Synergistic Effect of Short Reinforced Fibers and Gamma Rays on the Thermal and Mechanical Properties of Waste Poly(propylene) Composites

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ABSTRACT: Compressed molded waste poly(propylene) was reinforced with short carbon and/or glass fibers for investigation. The prepared composites were γ-irradiated to estimate the role of the ionizing radiation as a compatibilizing agent. TGA and DSC were used to investigate the influence of exposure dose and the incorporation of short fibers on the thermal parameters of the prepared composites. The mechanical properties of different composites were also studied. It was observed that the mechanical and thermal parameters were highly affected by the kind of incorporated fibers and γ-irradiation. The structural and morphological studies were made by means of XRD and SEM to investigate the structure change caused by the incorporation of short fibers and exposure to γ-irradiation. The results show that the irradiation of carbon fiber–containing composite magnified its thermal stability and its tensile strength. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 1741–1747, 2005

Key words: γ-radiation; fibers; composites; waste poly(propylene); thermal parameters; mechanical properties

INTRODUCTION

The use of plastics has substantially increased over the last few decades in most areas of life with a profusion of applications. The increase in the use of plastics has been accompanied by a huge increase in the generation of plastic wastes, which is an environmental threat. Recycling of such wastes is the reasonable way to overcome that serious threat by converting plastics waste into valuable reproducible materials.[1–3]

Short reinforced fibers (SF) have become very important materials because of their processing and technical advantages such as stiffness and tensile capacity. The most common type of fibers in the structural applications are glass fiber, aramid, and carbon fiber.[4,5] Polymer composite formation is a way of improving deficient properties of the waste polymers such that the incorporation of one or more distinct fibers into a single matrix leads to the development of hybrid composites with a great diversity of material properties. Many researchers have described the potential advantages of incorporation of fibers in a polymeric matrix. Such regenerated and modified properties have made polymer composites of great interest in many applications.[6–9] The attainment of desirable properties mainly depends on the extent of adhesion between composite components.[10]

Compatiblization is the way to create a better interaction between otherwise incompatible surfaces at the molecular level. Bridges forming double-face chemicals and surface treatment such as Corona and flame treatments, plasma modification, or surface grafting are the most common modern methods of composite compatibilization.[11–13]

Ionizing radiation offers a unique solution for the improvement of composite compatibility stemming from its ability to alter the structure and properties of bulk materials and its applicability to all polymers types. On exposure to ionizing radiation, its energy absorbed by the polymer material and active species such as radicals are produced, thereby initiating various chemical reactions.[14,15] There are two fundamental processes resulting simultaneously from these reactions. (1) crosslinking, where polymer chains are joined and a network is formed; and (2) degradation, where the molecular weight of the polymer is reduced through chain scission.

The object of the investigation described in this article was to study the effect of γ-radiation on the thermal and mechanical properties of reinforced waste poly(propylene) with short glass (SGF) and/or carbon (SCF) fibers. The change in thermal behavior of the prepared and irradiated composites was investigated. The mechanical properties of such composites is described. X-ray diffraction (XRD) and SEM were used to estimate the structural and morphological changes

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TABLE I
Detailed Compositions of the Prepared Waste PP Composites

Sample code	Composition (pph)		
	Waste PP	Carbon fiber	Glass fiber
WPP	100	—	—
PP1	100	20	—
PP2	100	—	20
PP3	100	10	10

resulting from the incorporation of SF and/or γ-radiation.

EXPERIMENTAL

Materials

The materials used in this investigation were recycled poly(propylene), kindly provided by the Coca-Cola Co (Budapest, Hungary) and chopped SGF and SCF (commercial-grade) obtained from Zoltek Co. (Budapest, Hungary).

Specimen preparation

The composites were prepared by feeding the chopped SGF and SCF into the polymer melt using a twin-screw extruder (Plasti-corder, PL 2100; Brabender OHG, Duisburg, Germany) (Table I). The six heating zones were set to 210, 210, 200, 200, 200, and 200°C, then the extruded strands were chopped into granules. The dried regrinds had an MFI (melt flow index) value of 15.3 g/600 s at 2 kg and 190°C by using Zwick machines (Z020; Zwick, Bamberg, Germany). All of the specimens were compression-molded. Series of different composites with and without interfacial agent were obtained. Afterward, plies 1 mm thick were prepared by compression molding of the compound at 190°C and then cooled under controlled conditions in a Collin P200E press at pressure 150 bar.

