Study on Mechanical Properties of Perlite-Filled Gamma-Irradiated Polypropylene

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ABSTRACT: This study covers the preparation and characterization of perlite-filled polypropylene (PP). The compositions of 15, 30, and 50 % by weight perlite–PP composites were prepared by melt-mixing. The PP used in this study was either applied in the virgin form or γ-irradiated in air at the doses of 10, 25, 50, and 100 kGy to determine the effect of oxidative degradation in composite properties. Furthermore, the active sites containing oxygen produced by γ-irradiation in PP may provide a possible enhancement by the interfacial interaction between perlite and PP. An initial sharp drop in torque readings during the melt-mixing of perlite–PP composite preparation indicated an extensive chain scission and degradation by γ-irradiation. The thermal properties of the composites were characterized by DSC. The ultimate tensile strength and elongation and also impact strength decreased in all composites with γ-irradiation. Yet, these changes appeared not to be faster than was the change in unfilled PP upon irradiation. Scanning electron microscopy revealed an interfacial adhesion between perlite and irradiated PP while virgin PP did not show any evidence of adhesion. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 2670–2678, 2001

Key words: perlite-filled polypropylene; γ-irradiation; mechanical and thermal properties

INTRODUCTION

Polypropylene (PP) is still in the first place among the plastics, being the largest and fastest-growing plastic material because of its low cost, versatile properties, and commercial applications. PP has a low surface energy with a high inertness toward chemicals. Its sensitivity to thermal and photooxidation, poor hygroscopicity, inadequate compatibility with other synthetic polymers, and weak adhesive characteristics to other conventional materials are relevant physical properties.

Especially, PP and its composites with metals or inorganic fillers usually possess weak adhesion. It is a very popular research area to improve the adhesion between any polyolefin matrix and fillers through functionalization of polyolefins or by applying coupling agents.[1–10]

Inorganic flakelike fillers (talc, mica, kaolin, perlite, etc.) can be compounded with commercially available thermoplastics to improve the physical and mechanical properties.[2–9] The interfacial adhesion between a polymer and a filler is also one of the most crucial factors affecting the final properties of the composites. Therefore, it becomes necessary to modify either the filler by using coupling agents or the polymer by functionalization to promote a good adhesion between them.[1,10,11]

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High-energy irradiation can be used to produce active groups on the widely used thermoplastics and rubbers. However, it can also cause embrittlement at high radiation doses and, especially, the failure strain decreases dramatically with a loss of flexibility while the hardness increases. Energetic radiation (gamma, electron beam, etc.) results in crosslinking and chain scission through radical reactions, almost equal magnitudes in PP if oxygen is absent in the medium. These radical reactions can also initiate oxidative degradation when oxygen is present. Indeed, the chain scission and oxidative degradation become the predominant process in an atmospheric medium and new active groups on the polymer chain containing carbonyl, hydroxyl, acid, aldehyde, and hydroperoxide groups are also produced inevitably by the high-energy radiation as explained elsewhere.[12]

In this work, perlite-filled γ-irradiated and nonirradiated PP composites were prepared by the melt-mixing process. High-energy irradiation of PP was carried out for two purposes: (a) to enhance the interfacial interaction between perlite and the active sites containing oxygen produced by γ-irradiation in PP and (b) to understand the variation of the properties studied in irradiated PP composites, where, occasionally, irradiated PP should possess a degree of degradation, both chain scission and oxidation. Since perlite, a volcanic glasslike rock, inherently contains active hydroxyl groups, it is then expected that the interaction could be improved if the main matrix PP contained active sites containing oxygen. The mechanical, thermal, and flow properties and the morphology of γ-irradiated-PP–perlite composites were studied and the results are presented in this article.

EXPERIMENTAL

Materials

PP (coded as MH-418), a product of the Turkish Petrochemical Industry (PETKİM; Izmir, Turkey), was used and it contained an antioxidant. The perlite filler was supplied by ETIBANK, Cumaovası Perlite Plant (Izmir, Turkey). The PP used in this study had a melt flow index of 4.2 g/10 min and a density of 0.90 g/cm^3. The chemical composition and some physical properties of the expanded perlite were already given in our previous works[6,7] and it was basically composed of oxides: silica, alumina, and other oxides (SiO_2 71–75 %; Al_2O_3 12.5–18 %; Na_2O 2.9–4.0 %) with a surface area of 1.88 m^2/g and hardness (Mohs) of 7.0.

Sample Preparation and Testing

PP granules were irradiated at four different doses, 10, 25, 50, and 100 kGy, in a Co-60 source (Gamma Cell 220, Atomic Energy of Canada Ltd.). The average dose rate throughout the irradiation experiments was 3.6 kGy/h.

Before the application of the received perlite into the polymer matrix, it was sieved after drying at 100°C in an oven for 24 h and then the sieve fraction under 400 mesh was collected and used. The average particle size was measured as 5.0 μm by a Shimadzu SA-CP3 analyzer based on the sedimentation technique.

