

Mechanical, Thermal, and Structural Characterization of Poly(ethylene terephthalate) and Poly(butylene terephthalate) Blend Systems by the Addition of Postconsumer Poly(ethylene terephthalate)

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ABSTRACT: The focus of this study was mainly on the use of scrap poly(ethylene terephthalate) (PET) in poly(butylene terephthalate)-rich blend systems. A good combination of tensile and impact properties was observed in the newly formed blend system with scrap PET. The morphology depicted controlled and well-dispersed phases. The thorough mixing of the constituents was observed in the thermal study. For this innovative blend system, an attempt to correlate the

mechanical, thermal, structural, morphological properties and the chemistry of the blend system seemed to be technoeconomical. This study contributed to the recycling of waste material. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 928–934, 2010

Key words: blending; differential scanning calorimetry (DSC); extrusion; mechanical properties; recycling

INTRODUCTION

Polymer blending is an established technique in the field of polymer technology. Poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) blends have the advantages of the low cost of PET and the rapid rate of crystallization of PBT. PET and PBT belong to a similar family of aryl groups and form stable blends without the need for a compatibilizing agent, although there is a large difference in their crystallization rates.

The growing end-use applications of polymeric materials have been witnessed by all industrial sectors in the last 2–3 decades. The trend continues today. Traditional materials are speedily being replaced by advanced plastics and new-generation polymeric materials for reasons such as higher strength-to-weight ratios, cost effectiveness, and comparative ease in processing. In polymer synthesis, the blending of the constituents is a versatile technique of designing tailor-made materials and gaining the added advantage of the superiority of the properties. In this study, scrap PET was used as one blend constituent. For the sustainable growth of the food and beverage packing industries, the recycling of PET is highly recommended. This will also contribute to the environmental aspect. This dual purpose will thus be

served by the creation of blends with recyclable PET materials. The detailed investigation of this system helped in the development of a scientific and technical base for various engineering applications. It also helped in the development of the interrelationship between the structural, mechanical, thermal properties and the chemistry of the polymer blends.

Various researchers have studied the PET/PBT system. Mishra and Deopura¹ studied the rheological behavior of PET/PBT blends and correlated the viscosity with composition and also predicted the theoretical compatibility of the system using interaction parameters and the free-energy-of-mixing approach.² The detailed characterization of basic PET/PBT blend systems was carried out by Arvinthan and Kale.³ They unveiled data of the systematic variations of properties with composition for PET/PBT blends.

A detailed chromatographic investigation of PET/PBT blends with the addition of triphenyl phosphate was done by Jacques et al.,⁴ who reported the molecular weight increment. In view of the use of recycled PET materials, Chaudhari and Kale⁵ studied the impact modification of scrap PET by a polyolefinic elastomer with poly(ethylene-co-acrylic acid) as a compatibilizer and reported an improvement in the impact properties. Xanthos and Patel⁶ also studied the recycling of PET using additives such as unmodified and maleated polyolefin elastomers and styrene-olefin block copolymers for modifying the properties of the waste PET.

Oromiehie and Mamizadeh⁷ studied the recycling of PET beverage bottles using polypropylene

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functionalized with maleic anhydride as a modifier, and an improvement in the properties were reported. Evstatiev et al.⁸ studied microfibrillar-reinforced composites of low-density polyethylene (matrix) and recycled PET (reinforcing material). The impact strength of low-density polyethylene was enhanced by 50% after reinforcement with recycled PET.

The systematic study of virgin PET and PBT has been done by various researchers.^{3,9} They have reported improved properties in blend systems with more than 40% PBT. The purpose of this study was to further extend this research by the addition of postconsumer PET in different proportions and by the correlation of the mechanical, thermal, and structural properties of the newly formed blend systems. Such a study has not yet been reported in the literature. This study was also useful for maintaining the ecological balance and for taking into account the environmental aspects.

EXPERIMENTAL

Materials

Commercial molding-grade PET was supplied by ASPET Edge (South Asian Petrochem, Ltd., Haldia, WB, India). PBT was supplied by BASF Ultradur (Kuantan, Malaysia) and was Ultradur B 2550 grade.

