Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 18 Oct 2010

To cite this article: J. Reyes-Romero, E. Davidson, C. Albano*, D. Moronta & P. Reyes-Turcu (2004): Irradiation on Polyolefins/Woodflour: An ESR Study, Molecular Crystals and Liquid Crystals, 418:1, 181-187

To link to this article: http://dx.doi.org/10.1080/15421400490479262

Mol. Cryst. Liq. Cryst., Vol. 418, pp. 181/[909]–187/[915], 2004

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490479262

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IRRADIATION ON POLYOLEFINS/WOODFLOUR: AN ESR STUDY

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We have exposed the Polypropylene + virgin-High Density Polyethylene + woodflour and Polypropylene + recycled-High Density Polyethylene + woodflour woodflour composites under gamma irradiation to integral doses from 10 to 70 kGy at the constant dose rate of 4.8 kGy/h. ESR Spectroscopy was carry out. The nature of free radicals after two days of air storage induced by gamma irradiation is discussed. The peak to peak resonance line width, and his dependence with the integral dose on gamma irradiation, is discussed. The concentration radicals has been estimated for a group of singles lines, characterized by the same giromagnetic factor value, by direct numerical double integration.

INTRODUCTION

The polyolefins are a very interesting class of technological polymers use for a very large variety of applications, including composites. Between

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these materials, the polyethylene (PE) and the polypropylene (PP) are polymers massively used in the industry.

Polymers exposed to ionizing radiation, even at low doses, often undergo structural changes accompanied by molecular crosslinking, grafting and chain scission reaction [1–2]. Physically, the success achieved by the irradiation of plastics is based on the fact that it currently represents the only technique, which allows introducing energy into the material to generate favorable changes, provided it is used in the proper doses.

Electron Paramagnetic Resonance Spectroscopy (ESR) is a valuable tool in the identification of free radicals and in the investigation of the kinetics of their reactions, we have studied the dependence of resonance spectra parameters on the dependence with the integral dose of irradiation for composites with and without woodflour filler. The free radicals concentration, the double integral of the resonance line S, has been estimated, at 20°C, for a group of single lines, characterized by the same g value, by direct numerical double integration using the relation: $S = kIH_{PP}^2/mA$, where k is the shape factor, estimated using the slope method, I is the resonance line amplitude, m is the mass of the sample and A is the gain of the spectrometer.

EXPERIMENTAL

The materials used in this work are polypropylene (ρ: 0.91 g/cm^3, MFI: 7.0 g/10 min, 230°C and 2.16 kg load) produced in Venezuela by Propilven; virgin high density Polyethylene (v-HDPE, ρ: 0.91 g/cm^3, MFI: 6.3 g/10 min, at 190°C and 2.16 kg load), produced in Venezuela by Resilin and recycled high density polyethylene (r-HDPE) supplied by Plásticos MyM were used. A mix of some types of hard wood flour supplied by Maderas Unidas Sawmill, Zulia-Venezuela, was used too. The average particle sizes of the woodflour used were 20 mesh and 40 mesh in a 50/50 wt%.

Composites of PP + HDPE (80/20) with 40 wt.% of woodflour were prepared [3]. Composites of PP + v-HDPE + woodflour and PP + r-HDPE + woodflour (previously the wood flour was dried for 48 h at 65°C) were mixed in a one-stage process in a W&P intermeshing co-rotating twin screw extruder at 165°C and 110 rpm. The samples were irradiated with γ-rays at integral doses of 10, 25, 50, 60 and 70 kGy using a dose rate of 4.8 kGy/h in air, at room temperature with a ^{60}Co source.

ESR measurements were carried out using the Varian E-line-X ESR spectrometer at 100 kHz modulation frequency. All samples were measured at room temperature, 20°C, in the TE-102 rectangular cavity at a microwave power level of 30 mW.

