatic phosphites, are commonly used as antioxidants in polymer applications. These compounds react readily with oxygen to form the corresponding phosphates,⁶

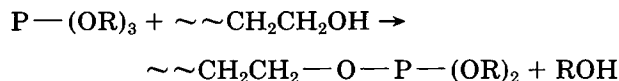


In addition to this reaction, there are numerous reports of phosphites involved in exchange reactions. For example, trialkyl phosphites have been reported to undergo an uncatalyzed alcohol exchange reaction when heated with aliphatic alcohols to yield tertiary phosphites containing different alkyl groups,⁷

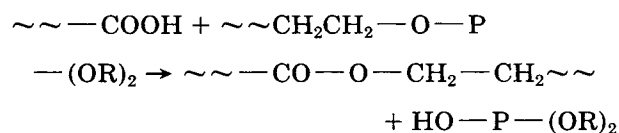


Similarly, triphenyl phosphite (TPP) has been used as a modifier for epoxy resins.⁸ It acts as a curing agent by reaction with the resin's hydroxyl groups through an exchange step as outlined above. In this case, the trifunctional phosphite acts as a cross-linker and becomes chemically bound into the polymer system that forms.

Another reported exchange reaction involves the melt processing of PET in the presence of small amounts of TPP.⁹ This process leads to the chain extension, or increased molecular weight, of PET and is proposed to take place in two steps. First, the phosphite rapidly reacts with the hydroxyl end groups of the PET by replacing one phenoxy group from the TPP,



Second, a slow reaction takes place between the alkyl-diphenyl phosphite and the carboxylic end groups of PET, forming an ester bond between the carboxyl and alkyl groups, and producing diphenyl phosphite as a reaction by-product.



Subsequently, the diphenyl phosphite tautomerizes to its more stable pentavalent bonded form of diphenyl phosphate,



Thus, in this case, the phosphite acts only as a catalyst for the increase in molecular weight of PET and is not incorporated into the polymer structure.

It is reasonable to expect that similar phenoxy-alkoxy exchange reactions take place in the present polyester blend system. The reaction of the phosphite with the hydroxyl groups of the polyesters is known to be rapid⁹ and is most likely a random process. The phosphite is trifunctional. It can react with the hydroxyl groups among three different chains of any combination of PET and the copolyester elastomer, between two chains, or with only one chain. Subsequently, one would expect continued reaction with the carboxylic end groups as outlined previously or simply a rearrangement of the phosphites into their more stable pentavalent bonded forms, which results in the coupling of chains through the

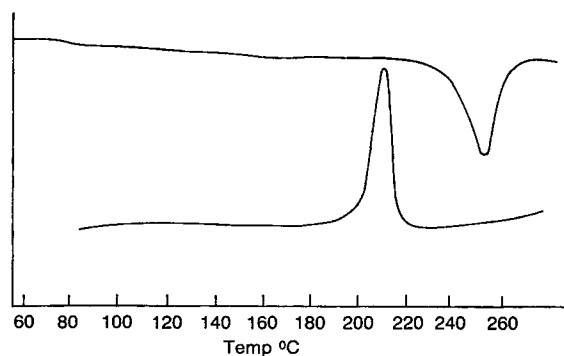
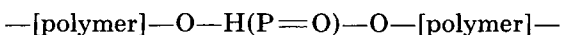


Figure 11 Differential scanning calorimetry (DSC) of high-impact strength PET containing talc (Formulation 2 Table VII).

phosphorus. Thus, one can picture the formation of a complex network structure. In looking at the solution spectrum in Figure 6, one observes as many as eight resonances in the -10 to $+10$ ppm region, confirming that the final phosphorus species are varied.

The primary signal of the 7033 sample exhibits a chemical shift of 4.0 ppm and a phosphorus-proton coupling constant (J_{PH}) of 675 Hz. This value is comparable to the alkyl substituted phosphates of the form, $H-(P=O)-(OR)_2$, listed in Table II. Thus, it is consistent with the presence of an exchange reaction between the phosphite and the polymers, which yields polymer chains coupled through the phosphorus,



Having examined the chemistry associated with the principal peak, our attention turned to the examination of the solubility characteristics of these polymers in chloroform. The elastomer is soluble in chloroform while the PET is not. A quantitative analysis of the copolyester elastomer component in the extracted residues was performed using a Bloch decay solid-state ^{13}C experiment, where integrated signals are compared to samples of known weight. The extracted sample of 7030 shows no residual elastomer present, while the extracted samples of 7033 shows one-third of the elastomer still present. Since crosslinked networks can have a great variety of structures, this experiment provides some indication of the amount of the copolyester elastomer that is coupled to the PET. One would expect that this parameter may correlate with the final bulk physical properties, as it provides an indication of how tightly knit these polymers become after processing.

