

Thermal and Morphological Behavior of Irradiated Composite Materials Based on Injection-Moulded Recycled Polyethylene Terephthalate

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ABSTRACT: The effect of gamma irradiation and short glass fiber (SGF) on the thermal and morphological behavior of the recycled poly (ethylene terephthalate) (rPET) in the presence of reactive additive (epoxy resin, 2 wt %) has been investigated. Characterization of the resulted composites to evaluate the effect of incorporation the SGF and irradiation by means of differential scanning calorimetry, X-ray diffraction, thermal gravimetric analysis, and scanning electron microscopy (SEM). The results show that the SGF and epoxy resin behave as nucleating agents for the crystallization of rPET. A noticeable increase in the rPET thermal stability in the presence of both SGF and epoxy resin has been observed. Furthermore, the rPET melting

temperature (T_m) slightly decrease in the presence of the SGF and remains nearly constant with the incorporation of the epoxy resin. On the other hand, the rPET crystallinity percent (X_c) decreases in the presence of SGF and gamma irradiation. The SEM showed that a layer of epoxy resin was coated onto the SGF in the rPET matrix. This coating layer raises the interfacial shear strength between the fiber and polymer matrix and also increases with gamma irradiation. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 3974–3980, 2008

Key words: glass fiber; reinforced recycled PET; thermal and morphological properties

INTRODUCTION

Plastics, in the past few decades, have entered overwhelmingly and diffusely into our lives, being widely used particularly in the fields of packaging and building. This has caused increasing concern regarding the environment in relation to the problem of plastic waste disposal. The recycling of plastic waste coming from a separate collection of municipal solid waste can be a convenient way to solve the problem of land filling this large amount of material and has therefore become not only desirable but also increasingly mandatory.¹

In particular, polyethylene terephthalate (PET) is extensively used for the production of fibers, films, and bottles for water and other beverages (especially carbonated drinks) as well as containers for other edible products because of its combination of unique physical, mechanical, and permeant properties, as well as processability.² One way of the recycling process is by melting the milled bottles but in the course of this process, the properties of the material deteriorate because of the molecular chains degradation resulting from the high temperature, the presence of humidity, and contaminations.^{3–5}

An important application of recycled PET to be considered is to obtain reinforced composites. The use of reinforcement of polymeric materials by short fibers has grown rapidly over the past 30 years. The first polymeric composites to use chopped glass fibers were based on unsaturated polyesters and epoxy acrylate, but recently thermoplastics materials have gained acceptance.⁶ Many studies dealing with short-fiber reinforced engineering plastics, such as poly(ethylene terephthalate) (PET),⁷ polycarbonates,^{8,9} have been reported. Glass fibers are the most used reinforcing materials in structural reinforced thermoplastics. They have many desirable characteristics such as low cost, high tensile strength, high chemical resistance, and excellent insulating properties.^{10,11} As a consequence, composites based on thermoplastics and glass fibers have similar advantages.^{12–14} The mechanical properties of glass fiber reinforced thermoplastics are affected not only by the interfacial adhesion between glass fiber and polymeric matrix but also by the length and the diameter of the fibers as well as by their volume fraction, orientation, and distribution in the composite.^{15–19} Good interfacial adhesion is necessary to transfer the stresses from the polymeric matrix to the reinforcing glass fibers; however, the different hydrophilic/hydrophobic characteristics between the glass fibers and the thermoplastics result in poor interfacial adhesion and mechanical properties of the composites. Therefore, this situation needs to be controlled by coupling

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agents or reactive additives that are normally used to improve the adhesion between the fibers and the polymeric matrix such as epoxy resin.⁷

High-energy radiation is a well-known technique for modification of polymers. However, little work concerning the effects of irradiation on the properties of polymer blends has been done. Many polymer blends are immiscible on the molecular scale and form heterogeneous systems. There have been a few attempts to improve the miscibility by using radiation to modify of one or both polymers.^{20–22} Blends of HDPE, which easily crosslinks when exposed to radiation, and PET, which crosslinks at higher doses, due to the aromatic group, were irradiated and the effect of formation of the crosslinked copolymer was observed. Also, polymer was oxidized by irradiating in air, then heated to destroy peroxides formed by this irradiation and to form polar groups in the HDPE, and then extruded together with PET. The mechanical and thermal properties of these blends with the oxidized PET are presented.