Gamma radiation treatment

The samples were submitted to gamma irradiation in air at room temperature and in ambient humidity. The absorbed doses were 30, 40, and 50 kGy at an irradiation dose rate 5–7 kGy/h.

Thermogravimetric analysis (TGA)

A Type TGA-50 TGA system (Shimadzu, Kyoto, Japan) in nitrogen atmosphere at 20 mL/min was used in this study in the temperature range from ambient to 600°C at a heating rate of 10°C/min.

Differential scanning calorimetry (DSC)

A Shimadzu Type DSC-50 DSC system in nitrogen atmosphere at 20 mL/min was used in this study in the temperature range from ambient to 250°C at a heating rate of 10°C/min.

X-ray diffraction (XRD) measurements

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

Scanning electron microscopy (SEM)

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

Mechanical testing

Dumbell-shape specimens (50 mm long and 4 mm neck width) were used for the measurement of the ultimate tensile strength and elongation at break using a model 944 KVA 0400 apparatus (Comten Industries, Pinellas Park, FL) according to the standard methods. The crosshead speed was 10 mm/min.

RESULTS AND DISCUSSION

Thermal behavior

Thermogravimetric analysis

Thermogravimetric analysis was carried out to investigate the effect of the presence of SF on the thermal stability of the waste poly(propylene) (WPP) compos-

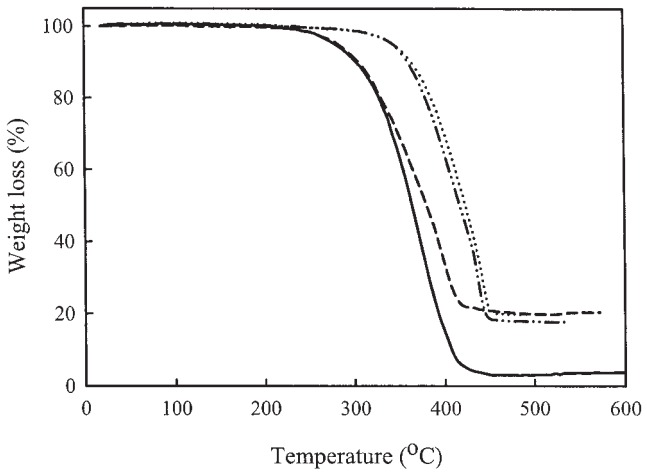

Figure 1 TGA plots of different waste PP composites: (—) WPP; (– – –) PP1; (· · ·) PP2; (– · · –) PP3.

TABLE II
Thermal Stability of Different Waste PP Composites Compared with Those Exposed to 50 kGy

Temperature (°C)	Remaining weight (%)							
	WPP		PP1		PP2		PP3	
	0 kGy	50 kGy	0 kGy	50 kGy	0 kGy	50 kGy	0 kGy	50 kGy
50	100	100	100	100	100	100	100	100
100	100	100	100	100	100	100	100	100
150	100	100	100	100	100	100	100	100
200	100	100	100	100	100	100	100	99
250	99	94	100	99	99	99	100	98
300	91	80	99	97	92	97	99	96
350	62	44	94	92	72	90	93	88
400	16	3	69	73	36	75	63	16
450	3	3	21	28	21	40	20	10
500	3	3	20	15	20	20	20	10
550	3	3	20	15	20	15	20	10

ites and to study the benefits of applying the ionizing radiation. TGA curves of the WPP and its composites with SGF and/or SCF are given in Figure 1 and the data of the thermograms are summarized in Table II. TGA curves show that WPP and its composites possess only one degradation step. Also, the thermal stability of the WPP increases by the incorporation of reinforced fibers. Thermal stability of WPP composites varies with the type and amount of the SF included in the composite. The presence of SCF, PP1, possesses the lowest thermal stability among the investigated composites whereas the inclusion of SGF, PP3, increases the thermal stability and it increases with increasing SGF, PP2, content in the composite. Figure 2 shows the TGA curves of waste WPP and its composites exposed to 50 kGy to investigate the effect of γ-irradiation on its thermal behavior. The curves show that the thermal stability of WPP and its composites with SGF, PP2, decreases by γ-irradiation, whereas the incorporation of SCF with SGF, PP3, resulted in increasing its thermal stability. Meanwhile, the irradiated PP1 possesses the highest thermal stability among the investigated irradiated composites.