Identification of some of the smaller peaks in the -10 to $+10$ ppm region of the solution spectra can be made in conjunction with the examination of the chloroform solubility of these polymers. The ^{31}P -NMR solution spectra of the extracted residues dissolved in *m*-cresol are shown in Figure 7. These spectra reveal species that are chemically bound to the PET. For the 7033 sample, we observe three resonances with chemical shifts of 8.6, 5.1, and -2.7 ppm and corresponding J_{PH} s of 732, 643, and 0 Hz, respectively.

The origin of the different peaks in the extracted residues can be determined by comparison to the chemical shift and coupling constant data shown in Table II. The large J_{PH} of 724–732 Hz observed for the 8.6 ppm resonance suggests that it has one aryl

group associated with it. This may represent phosphite that has reacted with one chain end and subsequently rearranged to a more stable phosphate form. The signal at -2.7 ppm shows no proton coupling and, thus, is associated with a phosphate of the form, $O=P-(OR)_3$, where the Rs are alkyl groups. These species arise from phosphite that has undergone three phenoxy-alkoxy exchanges and then reacted with oxygen to form the corresponding phosphate. It represents the coupling of three polymer chains. The resonance at 5.1 ppm appears consistent with another dialkyl substituted phosphate of the form $H(O=P)-(OR)_2$ and, thus, is associated with the coupling of two polymer chains. The observation that the principal species associated with the signal at 4.0 ppm in the 7033 sample is completely extracted suggests this resonance is associated with the coupling of two copolyester elastomer chains.

There is some discrepancy between the results of this study and the results of Aharoni et al., who studied the reaction of PET with TPP.⁹ The primary species reported in their study for PET melt extruded in the presence of TPP is diphenyl phosphate (DPP), which is the by-product of the chain extension reaction. This material has a chemical shift of 0.1 ppm and a J_{PH} on the order of 740–750 Hz. We see very little evidence of this product in our materials; however, this does not mean that this reaction has not occurred. Our processing conditions possibly result in the further reaction of the DPP if it forms. DPP is reported to undergo similar exchange reactions as TPP, although at a much slower rate.⁹ In light of this possibility, chain extension could be present in our materials which is not visible in the ^{31}P -NMR spectra of the final materials. Future research, where materials are studied as a function of the different processing conditions, will illuminate whether this occurs in the polyester blends. Nevertheless, the presence of signals in the -10 to $+10$ ppm region is representative of the coupling of the different polymer chains. These couplings enhance the compatibility of the polymers and result in the improved physical properties of the blends.

Mechanical Properties

The mechanical properties of select formulations of PET and its blends with polyester elastomers were investigated. In addition to the blended formulations, mechanical property measurements were also conducted for PET samples molded from pellets as received (Eastman Kodak) and for high-impact-strength PET (Rynite SST, DuPont) also molded

from the pellets as received. The properties investigated include impact strength, tensile, and flex modulus properties described below.

Notched Izod Impact Strength

The impact strength was measured by two methods: the Izod pendulum and the constant velocity dart (Rheometrics). The notched Izod impact results of the different PET formulations at room temperature are shown in Table III. PET molded from the pellets as received had an impact strength of 16 J/m. Addition of Mistron vapor talc raised the impact strength only slightly to 25 J/m (Formulation 1, Table III). However, addition of 22 to 23% glass with and without TPP raised the impact strength values to 66–68 J/m (Formulations 2 and 3, Table III). Further improvements of impact strength were accomplished by blending with polyester elastomers. The addition of copolyester 5526 at 80/20 and copolyester 4074 at 70/30 PET/copolyester ratios improved the impact strength only marginally to 26–27 J/m (Formulations 4 and 10, Table III). But the addition of the copolyester at 70/30 ratio and the incorporation of 23.1% chopped glass fiber raised the impact strength value to 177 J/m (Formulation 12, Table III). A more dramatic improvement in impact strength to 206 J/m (Formulation 6, Table III) was obtained when TPP was added to the PET blend containing copolyester 4074 and chopped glass.

The most dramatic improvement of impact strength to 973 J/m was obtained when a core/shell polyester consisting of poly(butyl acrylate) and poly(methyl methacrylate) was added to PET at a ratio of 65/35 by weight (Formulation 8, Table III). Addition of glass to the above blend lowered the impact strength to 124 J/m (Formulation 9, Table III). Reducing the polyacrylate concentration in PET from 65/35 to 80/20 drastically reduced the impact strength to 47 J/m (Formulation 7, Table III).