Nonirradiated and irradiated PP were mixed with perlite at different weight percentages of perlite (15, 30, and 50 % by weight, and the volume fraction of the filler was varied at 6.8, 16.1, and 29.3, respectively) in the mixing head of a W3OH of a Brabender Plasticorder PLV-151 (Germany).

The oil-bath temperature of the Brabender was adjusted to 190°C and the mixing was carried with a rotating speed of 60 rpm for 10 min to obtain complete dispersion of the perlite particles and better adhesion. Plate samples, 2.0 mm thick, from these mixtures were prepared by compression molding at 190°C and 1400 kg/cm^2 between steel plates. The temperature was allowed to decrease to 150°C at the same pressure, and then the mold was cooled outside to room temperature.

Tensile tests were performed in an Instron tensile testing machine (TM 1102) with dumbbell-shaped standard samples cut from 2.0-mm-thick plates at room temperature. The draw and strain rates for the elastic modulus were 0.31 cm/min and 0.089 min^{-1}, respectively, whereas for the ultimate properties, they were 5.0 cm/min and 1.429 min^{-1}, respectively. The gauge length was kept constant at 3.5 cm for both testings.

The same compression technique was used to prepare samples (60 × 7.5 × 4.0 mm) for impact-strength tests in a special steel mold, according to ASTM D256-78. Charpy impact testing on unnotched samples was carried out using a plastic impact machine (type H20) at room temperature. Impact strength values, the averages of at least five measurements, were provided in terms of kN/m.

Flow Properties: Brabender Torque Data Evaluation

The recordings obtained from the Brabender torque rheometer were evaluated for 5 and 10 min of mixing according to Goodrich and Porter.[13] The viscosities were represented according to the low shear rate from the equation

$$\eta(\text{poise}) = 360\, M\,(\text{mg})/S\,(\text{rpm})$$

where M is the torque in meter grams, and S, the speed of rotation in rounds per minute. The melt-viscosity values calculated from the Brabender should be considered as an approximate approach, as noted by Goodrich and Porter.[13]

Thermal and FTIR Analyses

Thermal analysis data of filled specimens were obtained from differential scanning calorimetry (DSC), using a Perkin–Elmer D-4. The variation of the melting point of the PP composites was determined on 5-mg samples at a heating rate of 10°C under a nitrogen atmosphere.

Nonirradiated and irradiated PP thin films (about 100 μm) were also examined in an FTIR, Nicolet 510, to follow the formation of active sites in the polymer, like carbonyl, hydroxyl, etc. The carbonyl band index (COI) was defined as the ratio of the absorbances of the carbonyl peak at 1725 cm^{-1} to the reference peak absorbance of δ (CH$_3$) at 1453 cm^{-1} to eliminate the effect of small changes in the sample thickness.

Surface Analysis

The fracture surfaces of the PP–perlite composites were examined by a JEOL-JSM–640 (Japan) scanning electron microscope (SEM) after applying a gold protective coating .

RESULTS AND DISCUSSION

Infrared and Thermal Characterization

The major effect of high-energy radiation in an ambient condition on PP is the oxidative degradation accompanied by chain scission.[14,15] FTIR spectra of the nonirradiated and irradiated PP are given in Figure 1. The increased intensity of the carbonyl peak (at 1725 cm^{-1}), in terms of the carbonyl index, with the dose of irradiation is shown in Figure 2. A large jump at a 25-kGy dose
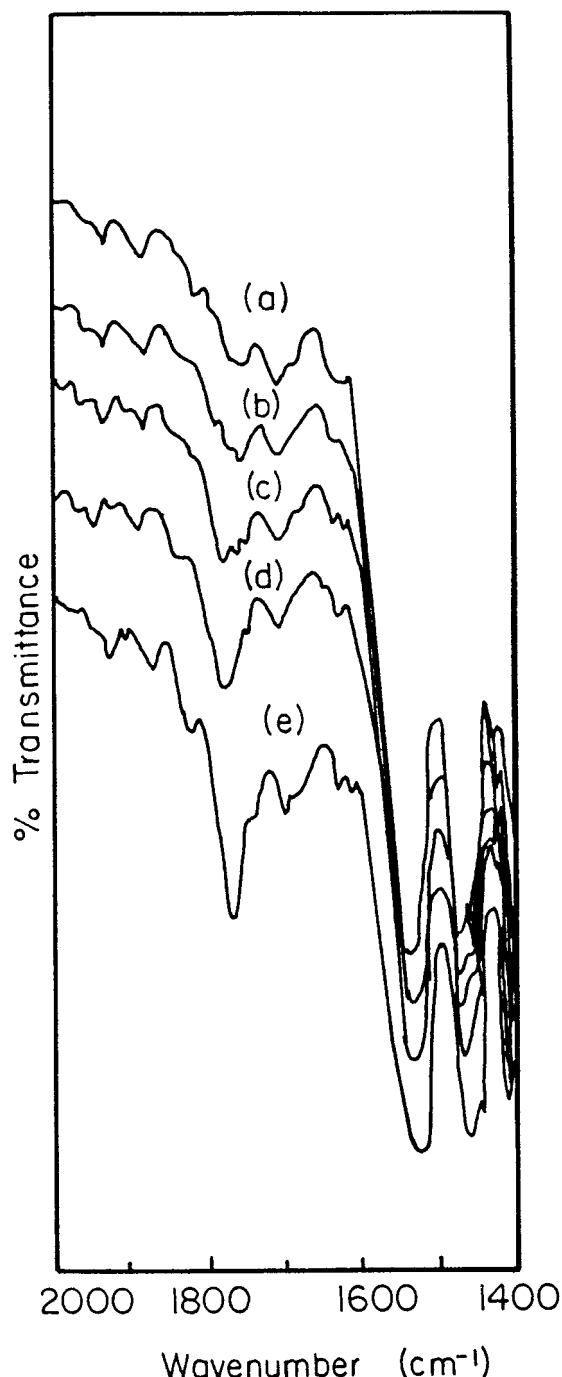