The main purpose of this work is studying the effect of gamma irradiation and short glass fiber (SGF) on the thermal and morphological behavior of recycled poly (ethylene terephthalate) (rPET) in the presence a reactive additive (epoxy resin, 2%). The study has been carried out by differential scanning calorimetry (DSC), X-ray diffraction (XRD), thermo gravimetric analysis (TGA), and Scanning electron microscopy (SEM).

EXPERIMENTAL CONDITIONS

Materials

Most of the soft drink PET bottles used in Hungary are made of KOSA PET 1101 PET type ($M_n = 27$ kg/mol, $M_w = 65$ kg/mol, density 1.168 g/cm³). The melt flow rate (MFR) was 28.9 cm³/10 min measured by the ISO 1133 S standard at load 2.16 kg and 280°C, MFR (at identical conditions) is 33.8 cm³/10 min. The reactive additive applied was the epoxy resin of Ciba-Geigy, with a molecular weight approximately about 400 g/mol. The resin was dissolved in acetone 70 Vol % by spraying on the surface of the commingled composite partners then dried it at 80°C for 3 h to evaporate the solvent.

The glass fiber was an E-type short fiber from Zoltek Hungary, with length 10–15 mm and its diameter was 8 μm.

Processing of samples

The waste PET washed dried and chopped in particles of 4 mm main size dried again before use at 140°C for 5 h. The MFR of rPET was slightly more

TABLE I
Detailed Compositions of the Prepared rPET Composites

Sample code	Composition (PPh)			Irradiation dose (kGy)
	rPET	Glass fiber	Epoxy resin	
rPET	100	–	–	–
rPET _{irr}	100	–	–	5
rPET1	100	10	–	–
rPET2	100	20	–	–
rPET3	100	10	2	–
rPET4	100	20	2	–
rPET3 _{irr}	100	10	2	10
rPET4 _{irr}	100	20	2	10

than 100 g/10 min material. After mixing, the dry composites were irradiated by Co-60 gamma rays of 1.8 PBq gamma sources of the Institute of Isotopes and Surface Chemistry of the Hungarian Academy of Sciences, Budapest. The irradiation dose was 10 kGy and the dose rate is 1 kGy/h in air at ambient temperature. The extrusion is not homogenous, thus heating the free radicals may initiate bridge-formation reactions between the phases of recycled matrix and reinforcing fiber the temperature zones; 250, 255, 260, and 265°C and total dwelling time 150 s. This processing step was performed with a computer assisted Brabender twin screw extruder (Plasticorder PL2100).

The injection molding of the samples has been performed on an Arburg All rounder with computer assisted injection molding machine at conditions according to the ISO 527-2:1993(E) standard at 270°C (Table I). We must note that the rPET without additives was not injectable; because of the extremely low melt viscosity; and consequently those samples were press molded.

Thermo gravimetric analysis

The thermal properties of all composite were investigated by TGA under nitrogen atmosphere at flow of 20 mL/min of pure nitrogen gas and the heating rate was 20°C/min from ambient up to 600°C by TGA-50 system (Shimadzu, Kyoto, Japan).

Differential scanning calorimetry

A Shimadzu Type DSC-50 DSC system in nitrogen atmosphere was used in the temperature range from ambient to 300°C at heating rate of 10°C/min. The degree of crystallization of the composite was evaluated from the relative ratio of the value of fusion heat of the composite to the fusion heat of PET ($\Delta H_{\text{PET}} = 121.2$ J/g).²³

