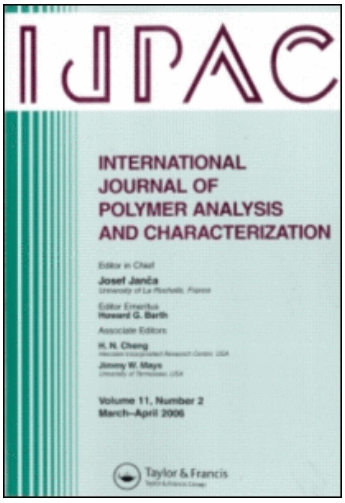

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Improving the Compatibility of Polycarbonate/ UHMWPE Blends through Gamma-Ray Irradiation

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Abstract: Gamma-ray irradiation treatment in air has been used as an alternative to the common surface treatment of ultrahigh molecular weight polyethylene (UHMWPE) powders to induce some oxygen-containing groups onto the molecular chain of UHMWPE to enhance its compatibility with polycarbonate (PC). The effect of gamma-ray irradiation on the structure and properties of UHMWPE was studied by FTIR, gel content measurement, mechanical property testing, and melt flow rate measurement. The mechanical properties and compatibility of polycarbonate/gamma-ray irradiated UHMWPE (γ-UHMWPE) blend were also studied. The experimental results show that gamma-ray irradiation partly causes oxidative degradation of UHMWPE and the content of oxygen-containing groups increases with irradiation dose. The surface hydrophilicity of UHMWPE is improved due to the presence of oxygen-containing groups. SEM observation of the fractured surface of the PC/UHMWPE blends indicates the compatibility is improved through γ-ray irradiation. Meanwhile, improved fracture toughness and mechanical strength can also be achieved; both yield and notched impact strength of PC/γ-UHMWPE blends are greatly increased from 39.7 MPa and 9.9 kJ/m^2 to 49.2 MPa and 24.9 kJ/m^2, respectively, compared with the

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PC/UHMWPE (85/15) blend. Gamma-ray irradiation treatment is efficient for enhancing the compatibility of polycarbonate/UHMWPE blends.

Keywords: Blend; Compatibility; Gamma-ray irradiation; Polycarbonate; UHMWPE; Ultrahigh molecular weight polyethylene

INTRODUCTION

Polycarbonate (PC) and ultrahigh molecular weight polyethylene (UHMWPE) are two important commercial polymers. Polycarbonate (PC) has found many uses because it combines a high level of heat resistance and dimensional stability with good insulating properties. Unfortunately, it is sensitive to notch and exhibits poor solvent resistance. In addition, PC is very difficult to fabricate from the melt due to its exceptionally high viscosity. This fact limits its application in many fields. In order to overcome these drawbacks, PC is usually blended with some olefin polymers, such as polyethylene (PE), polypropylene (PP), or thermoplastic rubbers, e.g., ethylene-1-octylene copolymer.[1–3]

Compared with other kinds of polyolefins, UHMWPE has several attractive properties, such as high strength and modulus, good wear resistance, good chemical resistance, insensitive to notch, and excellent impact strength at low temperature. Blending and alloying of PC and UHMWPE offer an opportunity to convert their blends into materials with specific applications. However, PC and UHMWPE are thermodynamically immiscible, and their blends usually display unstable morphology and poor mechanical properties compared with the raw materials. The conventional approach to solve this problem is to incorporate a compatibilizer into the blended system. Most of compatibilizers are polyolefins functionalized with maleic anhydride or acrylic acid, which form bonds at the interface.[3,4] However, the grafting techniques have some disadvantages, such as requiring complex and elaborate procedures as well as chemical pollution. Furthermore, residue graft monomers and other auxiliaries might negatively affect the thermal, electrical, and mechanical properties of blends.

Radiation processing of polymers receives increasing interest because it offers a way to modify the molecular structure of polymers as an alternative to the traditional chemical methods.[5] Xu and his research group used γ-ray irradiation in air to introduce some oxygen-containing groups onto the molecular chain of the polyolefin, thus significantly improving the compatibility and mechanical properties of their blends with muscovite and $Mg(OH)_2$.[6–8] Valenza and Spadaro[9] utilized gamma irradiation to introduce some oxygen-containing groups onto the molecular chain of linear low density polyethylene (LLDPE), and improved its compatibility with polyamide.