Figure 1 FTIR spectrum of nonirradiated and irradiated granule PP: (a) nonirradiated PP; irradiated PP: (b) 10 kGy; (c) 25 kGy; (d) 50 kGy; (e) 100 kGy.

shows how the oxidation becomes very intense, as calculated from the carbonyl index, where the internal reference peak intensity (at 1453 cm^{-1}) remained almost unchanged.

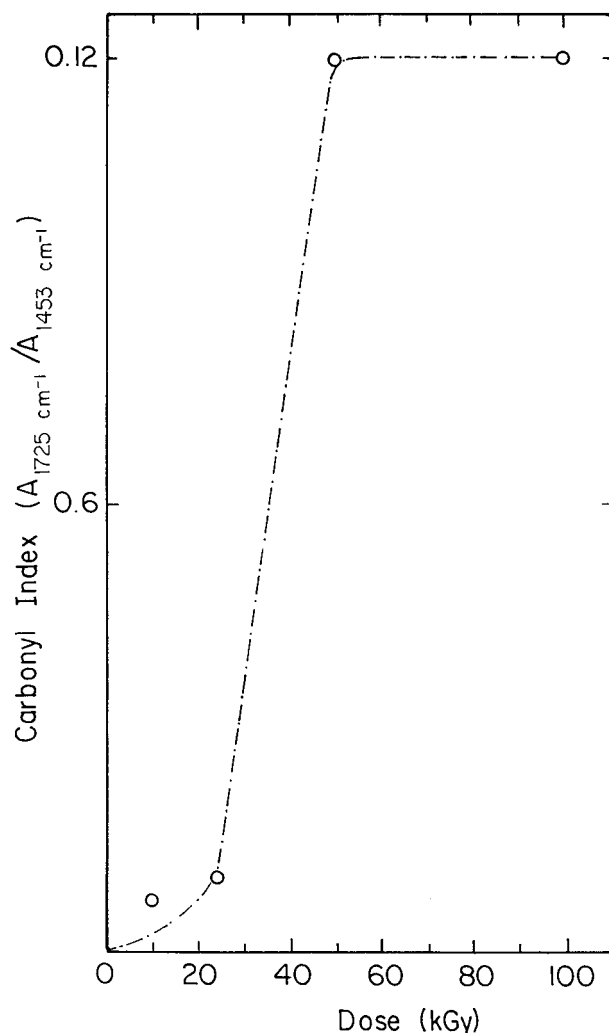Since the irradiation was carried out on common commercial granular PP, the progress of ox-

Figure 2 Carbonyl index development in PP with absorbed dose.

which was measured as the highest value at 25 kGy. This crosslinking, however, did not cause any processing problem to obtain PP–perlite compounds and, finally, films and sheets. Indeed, the decrease in the melt flow of pure PP with irradiation in air [see Fig. 4(a,b)] indicated extensive chain scission rather than crosslinking, except that the largest experimental scattering at the 25 kGy dose was observed.

The variation of the melting temperature (T_m) with the irradiation dose, for both the pure and perlite-filled samples, is given in Figure 3. The melting point of the pure unfilled polymer decreased with the dose of irradiation. This depression of the melting point is simply due to the chain scission and oxidation processes, which inhibit the crystallization and also cause more defects in the crystal structure. This decrease in T_m becomes even higher by the addition of perlite into γ-irradiated PP compared to the pure PP T_m variation with the radiation dose. However, in nonirradiated PP, the addition of perlite increased the T_m from 165°C, unfilled PP to 172°C, 50% filled PP (see zero dose line or y-axis in Fig. 3), while, as noted above, the decrease in T_m with

idation was related to the diffusivity and solubility of oxygen and the oxidation was expected to initiate from the surface to the interior parts of the granules.[15] The jump in the carbonyl index, as shown in Figure 2, indicates that oxidation reaches some interior parts, but, as a whole, it remained quantitatively almost the same at 50- and 100-kGy irradiation doses. Note that these granules were passed through the Brabender mixer followed by compression molding to obtain thin films and sheets.