RESULTS AND DISCUSSION

Figure 1 shows ESR spectra of the mixtures PP + virgin-HDPE + woodflour and PP + r-HDPE + wood flour composites after two days of air storage. Both mixtures show ESR spectra at 0 kGy and this is resulting from the previous processing to which it has been subjected for the mixed process of, being observed a more intense signal when r-HDPE is had, which can be explained by a superposition of the effects of these and the

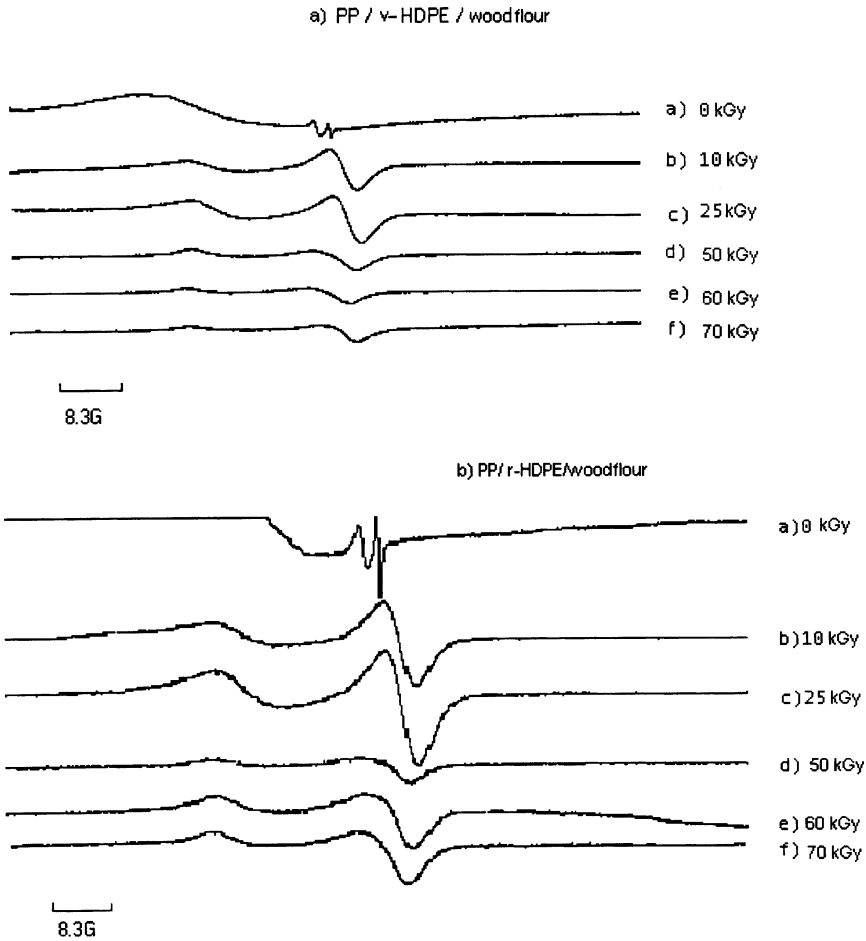

FIGURE 1 ESR spectra of PP/v-HDPE/woodflour and PP/r-HDPE/woodflour at different integral doses of γ-irradiation.

filter. Both ESR are asymmetrical singlets (Fig. 1) located around $g = 2.015 \pm 0.001$ and an splitting constant value of "a" between 22×10^{-4} T and 45×10^{-4} T characteristic of allyl, alkyl and peroxy radicals that are converted in carbonyl radicals after two days in air storage and at upper integral doses of gamma irradiation. The dependence of S on integral doses is given in the Figure 2a for PP + v-HDPE + woodflour and PP + r-HDPE + woodflour. From 0 kGy to 25 kGy, both mixtures show similar behavior but the double integral value of ESR line, S, of pristine mixture is a 50% of free radicals concentration of recycled mixture is observed as gamma irradiation dose is increasing. From 25 kGy to 70 kGy the S for PP + v-HDPE + woodflour value decreases as dose integral irradiation increases showing a minimum value at 70 kGy. On the other hand, the S for PP + r-HDPE + woodflour value decreases as dose integral irradiation increases from 25 kGy to 50 kGy, showing at 50 kGy the same S value observed at 0 kGy and then the free concentration of radicals increases again showing a minimum relative of 4.4% at 70 kGy. This is due, to that the free concentration of radicals for neat r-HDPE (Fig. 2b) is bigger than the free concentration of radicals for neat v-HDPE polymer (Fig. 2b) indicative of the predominant influence of r-HDPE on the polyolefin mixture studied. The Figure 2a shows a non linear dependence of free radical concentration as integral doses of gamma irradiation increases suggesting a complex process.