Impact Strength at Low Temperatures

The notched Izod impact strengths of some of the PET blends were determined at 0°, –15°, and –30°C. The results are shown in Table IV. The impact strength of PET by itself was hardly affected by the low temperature. This result is expected since PET has a glass transition temperature at about 80°C. Hence, even at room temperature, the amorphous region of PET is already in the glassy brittle state, and the impact strength of the polymer is dictated by the crystalline phase. The impact strength of PET containing glass fiber was higher than that

of pure PET at all temperatures. Again the impact strength of this polymer composite was not affected by low temperature. The commercial high impact strength PET (Rynite SST) contains about 30% glass fiber and an unknown concentration and type of an impact modifier. The impact strength of this polymer decreased gradually with temperature as seen in Table IV. A similar decrease of impact strength with temperature is observed for the PET containing the copolyester and glass. The most dramatic change in impact strength with temperature occurred for the PET containing the poly(butyl acrylate)–poly(methyl methacrylate) core/shell polymer. The extremely high-impact-strength values of 973 and 887 J/m measured at room temperature and 0°C for this polymer blend dropped down to 89 and 58 J/m at –15 and –30°C, respectively. Differential scanning calorimetry (DSC) curves show that the polyacrylate has a glass transition temperature (T_g) between 0 and –10°C.

Impact Strength Measured by the Constant Velocity Dart Method

The constant velocity dart measurements were performed using the Rheometrics instrument. The dart speed can be adjusted to values between 0.01 to 12.67 m/s. The mode of deformation of the tested sample is biaxial bending and the mode of failure is yielding and breaking. Three speeds were chosen for the investigation of the impact strength of eleven PET formulations, namely, 6.7, 0.67, and 0.067 m/s. Typical force versus travel and energy versus travel curves obtained by this method are shown in Figure 8. For each sample, the total energy, the total travel, and the ultimate force were obtained from plots similar to those shown in Figure 8 and are listed in Table V for the three dart speeds of 6.7, 0.67, and 0.067 m/s.

For PET, the impact strength, as measured by the total energy needed to break the sample, was 1.33 J at 6.7 m/s. As the dart speed was decreased, the sample showed higher impact values of 1.84 J at 0.67 m/s and 2.34 J at 0.067 m/s. As seen in Table V, the increase in impact strength was the result of the increase in force required to break the samples at those low speeds. The impact strength of PET increased to 2.3 J when 23% chopped glass fiber was added to it. Additional improvements in impact strength to 3.4–3.6 J were obtained when TPP is added to the PET containing the glass fiber. In this case, the higher impact strength resulted from the improvements in ultimate force and total travel.

Blending of PET with 19.4% copolyester 5526 actually reduced the impact strength to 0.34 J at 0.067 m/s dart speed. The impact strength of the blend rose to 1.78 J when TPP was added. High impact strength values of 7.9–9.8 J were obtained by blending with 22.4% copolyester 4074, 22.4% glass fiber, and 2.2% TPP. These impact strength values are comparable to those of the commercial high impact strength PET.

The highest values of impact strength were obtained from blends of PET with high concentrations of poly(butyl acrylate)–poly(methyl methacrylate) core/shell polymer. Blends of PET containing 25% acrylate had high impact strength values of 11.8 and 7.12 J at dart speeds of 0.067 and 0.67 m/s, respectively. Lower impact strength of 2.31 J was measured for the blend at dart speed of 6.7 m/s. Appreciably higher impact strength values were obtained when TPP was added to the blend. The blend of PET with the highest impact strength values of 25.5–27.9 J was obtained when the concentration of the acrylate was raised to 33.7%. From the data in Table V, it can be concluded that the very high impact strength of the PET–acrylate blends is the result of high strain to failure values. This is an indication of the excellent compatibility of these two polymers in forming the blends. Comparison of the results of the notched Izod impact strength (Table III) and the 6.7 m/s constant dart velocity impact (Table V) exhibits a good correlation between the two measurements as seen in Figure 9.