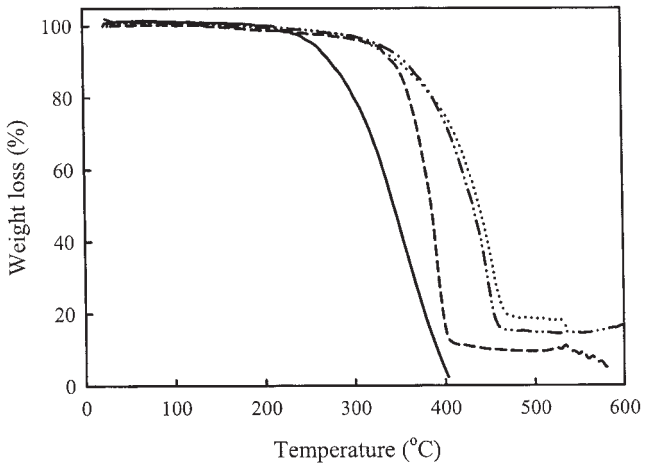

Figure 2 TGA plots of different irradiated waste PP composites exposed to 50 kGy: (—) WPP; (· · ·) PP1; (– – –) PP2; (– · · –) PP3.

The abovementioned results could be explained as follows: the increment of WPP thermal stability by incorporation of SF, attributed to the very high stability of the fibers, assists the polymeric matrix to survive at higher temperature.[16] The effect of γ-irradiation on the thermal stability could be explained in the scope of the molecular structure of the polymeric matrix, which is directly related to its thermal stability. The decrement in the thermal stability of WPP by exposure to ionizing radiation, presumably arising from some random degradation of PP chains, leads to the reduction of its stability. The presence of SGF did not affect nor was it affected by radiation process. On the other hand, the increase in the thermal stability of PP1 may result from the increase in the compatibility between SCF and polymer phases, which made the composite of higher homogeneity, and as a result its stability increases.

The results show the positive synergistic effect of γ-radiation and the incorporation of carbon fibers on the thermal stability of its composite with WPP such that the incorporation of SCF increases the stability of the composite and the use of γ-radiation magnifies such stability (Fig. 3).

Differential scanning calorimetry (DSC)

Figures 4 and 5 show DSC heating curves of WPP and its composites and Table III summarizes the thermal parameters obtained from such curves. All the investigated samples show only one melting peak, which is similar to that of pure poly(propylene). Such a result indicates that all composites are characterized by one crystalline form. Meanwhile, the presence of SF decreases both the melting temperature (T_m) and the

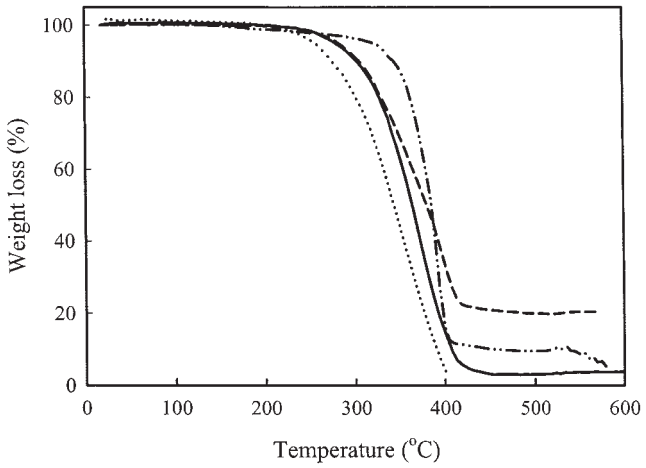

Figure 3 TGA plots of waste PP composites: (—) WPP; (· · ·) WPP exposed to 50 kGy; (– – –) PP2; (– · · –) PP2 exposed to 50 kGy.

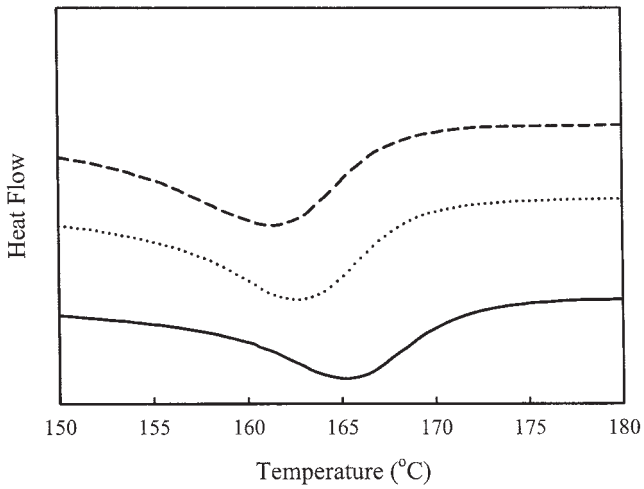

Figure 5 DSC thermograms of WPP–carbon fiber composite (PP1) exposed to different irradiation doses (kGy): (—) 0; (· · ·) 30; and (– – –) 50.