The possibility of crosslinking in granular PP was also checked by a simple solvent extraction in a Soxhlet apparatus. The extensive crosslinking apparently affected the processing and, hence, the addition of perlite. It was found that the crosslinking never exceeded 30% by weight,
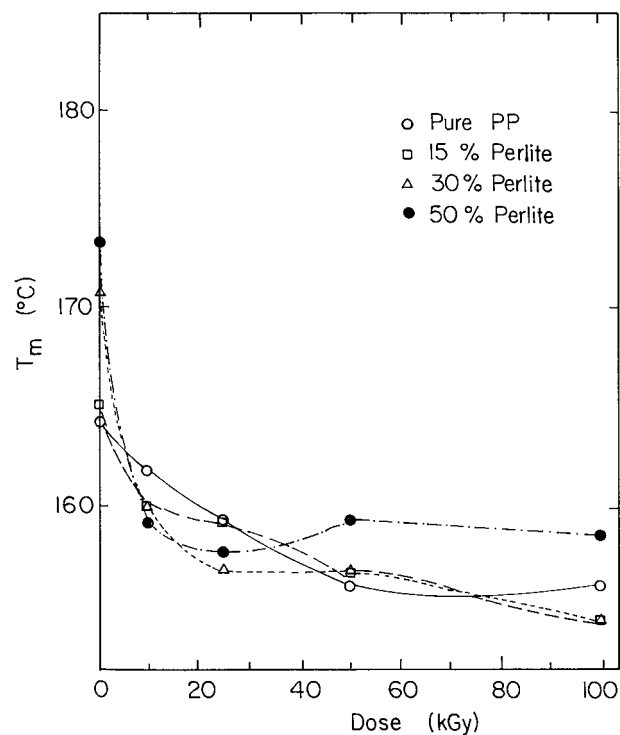

Figure 3 Variation of melting point (T_m) of PP, unfilled and perlite-filled, with respect to absorbed dose. (Symbols are given inside the figure according to percent perlite addition.)

the dose was very sharp and the T_m did not vary much afterward for higher doses for given compositions.

The increase in T_m of nonirradiated PP with perlite may be explained by the free volume created in the presence of perlite, which, in turn, caused enhanced crystallization. A similar result in talc-filled PP was observed in the melting temperatures under nonisothermal conditions and, yet, the isothermal conditions showed there was almost no change in the melting point after a recrystallization process.[16] This increase in T_m under a nonisothermal condition was explained by the nucleation activity of the talc filler. In addition, in our study, 50% perlite-filled irradiated PP composites still had the highest T_m values at 50 and 100 kGy compared to those of the other composites, but it obviously showed the largest depression with the dose because of extensive oxidation and chain scission.

Flow, Mechanical Properties, and SEM studies

The melt viscosity and torque variation in the mixing process with respect to the irradiation dose are given in Figure 4(a,b) for both 5- and 10-min mixing times. The sharp decrease in the melt viscosity for irradiated pure PP compared to the nonirradiated samples demonstrates the presence of extensive and inevitable chain scission. Higher radiation doses did not show any distinguishable change in the melt viscosity. Note that the addition of perlite to the irradiated PP did not result in any significant changes in the viscosity, while the nonirradiated PP–perlite composites had higher viscosity values than that of pure PP. The fluctuations and differences at a 25-kGy-irradiated sample melt viscosity for 5- and 10-min mixing times can be attributed to the presence of crosslinking in PP when compared to higher doses of irradiation. The melt-viscosity variation indicated that there did not exist a large difference between 5-min and 10-min mixing, but it was very obvious that a longer mixing time might result in better dispersion but also lower viscosity.

Stress–strain curves of some selected compositions are given in Figure 5(a,b) (note that the percent elongations in the x-axis are different in these figures). Upon irradiation, the mechanical behavior of pure PP suddenly changes. As shown in Figure 5(a), 10-kGy irradiation caused PP to be more rigid and this sample failed before the yield point. Irradiation caused an increase in the elas-
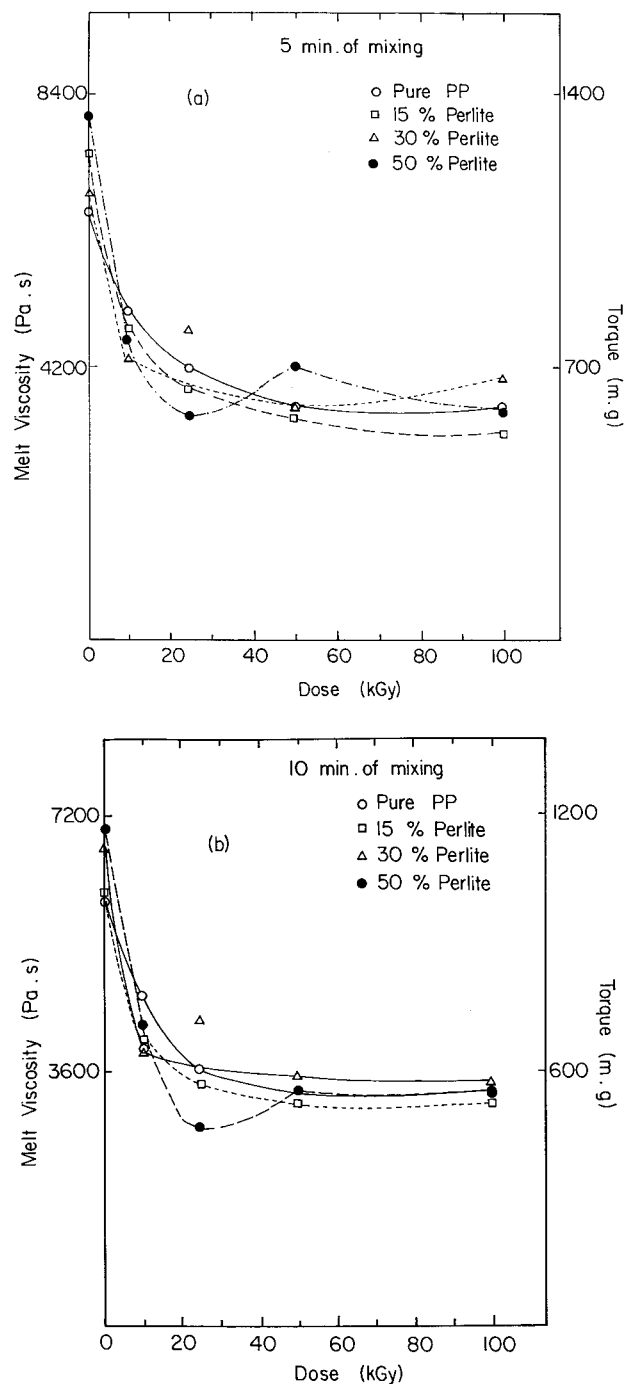