The postconsumer PET used in this study was in the form of PET bottle grinding scrap (natural) and was supplied by Shubham Trade Link (Mumbai, India).

Blends

Samples from four different blend systems were prepared for detailed analysis, as shown in Table I.

Out of these four blend systems, samples of two blend systems were prepared with a virgin PET and PBT blend (40/60) and postconsumer PET (blend system F), whereas the sample from the remaining blend system was prepared with a virgin PET and PBT blend (20/80) and postconsumer PET (blend system H). Samples of all of the blend systems were made by melt extrusion with a single-screw extruder ($\Phi = 25$ mm, where Φ is the diameter of screw, length/diameter ratio = 264). The constituent materials were thoroughly mixed and dried at 110°C for 4 h in an air-circulating oven before melt extrusion. The temperature profiles maintained during the

extrusion were 210°C for zone 1, 220°C for zone 2, 240°C for zone 3, and 260°C for the die zone. The screw speed was maintained at 40 rpm. The different blend systems and corresponding blend compositions are shown in Table I.

The extrudates were water-cooled and pelletized. These pellets were again dried before the injection molding in the air-circulating oven for 110°C for 2 h. Standard ASTM tensile and impact samples were molded with an Omega 80A 80W Ferromatic Milacron India (Milacron, Ahmedabad, India) hydraulic injection molding machine. The temperature profile was 215, 225, 250, and 265°C for zone 1, zone 2, zone 3, and the nozzle zone, respectively.

ANALYTICAL METHODS

Mechanical characterization

The tensile strength at yield (23°C) and elongation at break were measured with a universal tensile testing machine (model 8502, Instron, USA) according to ASTM D 638. The crosshead speed maintained was 50 mm/min.

The Izod pendulum impact resistance of the blend system was measured with a standard pendulum-type hammer mounted on a standard machine (International Engineering Industries India) according to ASTM D 256. A micrometer-operated notch cutter (Veekay Test Lab., Mumbai, India) was used to cut the standard-sized notch.

Thermal characterization

Differential scanning calorimetry (DSC) was used to determine qualitative and quantitative information about the physical and chemical changes that involved endothermic or exothermic processes or changes in heat capacity of the samples. The melting and crystallization and related thermal studies of the blend were done with DSC (9PT24 M, Mettler-Toledo, Albstadt, Germany). The scan procedure adopted for thermal analysis included the heating of the sample from 25 to 260°C at a rate of 10°C/min followed by the quenching and reheating of the sample at the same rate up to 260°C during the second scan.

Morphological characterization

Scanning electron microscopy was carried out with a Jeol (Tendo, Japan) model 6380A instrument. Samples were fractured under cryogenic conditions for the observation of the cross section. Samples were observed after platinum coating before installation in the scanning electron microscope chamber.

Fourier transform infrared (FTIR) studies

Qualitative chemical analysis and the identification of the functional groups in the blend sample were done

TABLE I
Blend Systems and Corresponding Blend Compositions

Sample	Blend system	Blend composition (w/w)
1	6S4F	60% scrap + 40% F
2	9S1F	90% scrap + 10% F
3	6S4H	60% scrap + 40% H
4	9S1H	90% scrap + 10% H