The Figure 3a shows the Hpp values for both composites on gamma irradiation from 0 kGy to 70 kGy. The dependence of the peak to peak resonance line width, Hpp, on the integral dose of gamma irradiation for both (PP + v-HDPE + woodflour and PP + r-HDPE + woodflour) mixtures exhibits increases values from 0 kGy to 10 kGy and from 25 kGy to 50 kGy and consequently the dipolar interactions are enhanced; and decreases values from 10 kGy to 25 kGy and from 60 kGy to 70 kGy suggesting the enhancement of exchange interactions [4–5]. In this competition between exchange and dipolar interactions, the former becomes dominant.

The dependence of the resonance line shape factor, k, on the degradation integral dose of gamma irradiation for, both, composites is illustrated in Figure 3b. The Figure 3b shows for PP + v-HDPE + woodflour that the resonance line shape factor, k, is Gaussean for samples degradated on gamma irradiation from 0 kGy to 70 kGy due to enhancement of dipolar interactions and free isolated radicals are observed in the composite. In addition, in this figure is observed for PP + r-HDPE + woodflour a transition from pure Gaussian line ($k = 2.2$) towards a pure Lorentzian line ($k = 4$) [4] on the irradiation range from 0 kGy to 10 kGy supporting the enhancement of exchange interactions and agrees with the dependence of free radical concentrations.

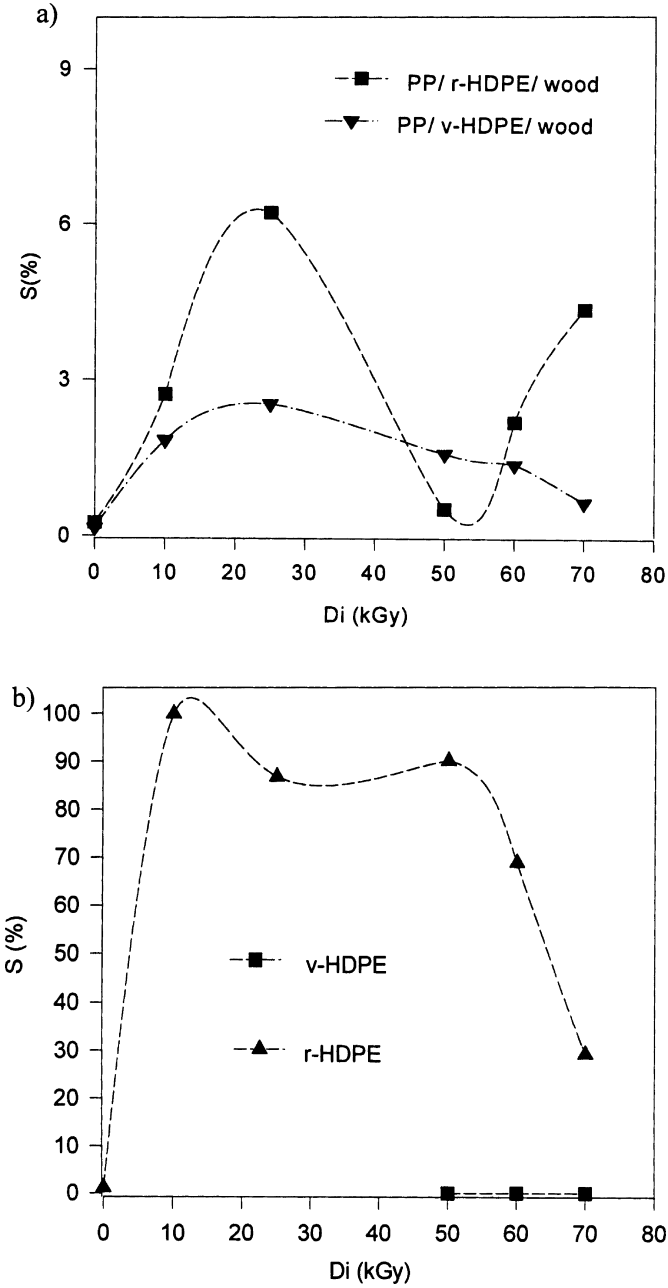

FIGURE 2 Dependence of the free radical concentration (S) on integral doses for a) composites and b) v-HDPE and r-HDPE.