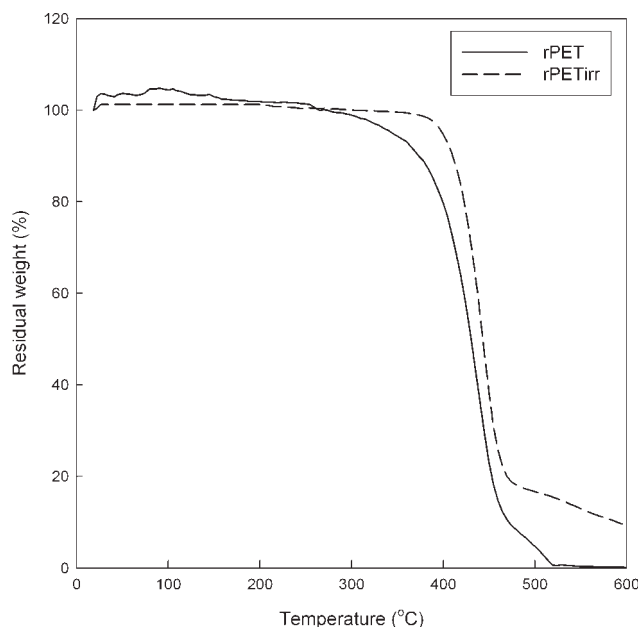


Figure 1 TGA degradation behavior curves for rPET and rPET_{irr}.

X-ray diffraction

Different samples were measured with a Bruker XRD (model; D8-advance), Germany. All the diffraction patterns were examined at room temperature and under constant operating conditions.

Morphological characterization

An ISM-5400 scanning electron microscope (SEM) (JEOL, Tokyo, Japan) was used for morphological observation of fracture samples in liquid nitrogen after vacuum coating with gold.

RESULTS AND DISCUSSION

Thermo gravimetric analysis

TGA is the most favored technique for comparing and ranking the thermal stability of the polymers. Figure 1 shows the TGA curves of unirradiated and irradiated rPET. In the TGA curves there is only one decomposition peak, a small initial weight loss between 100 and 300°C, which may be attributed to evaporation of water and the loss of dopant. The major weight loss observed between 300 and 500°C which may be explained to the decomposition of rPET backbone. It can be also noted that the thermal stability of rPET_{irr} was higher than rPET due to increase the crosslinking of the polymer matrix as a result of irradiation.

Figure 2 shows the TGA curves of rPET and its composites, the results are summarized in Table II. All composites has only one decomposition peak in

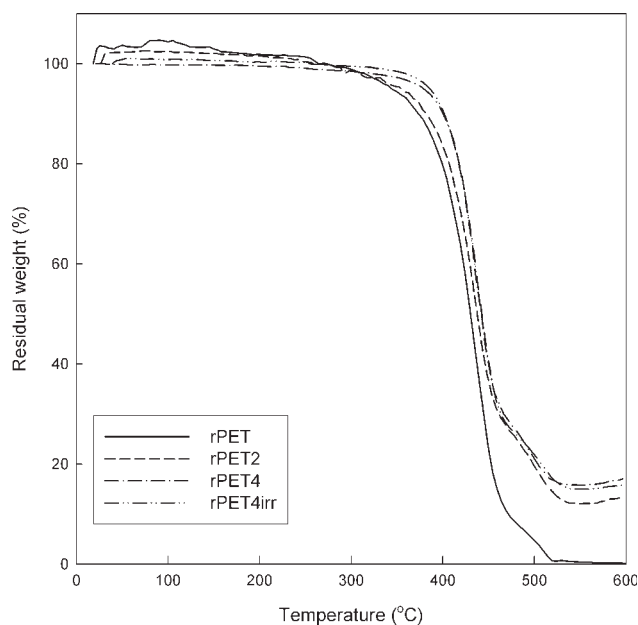


Figure 2 Effect of additive and irradiation dose on the TGA degradation behavior of recycled PET composites using 20% GF.

the TGA curves as aforementioned the given data shows clearly that rPET has the lowest thermal stability. The incorporation of the SGF into the composites improve its stability which increases with increasing the SGF content in the composite due to the high reinforcement of the polymer matrix by SGF to survive to the higher temperature.^{24,25} However, the maximum decomposition temperatures were observed for rPET1 and rPET2 which are 460 and 489°C, respectively, but for rPET2 is about 29°C higher than rPET1. On the other hand slightly increases in the thermal stability of rPET4_{irr} which may be due to occurrence of limit extent of the crosslinking of the loaded composites during its thermomechanical preparation.