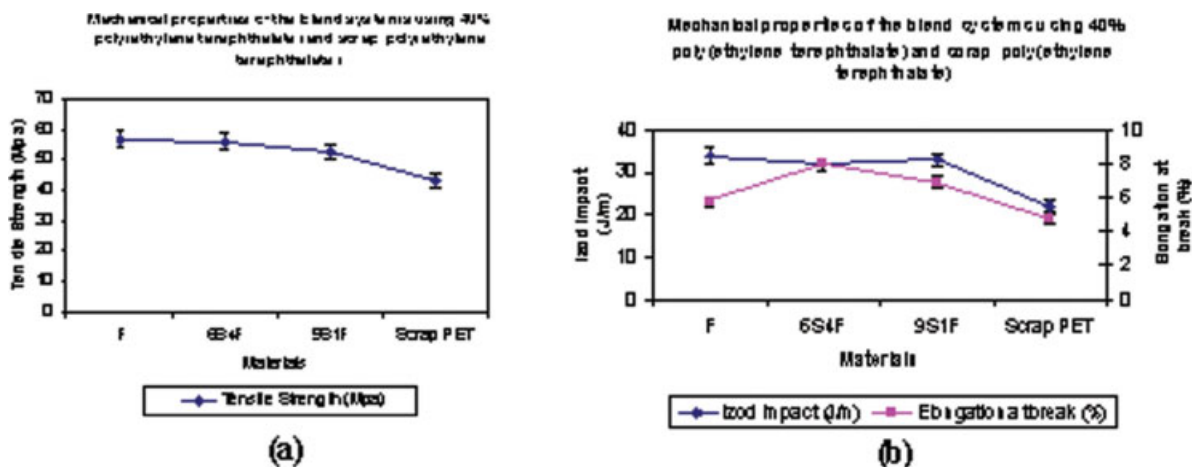


Figure 1 Mechanical properties in the blend system with F and scrap PET. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

with a PerkinElmer (Waltham, MA) FTIR spectrometer. Solid sample material was used for FTIR studies of the blend systems. A background scan was taken with KBr. The IR spectra were measured in transmission mode.

X-ray diffraction (XRD) studies

The crystallinity of the blend materials was evaluated with a PANalytical (Almelo, Netherlands) X-ray diffractometer with a copper anode with $K\alpha$ radiation. XRD of the blends and pure materials were recorded at room temperature over a range of 2θ from 10 to 120° with a 0.01° step size for the scan.

RESULTS AND DISCUSSION

Mechanical properties

The mechanical properties of the constituent blend systems F and H, which were also the results of our

previous study,⁹ were compared with the mechanical properties of the newly synthesized blend systems with postconsumer PET. An enhancement in the mechanical properties of the scrap PET was observed in both the F and H blend systems. It was clearly observed in the graphical behavior, which is shown in Figures 1(a), 1(b), 2(a), and 2(b). Compositional dependence was observed in the mechanical properties of the newly formed blend systems. Among the blend systems with F and H, superior mechanical properties were observed in blend systems with F (i.e., blend systems 6S4F and 9S1F). The recorded value of the tensile strength of 6S4F was almost equal to that of its F constituent system. The blend system 9S1F, with 90% scrap PET, showed the mechanical properties almost fully declining toward the constituent blend system F. It was superior to the 6S4H and 9S1H blend systems. The tensile strength of 9S1H was recorded to be slightly lower than the scrap PET, whereas the blend system showed a higher Izod impact strength than scrap PET. The crosslinking of

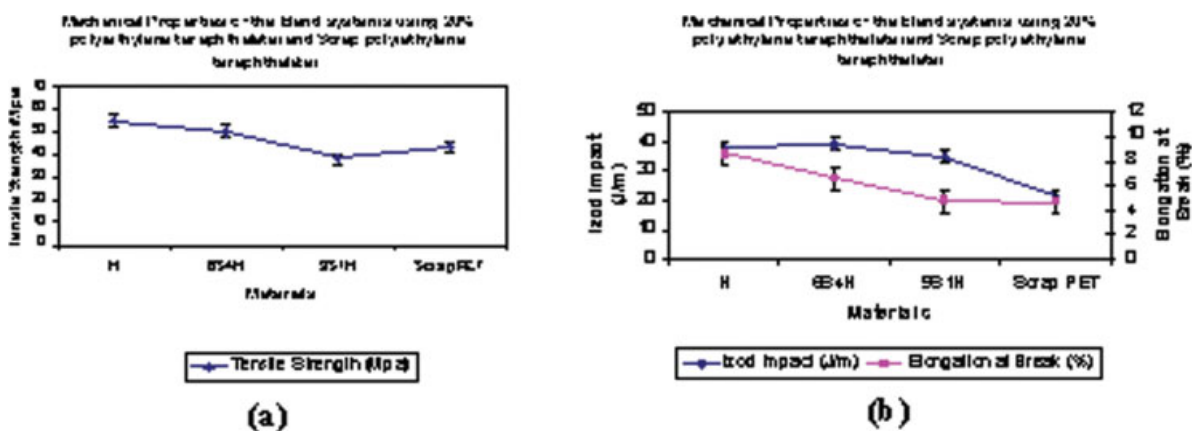


Figure 2 Mechanical properties in the blend system with H and scrap PET. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