Figure 4 Variation of melt viscosity with respect to absorbed dose for filled and unfilled PP: (a) viscosity measured at 5-min mixing time; (b) viscosity measured at 10-min mixing time. (Symbols are given inside the figure according to percent perlite addition.)

tic modulus of pure PP [Fig. 4(a,b)]. The elastic moduli showed a further increase with the addition of perlite, while the elongation decreased and the stress at break remained mostly unchanged.
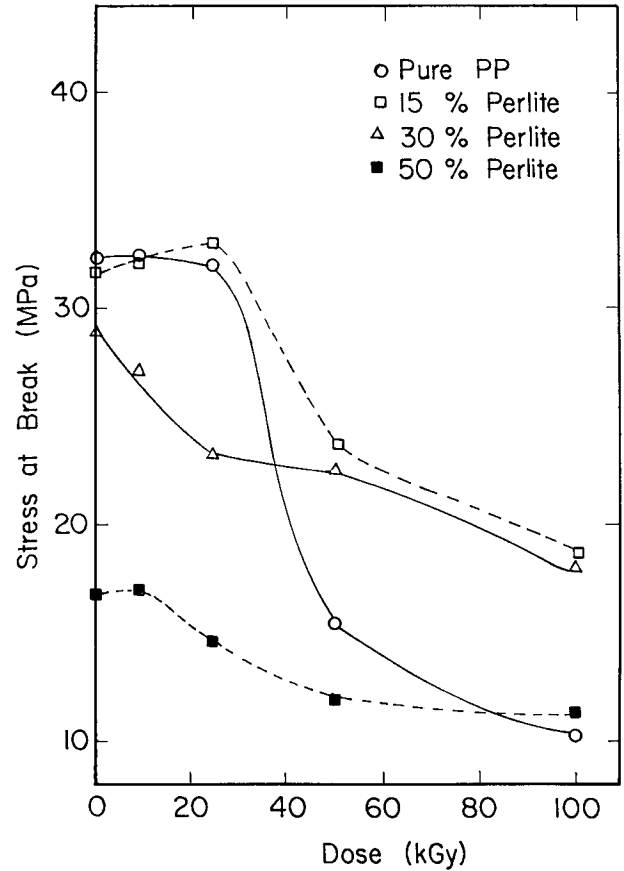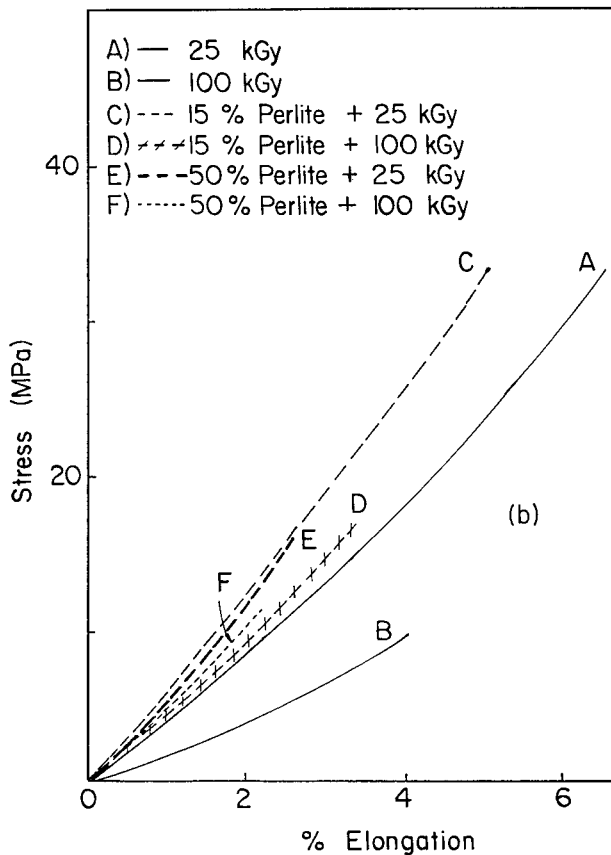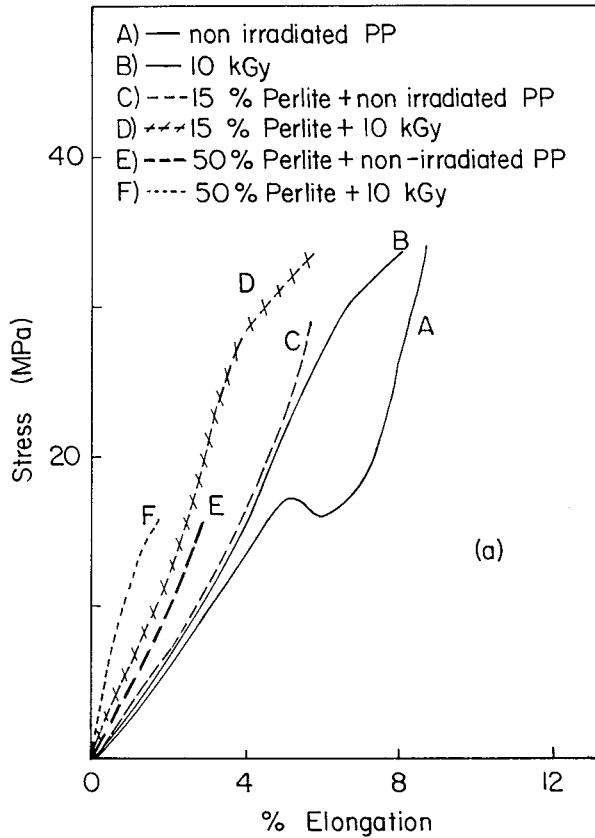
(a)