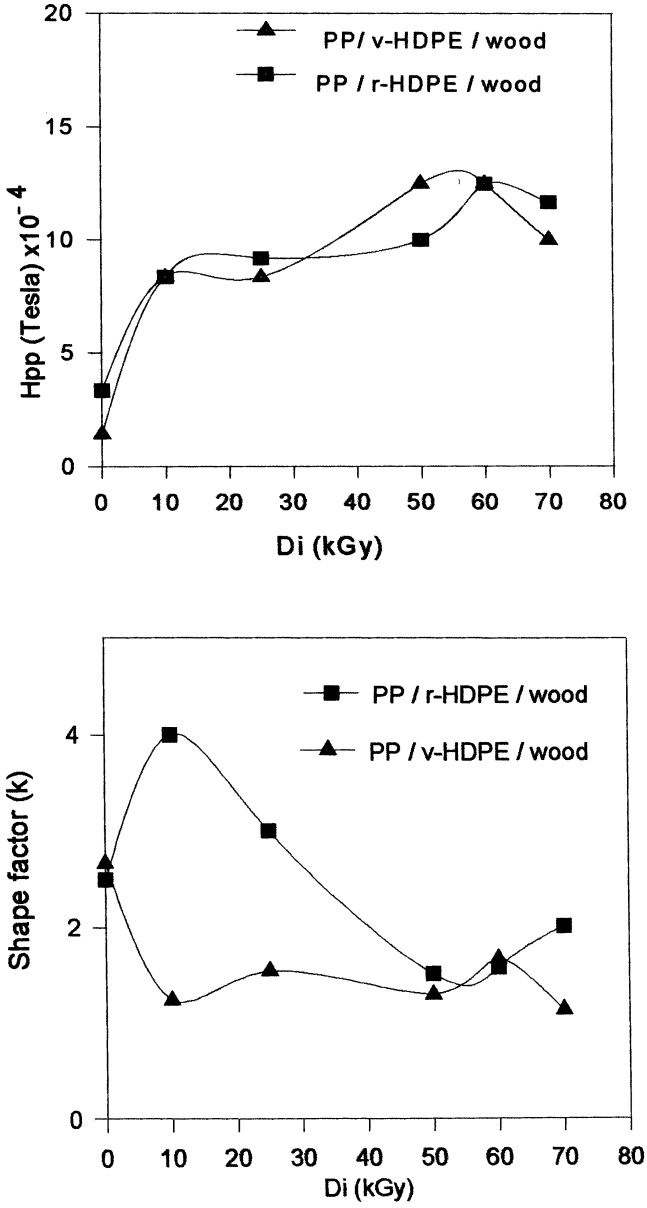

FIGURE 3 The dependence of Hpp and k versus integral doses for PP/v-HDPE/woodflour and PP/r-HDPE/woodflour.

The behavior of the mechanical properties [6] is in agrees with the behavior of the concentration of free radicals observed in the present research.

CONCLUSIONS

During the gamma irradiation of PP + v-HDPE + woodflour, PP + r-HDPE + woodflour composites, radicals' allyl, alkyl and carbonyl are generated. The resonance line position and structure, as well as the high stability at room temperature of the radicals observed in these samples, support this identification. No resonance signal at $g=4$ ascribed to free radicals pairs has been recorded suggesting that the concentration of free radicals pairs (if they exists) is low. No resonance signal near $g=2$ ascribed to free radicals formed in gamma irradiation cellulose [7] has been recorded suggesting not grafting processes between polymers and woodflour. The resonance line parameters (line, widths, line shape factor), suggests that dipolar interactions among free radicals are dominant as gamma irradiation integral doses increases.

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