It is also observed from the TGA analysis that, no residual was left for rPET while all rPET composites left a residue which increases with increasing the

TABLE II
Thermal Stability of rPET Composite at Different Compositions

Sample code	Temperature (°C) of different weight loss (%) (TWL %)							Residual (%)
	10	20	30	40	50	60	70	
rPET	372	398	411	422	430	436	444	0
rPET _{irr}	409	421	431	436	442	447	455	0
rPET1	381	406	420	430	440	446	460	9
rPET2	392	413	426	435	442	455	489	13
rPET3	398	415	425	434	440	448	458	17
rPET4	399	418	428	435	443	449	466	17.5
rPET4 _{irr}	400	417	426	435	444	450	468	15.8

crosslink formation in the composite. In this procedure the recycled postconsumer waste is mixed with some (10–20%) chopped glass fiber plus a modest amount of reactive additive (2% epoxy-resin) and subsequently a small gamma dose (10 kGy) is applied to initiate a good adhesion between the composite partners. These results can be explained by the strong nucleation ability of the rPET and epoxy resin on polymer matrix.

X-ray diffraction

XRD was used to characterize the crystallographic structure of rPET and the influence of both SGF and irradiation on the crystal structure of rPET. Figure 3 shows the XRD patterns of rPET, rPET1 and rPET2. From the patterns, a broad diffraction peak was observed at about $2\theta = 19^\circ$ for rPET. A slight but distinct shift of the peak position to higher angle was observed for rPET1 and rPET2 indicating the reduction of the lattice space. It can be also observed that the intensities of peaks have been reduced with line width broadening indicating the development of amorphisation. The intensity of rPET2 peak was lower than that of rPET1. These results show that the number of micro crystallites becomes smaller with increasing GF concentration and reduces the perfection of crystals.

The XRD patterns of rPET1, rPET3 and rPET3_{irr} composite is shown in Figure 4 to evaluate the effect of D411 and irradiation. It can be seen from the figure that the composites shows a peak lump between

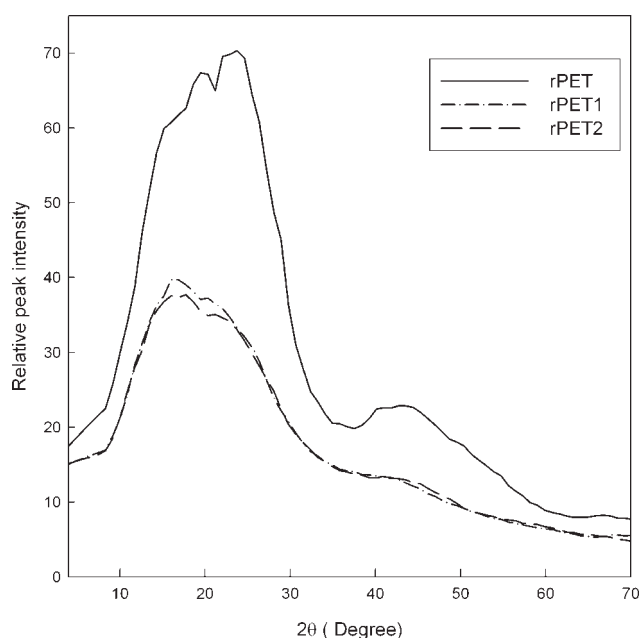


Figure 3 XRD pattern of rPET composites with different SGF ratios.