enthalpy melting values (ΔH) of the composite. Furthermore, the data show that the melting temperature also decreases by γ-irradiation. The decrement in melting temperature could be explained by understanding the Gibbs–Thomson relationship, which correlates the decrease in melting temperature to the decrease in the crystallites in the composite.[17,18] In this case, radiation causes a decrease in the length of the macromolecular chains, crosslinking, and other modifications in the crystal domains and as a result a decrease in melting temperature takes place. The decrease in the crystallites might be attributed to a hindrance of the crystallite growth attributed to presence of the fiber. The decrease in melting temperature by exposure to irradiation may arise from a further decrease in the crystallite growth.[19]

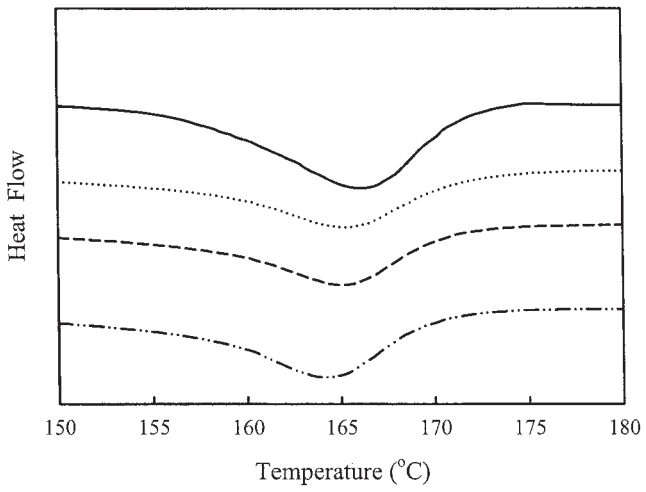

Figure 4 DSC thermograms of different waste PP composites: (—) WPP; (· · ·) PP1; (– – –) PP2; (– · · –) PP3.

Generally, melting onset and melting peak width (ΔT_m) are related to the least stability and distribution of crystallites, respectively.[20] Table III also shows a clear decrease of the melting onset resulting from the presence of the SF in the composites. It is also observed that PP1 and PP3 possessed higher stability than that of PP2. Data show the increase in the (ΔT_m) by the incorporation of the fiber with WPP. PP1 possesses the highest ΔT_m, which is increased by γ-irradiation. The aforementioned data mean that the irradiated carbon fiber–containing composite possesses higher thermal stability, which is in good agreement with data obtained from TGA.

XRD was performed to assess the influence of the incorporation of SF and γ-irradiation on the crystal structure of WPP. Such investigation could be considered as a good confirmation to results concluded from thermal analysis. The XRD pattern (Fig. 6) shows that all the investigated composites clearly display three major peaks, located at about the same 2θ values 14.1, 16.88, and 18.6°, revealing the presence of crystalline regions. The incorporation of short fibers in WPP did not show any new peak, thus implying the amorphous

TABLE III
Thermal Parameters of Unirradiated and Irradiated Composites Exposed to 30 and 50 kGy

Thermal parameter	Sample					
		PP1				
	WPP	0 kGy	30 kGy	50 kGy	PP2	PP3
Onset, °C	154	137	134	132	133.5	137.2
T_m, °C	166	165	162.6	161.5	165	164
ΔT_m, °C	20	38.6	39	40	42.5	40.1
ΔH, J/g	68.3	281.2	194	183	181.4	180.9

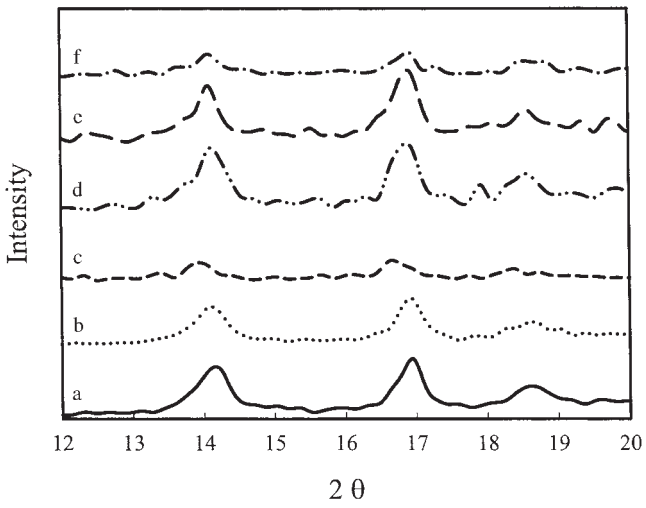

Figure 6 X-ray diffraction patterns of different waste PP composites: (a) WPP; (b) PP1; (c) PP2 compared with (d) WPP, (e) PP1, and (f) PP2 after exposure to 50 kGy.