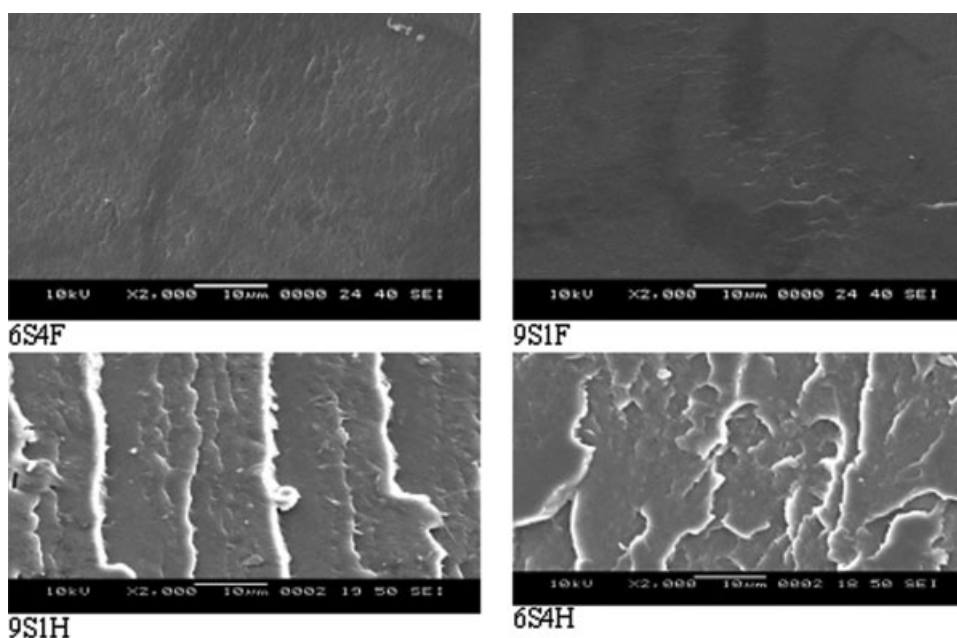


Figure 3 Microphotographs of the blend systems with scrap PET.

the polymeric chains in either chemical or physical form could be attributed to these enhanced mechanical features of the 6S4F blend system. The maximum cocontinuity of the phases and the related fine morphological structure of the blend systems 6S4F and 9S1F were also correlated with these enhanced mechanical characteristics.

Microstructural properties

Figure 3 shows the microphotographs of the newly formed blend systems with scrap PET along with F and H, respectively. A lamellar structure is clearly evident in this figure. A homogeneous and uniform morphology in all of the blend systems supported the miscibility of the components of the blend systems and was, thus, in agreement with the thermal studies. The very fine lamellae were observed in the blend system with scrap PET and F, as compared to the blend system with scrap PET and H. The superior mechanical properties of 6S4F and 9S1F were attributed to this appearance. The finer dispersion in this blend system thus led to the reduction in the interfacial tension by stabilization of the morphology. The maximum cocontinuity occurred when the distinction between the dispersed and matrix phases vanished. The cocontinuity contributed to the synergism of properties in the blend systems.¹⁰ Straight and longer lamellae were observed in the 9S1H blend system. The slightly poor tensile strength of the blend system 9S1H was correlated with this morphology. Comparatively shorter lamellae with nonuniform geometry were seen in the 6S4H blend system. The behavioral tendency of polymeric materials when subjected to tensile

loading is commonly expressed in two stages.¹¹ In the first stage of initial low loading, molecular chain sliding occurs, whereas, molecular chain breaking or intermolecular chain bridging occurs at higher load conditions. The ductile nature of the 6S4F blend system, indicated in Figure 1(b), was due to the occurrence of this two-stage process of deformation. The decrease in the values of percentage elongation in the remaining three blend systems clearly indicated the absence of the first stage (chain sliding) of mechanical deformation.