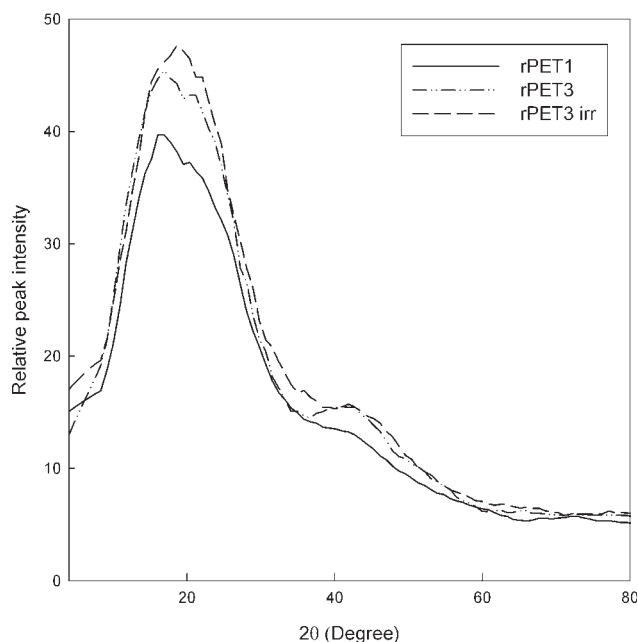


Figure 4 Effect of additive and irradiation on the XRD pattern of recycled PET composites.

19.5° and 16.9° , a distinct shift of the peak position to lower angle was observed for rPET3 and rPET3_{irr} composites which is associated with the increase the crystalline domain of rPET polymer matrix. The combination of rPET1 matrix with D411 increases the crystalline phase domain of the composite which more increases with irradiation (rPET3_{irr}). Also the intensity of the peak crystallinity increases in order of $rPET1 < rPET3 < rPET3_{irr}$. The change in the relative intensity and the shift of angular position can be explained by a change in lattice spacing.²⁶ The shifting in the diffraction peak position of the samples towards lower angle is because of developing the microstrain of rPET1 crystallites due to presence of D411 (rPET3) and irradiation (rPET3_{irr}).

Differential scanning calorimetry

The thermal properties of rPET and its composites were investigated via DSC and shown in Figures 5–7. The thermal parameter such as the glass transition temperature (T_g), the melting temperature (T_m), and the melting enthalpy (ΔH_m) obtained from the DSC studies are summarized in Table III. The results show that the T_m and T_g slightly decrease with increasing the SGF content in the rPET matrix. These results suggest that the SGF significantly affects the crystallization kinetics of the rPET matrix which agrees with the results obtained by Huda et al.²⁷ The nucleating effect of the glass fibers on the crystallization rate of rPET was demonstrated, moreover, these observations indicate that lower the T_g promotes a

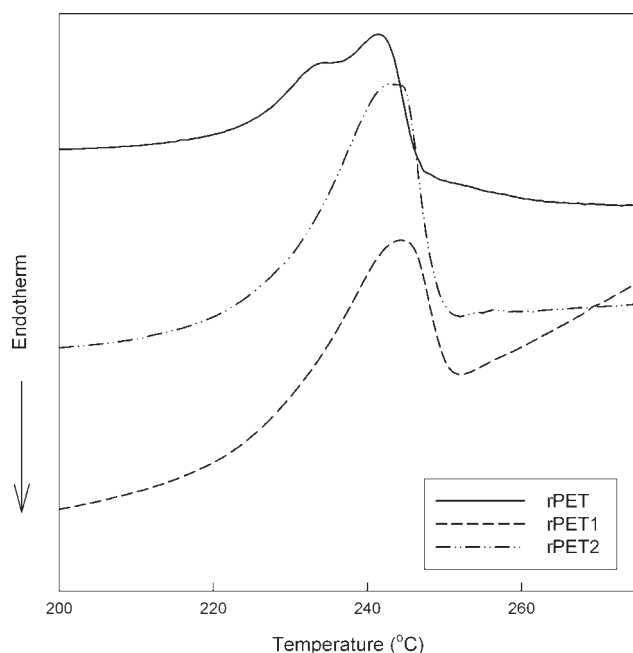


Figure 5 DSC thermographs of rPET composites with different SGF ratios.

change in the properties from hard and tough to soft and flexible.