nature of the fiber. Meanwhile, the incorporation of fiber as well as the exposure to γ-radiation decreased the intensity of the peaks; also, the decrement caused by glass fibers is more pronounced than that caused by carbon fibers. These results indicate the increase in the amorphous region by the incorporation of fibers in the PP matrix and that the amorphosity of glass is greater than that of carbon fiber. After exposure to γ-radiation, the intensity of the crysallinity peaks for all composites decreased, except that of PP1 and PP3, which could be correlated with a good adhesion between the SCF and WPP matrix, which may assist the growth of the crystalline structure.

Mechanical properties

Table IV shows the effect of irradiation dose and the incorporation of short fibers on the tensile strength of the prepared composites. The data show that the incorporation of the SF decreased the tensile strength of WPP from 315 to 261 and 280 kg/cm^2 in the cases of PP1 and PP3, respectively. On the other hand, the exposure to γ-irradiation raised the tensile strength of PP from 311 to 332 and 340 kg/cm^2 after exposure to 30 and 50 kGy, respectively. The most significant result is that of PP1. Although it possesses the lowest tensile strength before exposure to γ-irradiation, it shows the highest tensile strength after exposure to 50 kGy. On the contrary, PP3 possesses the highest tensile strength before irradiation and the lowest strength after irradiation.

TABLE IV
Tensile Strength Values for Waste PP Composites Exposed to Different Irradiation Doses

	Tensile strength (kg/cm^2)		
Sample	0 kGy	30 kGy	50 kGy
WPP	315	332	340
PP1	261	462	479
PP2	295	390	412
PP3	280	411	435

TABLE V
Elongation Values for Waste PP Composites Exposed to Different Irradiation Doses

	Elongation (%)		
Sample	0 kGy	30 kGy	50 kGy
WPP	7	5.5	5.1
PP1	8.4	2.5	2.3
PP2	7.5	3.2	3
PP3	7.9	2.9	2.7

The effects of radiation dose and incorporation of SF on the elongation percentage are represented in Table V. The elongation percentage decreases by γ-irradiation, whereas it increases by the incorporation of SF. PP1, which possesses the highest elongation percentage before irradiation, shows the lowest percentage after irradiation.

The results obtained from mechanical testing came as a confirmation for the foregoing results of this study. Such results could be explained as follows: on γ-irradiation, WPP underwent simultaneous chain scission and crosslinking. The slight decrease in the composite strength, accompanied by a reduction in the elongation percentage, indicates that the crosslinking is slightly higher than chain scission, forming a crosslinked region surrounded by broken chains. The presence of such a crosslinked island among the broken chains could also be considered as a reason for reduction of elongation percentage.

Morphological structure

Figure 7 shows SEM micrographs of WPP and its composites with SCF and/or SGF. WPP showed a smooth surface [Fig. 7(a)], although incorporation of SF deteriorated this smoothness [Fig. 7(b) and (c)]. Numerous voids, associated with the doping of fibers, can be readily seen in Figure 7(b) and (c). Also, the difference between SCF and SGF can be observed; the former is smaller in diameter than the latter.[21] It can be noted that fibers were aligned randomly to the mold flow direction. The random fibers would result in a lower toughness contribution to the composites. The effect of radiation on the morphology of the hybrid composite is shown in Figure 7(d) and (e). The micrographs indicate some short fibers are firmly adhered to the matrix, resulting in good adhesion and changes in the surface attributed to the radiation, although PP1