Tensile and Flexural Properties

The peak and ultimate (break) tensile stress, tensile strain, and the flexural modulus of the PET and its blends with polyester elastomers were obtained using the Instron tester at a crosshead speed of 5.08 mm/min. The results are shown in Table VI. The PET exhibits very high ultimate stress values of 63 MPa and an ultimate strain value of 2.9%. The flexural modulus of the polymer is 3500 MPa. Higher values of ultimate stress to 98 MPa and flexural modulus to 6700 MPa were obtained when 23% glass fiber was incorporated into the polymer. However, ultimate strain dropped to 1.4% for this composite. Addition of 2.2% TPP to the PET–glass fiber composites improves both the ultimate stress and strain values. Blending with other elastomers to obtain high impact strength resulted in lower peak and ultimate stress values and lower flexural modulus values. However, as seen in Table VI, all the blends had relatively high peak stress (38–64 MPa), flexural

modulus (1800–3700 MPa), and ultimate strain (2.0–15%).

Environmental Stress Cracking

The environmental stress cracking of six PET formulations was investigated using the elliptical bending apparatus.³ In this apparatus, a gradually increasing strain is experienced by the sample in going from one end to the other. The following solvents were investigated for their effects on cracking the polymer samples under stress: toluene, acetone, methanol, ethylene glycol, monoethanol amine, *n*-heptane, and ethanol. The PET formulations investigated were amorphous PET, commercial high-impact strength PET (Rynite SST), and Formulations 2, 6, and 8 of Table III. The amorphous PET exhibited cracking at 0.68% strain in toluene, 0.72% in acetone, 0.70% in methanol, 0.98% in ethylene glycol, 0.99% in monoethanol amine, and 0.80% in heptane. The commercial high impact strength polymer showed no cracking in any of the solvents at strain levels up to 1.85%. Similarly, the glass fiber filled PET (Formulation 2, Table III) and the high-impact-strength formulations (Formulations 6 and 8, Table III) showed no cracking in any of the solvents up to a maximum strain level of 1.96%. Hence, crystalline PET and rubber modified PET formulations have good resistance toward stress cracking by solvent.

PET Formulations Based on Recycled Resins

In this last section of the paper, we will investigate properties of glass-reinforced engineering resins formulated with recycled PET and employing the high impact modifier package we developed. To start, we investigated resins based on virgin PET. The first formulation contained the copolyester aromatic phosphite impact modifier package, a small concentration of dilauryl thiodipropionate antioxidant, and 45 phr of $\frac{1}{8}$ in. chopped glass fiber (Table VII). The resulting material had an excellent notched Izod impact strength of 214 J/m but a low heat deflection temperature of 99°C. It was suspected that the low heat deflection temperature was due to incomplete crystallization during injection molding of the test bars. A differential scanning calorimetry run confirmed our suspicion. As seen in Figure 10, the sample exhibited a large crystallization peak at 108°C, which is about 40°C above its glass transition temperature. The sample heating rate, in this case, was 10°C/min. The samples exhibit a melting point at

259°C and recrystallizes upon cooling from the melt at 203°C.

We investigated the use of several organic and inorganic additives to enhance the rate of crystallization of PET. We found that a small concentration of talc (Mistron Vapor) is effective in enhancing the crystallization rate. Addition of 5 phr talc to the PET formulation (Table VII, Formulation 2) increases the heat deflection temperature to 158°C; however, the impact strength is reduced to 110 J/m. Both properties indicate higher sample crystallinity. DSC study of the injection molded sample containing the talc is shown in Figure 11. The heating curve does not show any crystallization occurring above the glass transition temperature. The cooling curve shows a recrystallization peak temperature at 212°C, 9°C above the recrystallization temperature of the sample without the talc.

This formulation of high-impact-strength PET containing the impact modifier package and talc as a crystallization rate enhancer was used to investigate the properties obtainable from recycled PET. Two grades of the recycled resin were available to us from soft drink bottle regrind: a clear resin and a green resin both in chip form. The molecular weights M_w of the two grades were determined. The results showed that the ratio of the M_w recycled/ M_w virgin is 0.94 for the clear grade and 0.92 for the green. Substituting the green grade for virgin resin in the high impact strength formulations, shown in Table VII, resulted in little effect on either the heat deflection properties or the impact strength.

Substitution of poly(butyl acrylate-methyl methacrylate) core/shell polymer for copolyester elastomer is advantageous from material cost considerations. However, a partial substitution is favored in order to maintain good low temperature properties. In the fourth formulation of Table VII,

we substituted two-thirds of the copolyester elastomer with the core/shell elastomer. The impact strength of this resin is maintained at 107 J/m, and the heat deflection temperature remains high at 167°C.

The use of recycled PET to make engineering resins with excellent properties is feasible. The above formulations are only examples of the use of a new compatibilizer technology in order to produce usable high-quality resins from recycled plastics.

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