It is possible to obtain the degree of the crystallinity ($X\%$) in the composite as the following: $X\% = \Delta H_m / \Delta H_m^o \times 100$; where: ΔH_m = experimental melting enthalpy (J/g) and ΔH_m^o melting enthalpy of a pure crystalline matrix; (121.2 J/g).²³ The data of ($X\%$)

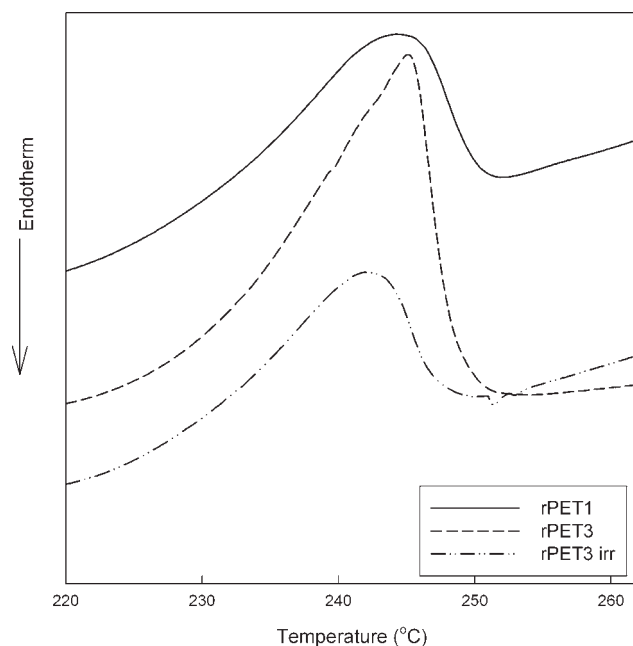


Figure 6 Effect of additive and irradiation dose on the DSC thermographs of recycled PET composites using 10% GF.

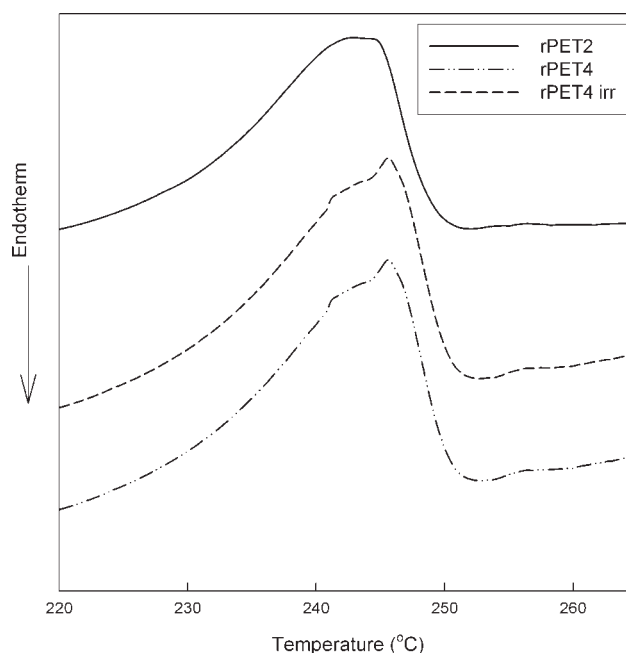


Figure 7 Effect of additive and irradiation dose on the DSC thermograph of recycled PET composites using 20% GF.

gives evidence the negative effects of SGF to the crystallinity of the composites which mainly provides the stiffness of a composite. Also the SGF hinder the diffusion and migration of rPET molecular chains to the nucleus surface of the composite. This can be explained that SGF acts as a heterogeneous nucleating agent for rPET.

Table III also shown that, the T_m of irradiated composite was lower than the unirradiated one. A decrease in the number of ties molecules of the amorphous regions and consequently weakens the interlamellar connections which result from the chain scission.²⁸ These changes could lead to the structural rearrangements to more defected crystallites with a probably smaller surface tension. The above thermal analysis data are in accord with the results obtained from XRD although the total content of crystal decreases.

TABLE III
Thermal Properties of Unirradiated and Irradiated rPET Composite at Different Compositions

Sample code	T_g (°C)	ΔH_m (J/g)	T_m (°C)	$X\%$
rPET	72.6	47.9	244.5	39.5
rPET1	68.2	38.3	243.5	31.6
rPET2	67.7	41.3	242.8	34.1
rPET3	68.5	39.9	244.2	32.8
rPET4	68.3	38.8	244.7	31.9
rPET3 _{irr}	68.5	37.7	241.8	31.1
rPET4 _{irr}	69.5	38.7	243.8	31.9