(b)

Figure 6 Variation of stress at break of nonirradiated and irradiated PP–perlite composites with respect to absorbed dose. (Symbols are given inside the figure according to percent perlite addition.)

At the highest irradiation dose, 100 kGy, the slope of the stress–elongation line was found to be smaller than that of the 25- and 50-kGy-irradiated perlite–PP composites, indicating slightly lower elastic moduli. Similarly, stress-at-break values were almost the same up to pure 25-kGy-irradiated PP and then decreased drastically to a very low value at 100 kGy. These results directly imply that a high irradiation dose, particularly after 25 kGy, ends with a noticeable loss of mechanical properties.

The variation of the stress and elongation at break for unfilled and filled PP with respect to the

Figure 5 Stress–strain curves of unfilled PP and composite PP: (a) stress–strain curves of pure PP and 15 and 50% filled (by weight) PP for 10-kGy irradiation; (b) stress–strain curves of pure irradiated PP and 15 and 50% perlite-filled (by weight) PP for 25- and 100-kGy irradiation.
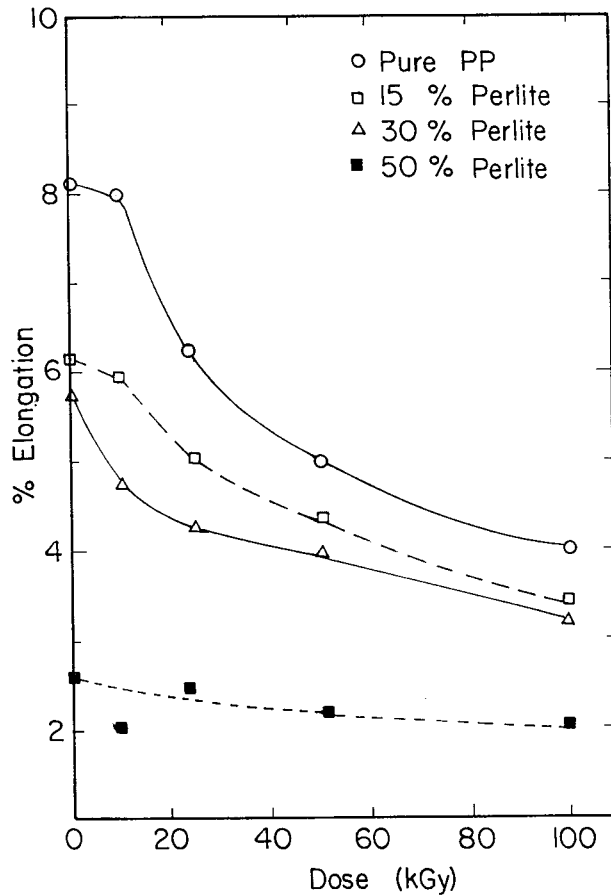
Figure 7 Variation of percent elongation at break of nonirradiated and irradiated PP–perlite composites with respect to absorbed dose. (Symbols are given inside the figure according to percent perlite addition.)