Thermal studies

Thermal analysis was performed to reveal the thermal transition of the blend systems. The DSC thermograms of all of the blend systems with scrap PET were reported with the single T_g value, which indicated that the constituent materials were miscible under amorphous conditions. The relevant data are shown in Table II. These values were compared with the

TABLE II
 T_g Values of the Constituent Materials and the Blend Systems with Scrap PET

Sample	Blend system	T_g (°C)
1	Scrap PET	75
2	Virgin PET	80
3	Virgin PBT	65
4	F	67
5	H	66
6	6S4F	72
7	9S1F	69
8	6S4H	60
9	9S1H	69

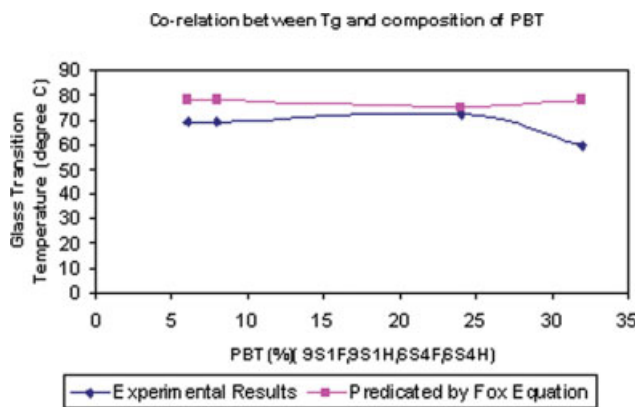


Figure 4 T_g observed and predicted by the Fox equation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

glass-transition temperatures (T_g 's) of the constituent materials. The glass transitions of all of the blend systems showed compositional dependence and were well in accordance with the Fox equation:¹²

$$1/T_g = (W_{\text{PET}}/T_{g\text{PET}}) + (1 - W_{\text{PET}})/T_{g\text{PBT}} \quad (1)$$

where T_g is the glass-transition temperature of the blend and W_{PET} , $T_{g\text{PET}}$, and $T_{g\text{PBT}}$ are the weight fraction of PET and the glass-transition temperatures of PET and PBT, respectively.

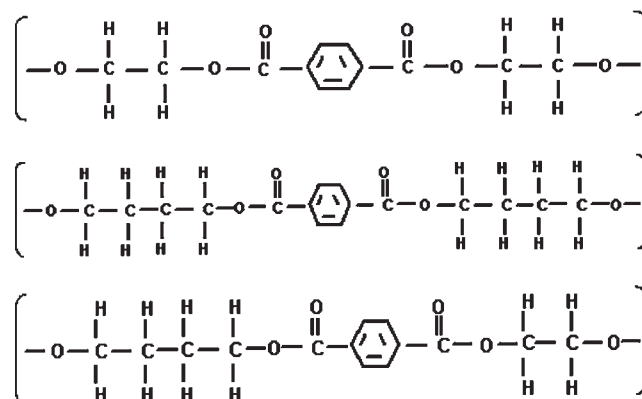
T_g decreased with increasing content of PBT. Figure 4 indicates the correlation between T_g and the composition of PBT. The T_g values from the experimental results obeyed eq. (1) satisfactorily. However, T_g of 6S4H deviated slightly more from its predicted result. The reduced specific interaction among the constituents might have resulted in a higher chain mobility. The various other thermodynamic entities from the DSC thermographs were not evaluated. DSC as a method of crystallinity determination is reliable for providing accurate crystallinity values for materials in an equilibrium state but fails for materials in a nonequilibrium state.¹³ Therefore, the crystallinity measurement and crystal morphological studies were carried out with the XRD technique.

FTIR studies

We detected and measured molecular vibrations by passing a beam of IR through the sample material. The transmitted light provided a wealth of information regarding the structure of the organic compound.