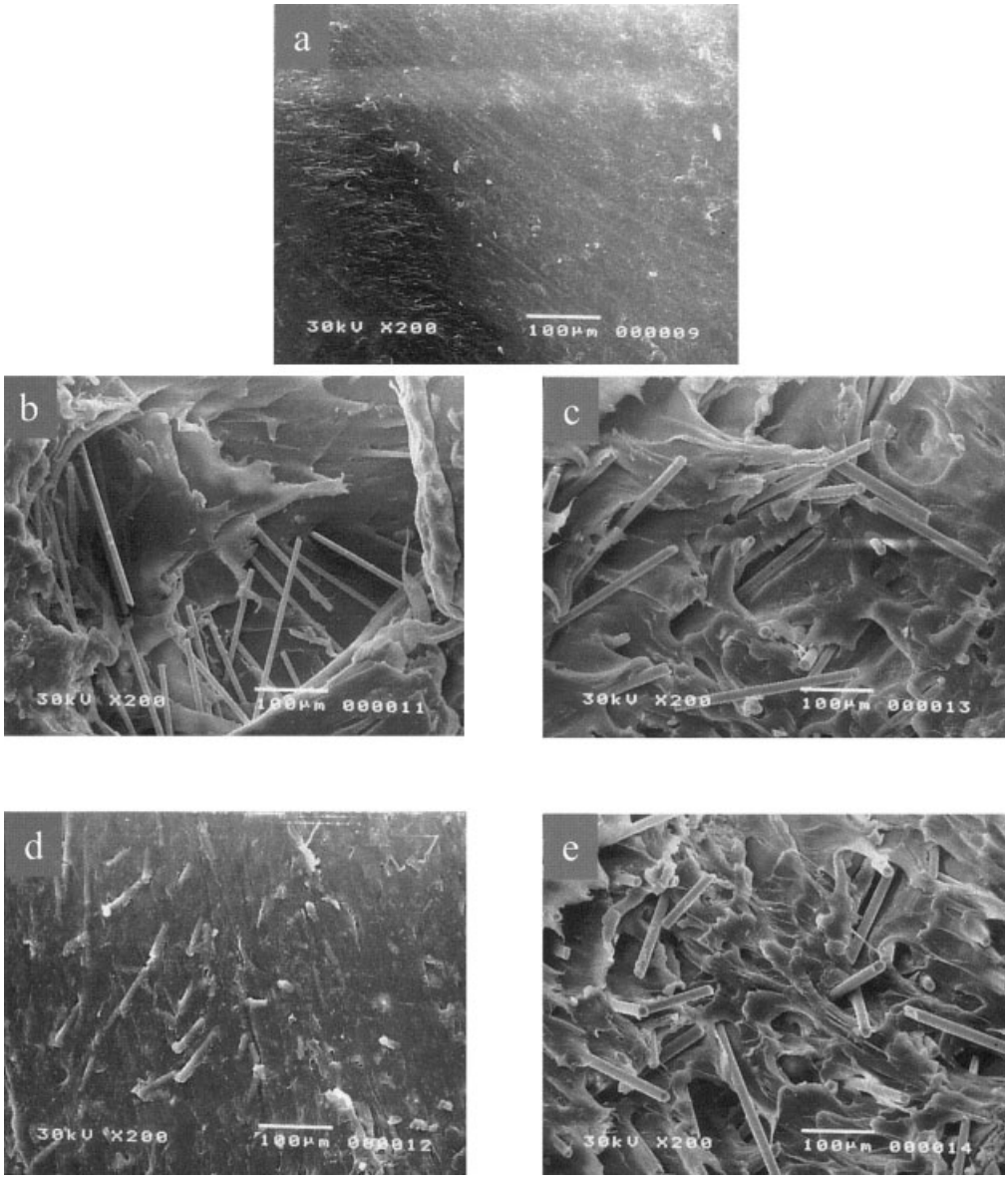

Figure 7 SEM micrographs of different waste PP composites: (a) WPP; (b) PP2; (c) PP1 compared with (d) PP2 and (e) PP1 after exposure to 50 kGy.

[Fig. 7(d)] has higher adhesion than that of PP2 [Fig. 7(e)]. Consequently, the positive synergistic effect on the toughness of WPP composites could be explained and confirmed with that obtained by mechanical tests.

CONCLUSIONS

Waste poly(propylene) composite was produced by γ-irradiation of compression-molded 20 pph carbon fiber within waste poly(propylene). The waste composite possessed high thermal stability and good tensile strength compared with those of waste poly(propylene). Such properties qualify it to be considered as an acceptable waste composite able to be used in the field of mechanical engineering. The results showed the efficiency of γ-rays as a compatibilizing agent. DSC and XRD studies showed that such improvement in the waste properties resulted from the increase in the active sites produced by exposure to γ-irradiation, which improve bonding between carbon fibers and the polymeric matrix. SEM micrographs also showed the good adhesion between the carbon fiber and polymeric matrix after exposure to γ-irradiation.

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