dose of irradiation of the PP matrix is given in Figures 6 and 7, respectively. The stress at break decreased almost half that of the nonirradiated PP after 50 kGy and even lower than that with a 100-kGy dose. The percent elongation variation with the dose was found to be even faster than was the stress at break just after 25-kGy irradiation. These are the inevitable results of high-energy radiation on a very sensitive and vulnerable polymer, PP.[14]

Addition of perlite into PP still appeared to give acceptable tensile strength values for 50- and 100-kGy-irradiated PP when the perlite content was 15 and 30% by weight, yet, at these high doses, the loss of strength is inevitable. At doses of 10 and especially 25 kGy, the stress at break for the 15 % perlite PP composite had almost the same value as that of the pure polymer (unfilled) within the experimental error limits. Better stress-at-break values observed in 15 and 30%

perlite compositions at high absorbed doses can be an indicator of an enhancement of the interaction between perlite and oxidized PP through oxygen-containing groups of PP and hydroxyl groups of perlite. A higher amount of perlite addition (50% by weight) did not result any improvement in the tensile strength of the pure PP, but, rather, resulted in a large drop, while other amounts caused a slight reduction in the strength. Concerning the variation for the 50% perlite composition, it was observed that the lower magnitude of the change in tensile strength with the dose was present.

The percent elongation at break showed a decreasing trend with the dose irradiation and also the filler content. Perlite addition to nonirradiated PP caused a sharp drop of elongation at break, from nearly 8% elongation of unfilled PP to 2.5% at 50% perlite addition. However, in irradiated PP samples, the dose of irradiation for a given perlite content was not very large, especially for 50% perlite samples.
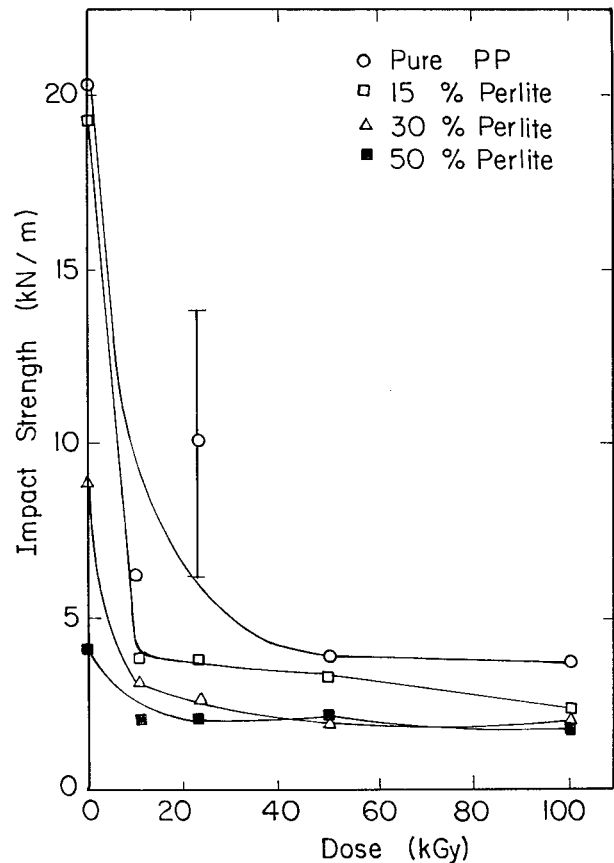

Figure 8 Variation of impact strength of nonirradiated and irradiated PP–perlite composites with respect to absorbed dose. (Symbols are given inside the figure according to percent perlite addition.)

The variation of the impact strength measured by the Charpy method only on unnotched samples with a perlite content with respect to dose of radiation is given in Figure 8. Addition of perlite into pure PP reduced the impact strength from 20 kN/m to a value lower than 5 kN/m. Due to the shrinkage problems in compression-mold sample preparation, the thickness of the samples was found to vary from 4.0 to 3.5 mm. Therefore, the results of the impact strength were presented in terms kN/m rather than J to avoid this small thickness difference that would affect the final impact strength if it were given in J. The approximate value of the impact strengths in terms of J varied from 0.6 to 0.15 J for 20 and 5 kN/m, respectively. The hard particulate filler caused a sharp decrease in the impact properties with a rapid crack propagation as noted in the literature.[2,17] The impact strength of irradiated pure PP also showed a very fast decrease, but it remained almost unchanged with the absorbed dose with the exception at the 25-kGy dose. We observed the highest fluctuation in the 25-kGy-irradiated PP, where a large experimental deviation bar was added only for this sample. This may partly arise from the radiation-crosslinked PP, which appeared to be still effective even after processing in melt and compression molding. The addition of perlite to irradiated PP showed almost no change in impact strength. The impact strengths are obviously almost the same with increasing dose and perlite content and lower than that of the values of pure and irradiated PP.