At the processing temperature of the blend systems, a possible chemical interchange reaction among the constituent materials was as shown in Scheme 1. The preferential formation of the block copolymers may have occurred in the initial stage of the interchange reaction. With the progress in the reaction, the block length might have been reduced, and further, random

copolymers may have prevailed in the final stage of the reaction.¹⁴ The results of FTIR alone have their own limitations for predicting the complete chemical compositional details. However, Figure 5 shows the characteristic IR spectra of the blend systems to identify the functional groups. The peak position was plotted versus the percentage transmittance. Sharp bands with high intensity were observed in the 6S4F blend system. The C—H stretching of the aromatic ring was confirmed at 3054 cm^{-1} . Similarly, the C—H stretching of the methyl group was confirmed at 2904 and 2964 cm^{-1} . Despite the use of scrap material with inferior mechanical properties, the superior mechanical properties of the newly formulated blend system was attributed to the formation of a certain amount of the block copolymers from the mix.¹⁵ For the aromatic compounds, the most characteristic C=C stretching bands were at 1600 , 1580 , 1500 , and 1450 cm^{-1} .¹⁵ The existence of this stretching was also confirmed in this study for all of the blend systems with a slight positive shift, that is, with peak values of 1613 , 1578 , 1505 , and 1452 cm^{-1} , respectively. The most prominent peak positions at 1719 cm^{-1} in 6S4F and 1720 cm^{-1} in the remaining blend systems were assigned to C=O stretching of the ester group. Because of the conjugation of the benzene ring, the peak position shifted slightly to a lower value than the standard assigned position of 1735 – 1750 cm^{-1} . C—O stretching was identified at 1102 and at 1264 cm^{-1} in these blend systems. The region 730 – 770 cm^{-1} was very helpful in identifying the type of substitution on the aromatic ring.¹⁶ A sharp peak at 727 cm^{-1} was prominent in these blend systems, which was indicative of monosubstitution. The peak positions at 1370 and 1454 cm^{-1} represented the gauche conformation of CH_2 wagging and the ethylene glycol segment, respectively.¹⁷ The peak position 1370 cm^{-1} was confirmed in 9S1F, 9S1H, and 6S4F, whereas the peak position at 1454 cm^{-1} was evidenced in all of the newly formulated blend systems. This relaxed form was correlated with the amorphous



Scheme 1 Possible chemical interchange at the processing temperature.

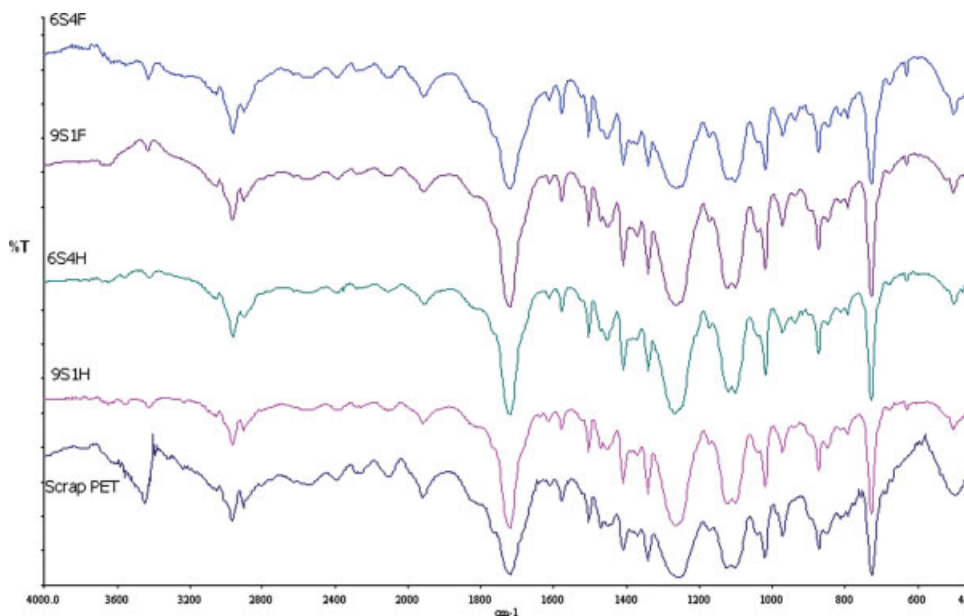


Figure 5 FTIR spectrographs of the blend systems and scrap PET. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

halo of the XRD diffractographs of the newly formulated blend systems. The peak position at 3430 cm^{-1} , which corresponded to O—H stretching, was prominent in scrap PET and did not appear in the newly formed blend systems. The overall inferior properties of the scrap PET were mainly due to recycling and allied thermal degradation.¹⁷ The presence of the contaminants and adhesives, moisture, and so on generated acidic compounds was responsible for catalyzing the hydrolytic ester bond cleavage at the processing temperature. This resulted in lowering of molecular

weight along with increase the carboxylic end groups.¹⁸ The decrease in T_g of scrap PET as compared to virgin PET was correlated with this result. Extra peaks beyond the parent peaks were not observed in either blend system.