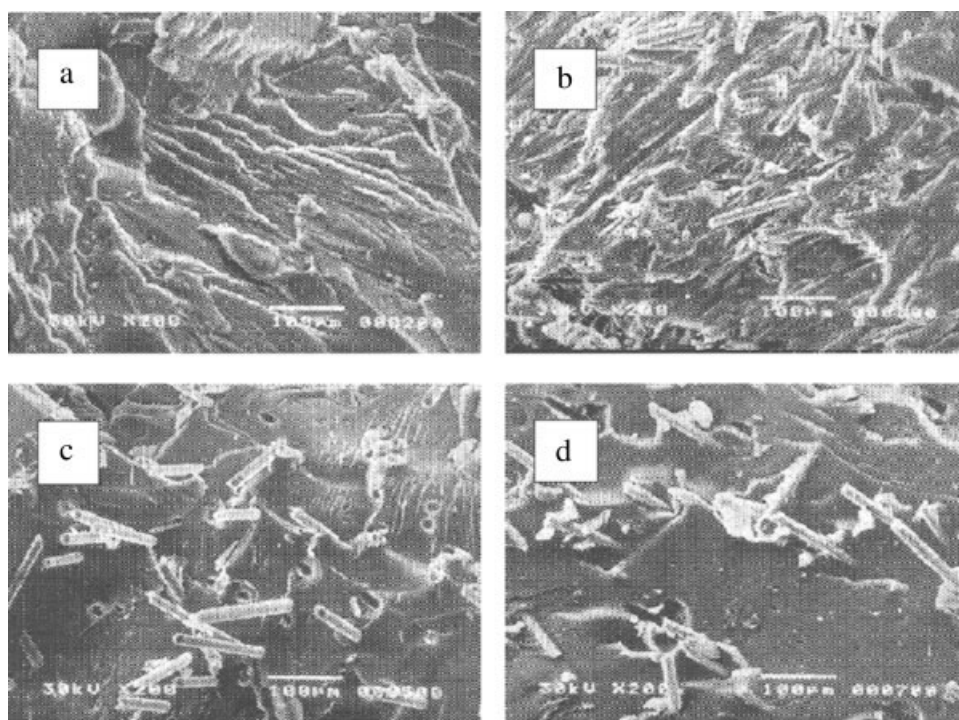


Figure 8 SEM micrographs of different rPET composites: (a) rPET; (b) rPET1; (c) rPET3, and (d) rPET3_{irr}.

Morphological structure

The morphology of the fractured surfaces of rPET, rPET1, rPET3, and rPET3_{irr} composites was investigated by SEM and shows in Figure 8. rPET specimen Figure 8(a) shows a relatively smooth topography. Incorporation of the SGF reduces the smoothness of rPET1 Figure 8(b), many fibers pulled-out but a relatively clean fiber surface appeared. The SGF were seen outside the fractured surfaces indicating that during the propagation, SGF are broken and pulled out the polymer matrix.²⁹ A higher magnification SEM micrograph of the interface shows that the glass fiber surfaces are clean but lack of the rPET matrix which indicates the low adhesion between them. The SEM studying of the fractured surfaces of rPET3 composites revealed less voids in the composite surface result from incorporation of D411 Figure 8(c). The effect of irradiation on the morphology of the hybrid composite is shown in Figure 8 (d). The micrograph indicates a smoother substrate may simply provide a more homogeneity; some of SGF are firmly adhered to the matrix, producing good adhesion result from irradiation. Consequently, a positive synergistic effect on the toughness of rPET composites could be explained.

CONCLUSIONS

The effect of gamma irradiation and SGF on the thermal stability and morphological behavior of the recycled poly(ethylene terephthalate) (rPET) in

the presence of epoxy resin; 2 wt % showed that the incorporation of the SGF into the rPET improve its thermal stability which increases with increasing the SGF content in the rPET matrix and slightly increases with γ -irradiation. On the other hand the crystallinity decreases with increasing the SGF content but combination of rPET1 matrix with epoxy-resin increases the crystalline phase domain of the composite which more increases with γ -irradiation. The melting temperature decreases with increasing SGF content and γ -irradiation. Scanning electron microscopy studies showed disintegration of SGF agglomerates after γ -irradiation.

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