Four fractographs of tensile-tested specimens of perlite-filled nonrradiated and irradiated PP composites are given in Figures 9–12. Nonirradi-
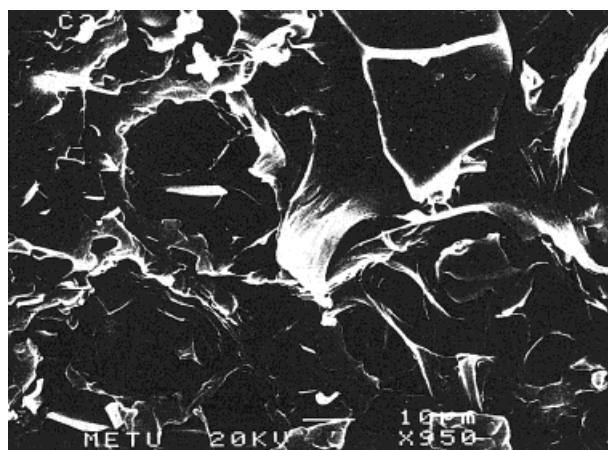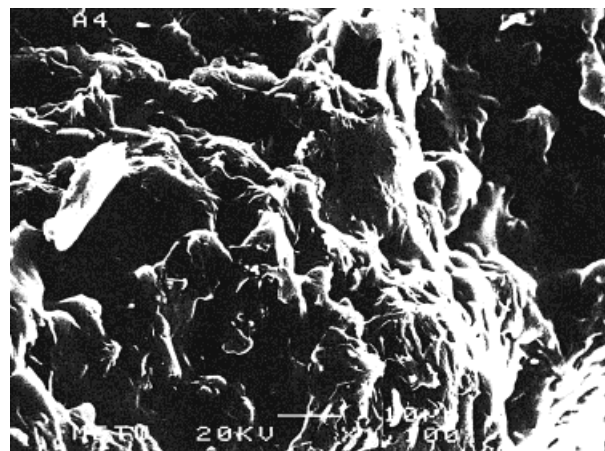

Figure 10 Fractograph of 50% perlite-filled 25-kGy-irradiated PP.

ated PP filled with 15 % perlite (Fig. 9) showed an indication of the orientation of the PP matrix upon tensile testing, and perlite particles (right upper part of Fig. 9) remained uninteracted and usually pulled out from the PP matrix, leaving holes. The composites of 25-kGy-irradiated PP with 50% perlite showed that perlite was covered with PP (Fig. 10), and the tilted fractograph of the same sample (Fig. 11) showed an adhered perlite particule to the matrix PP. The orientation of the polymer in this case was not present. No indication of the adhesion and orientation of PP were observed at the highest irradiation dose (Fig. 12) of the 15% perlite PP-containing sample, because of extensive degradation in PP.

CONCLUSIONS

Gamma-irradiation caused extensive chain scission and oxidative degradation to a certain ex-
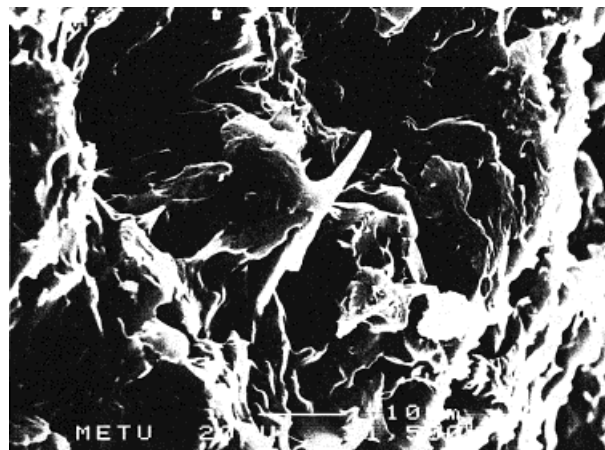

Figure 9 Fractograph of 15% perlite-filled nonirradiated PP.

Figure 11 Fractograph of 50% perlite-filled 25-kGy-irradiated PP, the tilted view.

Figure 12 Fractograph of 15% perlite-filled 100-kGy-irradiated PP.

tent. This was followed by FTIR, melting-point depression in PP, and also the sudden change in the viscosity of the melt flow with the radiation dose. The viscosity of the irradiated PP–perlite composites did not show any significant changes, while virgin PP–perlite composites had higher viscosities than that of pure unfilled PP. The ultimate strength of perlite-filled PP after a 25-kGy radiation dose was, obviously, better than that of pure unfilled irradiated PP. In general, the tensile strength was found to be improved with perlite addition at higher radiation doses, especially for 15 and 30% perlite compositions. The ultimate elongation also decreased with addition of perlite and the radiation dose but not as fast as observed in unfilled PP, especially when 50% perlite composites are considered. The impact strength, as can be expected, decreased with perlite addition for nonirradiated PP composites, but it was found that γ-irradiation for both unfilled PP and filled PP did not much alter the impact strength. SEM fractographs indicated that there existed a slight but very clear interaction between perlite and PP for irradiated PP.

In conclusion, the addition of mineral-filler perlite apparently improves the mechanical properties of γ-irradiated PP. Even at a high dose of irradiation, perlite addition resulted in substantially acceptable mechanical strengths, indicating better interfacial interaction compared to the variation of the mechanical properties in nonirradiated PP composites and the unfilled PP.

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