XRD studies

XRD crystallographs of the blend systems and the constituent materials are depicted in Figure 6. The semicrystalline nature of the F and H systems was

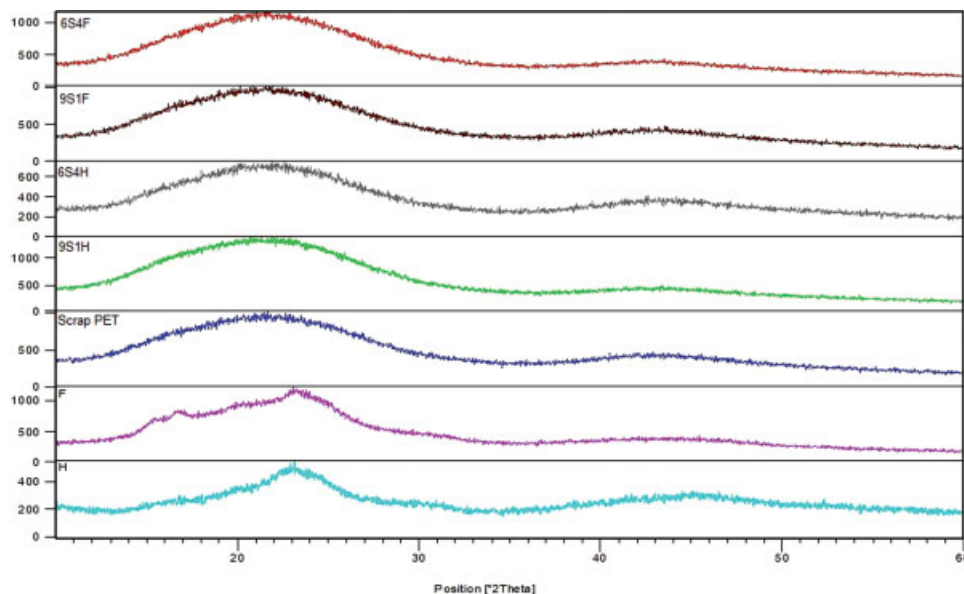


Figure 6 X-ray crystallographs of the newly formed blend systems and the constituent materials. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

recorded. The apparent degree of crystallinity was calculated from the ratio of integrated intensities under the crystalline peaks to the integrated total intensities.¹³ The crystallinities of F and H were found to be 32 and 10%, respectively. The amorphous nature of the material was reported in all of the newly formed blend systems. The process of crystallization was accompanied by increase in the density of the materials.¹⁹ The added advantage of reduced density, along with superior mechanical properties, was observed in this study. The unorganized chains in the newly formulated blend systems with scrap PET resulted in the halo diffractographs. Branching or crosslinking and conformational changes from trans to gauche form in the polymer chains might have resulted in the poor organization of the chains. The improvement in the mechanical properties was attributed to the effect of branching or crossing.²⁰ This study showed that the mechanical properties of the scrap PET were enhanced with F and H.

CONCLUSIONS

The enhancement of the mechanical properties of the scrap PET by the addition of the PET-PBT blend with 40 and 20% PET, respectively, might have been due to the formation of the block copolymerization and/or branching and partial crosslinking of the chains.¹⁹ A good combination of tensile strength and impact strength was observed in the newly formed systems. The use of scrap PET, even up to 90% in the virgin blend system (F), was found to be technoeconomically beneficial. The moderate proportion of the use of the scrap in the H blend system came out with encouraging results. However, with the increase in scrap PET in H (up to 90%), the tensile strength was slightly deteriorated compared with scrap PET. However, the system showed a higher

Izod impact strength than scrap PET. The complete correlation of the various properties was established in this study. This study on the use of recycled material strongly helped to move research ahead in the direction of ecological balance.

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