Recently, the effect of gamma-ray irradiation on UHMWPE[10–12] was investigated. The studies focus on radiation cross-linking and post-irradiation ageing. In such cases, oxidation degradation of UHMWPE is undesirable. According to the articles published on variation of polyethylene properties by gamma-ray radiation, it is obvious that cross-linking of UHMWPE can be expected as a result of low or moderate gamma irradiation doses at laboratory temperature in air.

This study utilizes the oxidative degradation of UHMWPE caused by gamma-ray irradiation, with the intention of avoiding the undesirable cross-linking of UHMWPE. Some oxygen-containing groups were introduced onto the molecular chain of UHMWPE through γ-ray irradiation in air. The effect of irradiation on the structure of UHMWPE and the compatibility with PC were studied. Meanwhile, high-pressure capillary measurement was used to study the apparent viscosity-shear rate relationship of PC/UHMWPE blends.

EXPERIMENTS

Materials

UHMWPE(M-II), with average molecular weight of 2.5×10^6 and mean particle diameter of about 300 μm, was supplied by Beijing No. 2 Auxiliary Agent Factory (Beijing, China). Polycarbonate, Lexan144R with melt flow index (MFI) 10.5 g/10 min, was obtained from General Electric Company.

Gamma Irradiation

Irradiation was performed at different doses (1, 10, 30, 50, 70, 100, and 150 kGy) with a ^{60}Co source at a rate of 1 kGy/h in air at room temperature.

Preparation and Injection Molding of PC/UHMWPE Blends

PC pellets were dried for 2 h under vacuum at 100°C to eliminate the hydrolytic degradation of PC during processing and dry-mixed with UHMWPE powders with predetermined proportions, and then the mixture was blended in a TSSL-25 corotating twin extruder (Chengguang Chemical Institute, Chengdu, China) with a screw diameter of 25 mm and a length/diameter ratio of 23. The temperature profile was set in the range from 220° to 250°C and the rotation rate of the extruder was 100 rpm. The extrudate in the form of a thread from a rod die was pelletized, dried, and injection molded into standard testing specimens according to ASTM standards in an injection-molding machine.

Gel Content Measurement

The gel fraction was determined according to ASTM D2765 method using a Soxhlet extractor and the xylene as a solvent. Samples were refluxed in xylene close to its boiling point (about 138°C) for at least 72 h, until the sample attained constant weight. The residue after extraction was taken as the gel content.

$$\text{Gel content} = W_2/W_1$$

where W_1 is the initial weight of the polymer and W_2 is the weight of the insoluble portion of the polymer in the gel.

FTIR Spectroscopy

Fourier transform-infrared (FTIR) analysis was performed using a Nicolet 560 series FT-infrared spectrometer. The samples were prepared by mixing 1 mg of UHMWPE powder and 100 mg of ground KBr and pressing it in a die, forming a pellet at 10 tons and 1 min. All infrared spectra were scanned from 4000 to 400 $cm^{-1}$with a resolution of 4 cm^{-1}.

Melt Flow Rate Measurement

Melt flow index (MFI) of γ-ray irradiated UHMWPE and unirradiated UHMWPE were measured according to ASTM D-1238–73 on a CS-127 melt flow indexer at 250°C under a load of 10 kg.

Contact Angle Measurement

Samples were pressed into films and then investigated through the contact angles of water drops on films with ErmaG-1 contact angle tester at room temperature. A 5 mL droplet of distilled water was deposited on the film surface with a microsyringe, and contact angle was measured. The value reported is the average of at least five measurements made at different positions of each film.

Mechanical Measurement

The tensile properties of the blends were examined with an Instron 4302 tensile machine at 23°C, the size of specimens followed the ASTM D 638 standard, and the crosshead speed was 50 mm/min. The impact strength

measurements were performed with a XJ-40A impact tester (Chengde Testing Equipment Co. Ltd., China) according to ASTM D 256. In each of the tests, at least five samples were tested and the average was reported.

Molau Tests

Molau tests were carried out on different samples. About 500 mg of the samples was put into 125 mL of chloroform. The test tubes were first shaken thoroughly and then left for 24 h for further observation.

Scanning Electron Microscopy Observation

Scanning electron microscopy (SEM) (JSM-5900, Jeol Ltd., Japan) was used to observe the morphology of the fractured surface of PC/UHMWPE blends. The fracture surface was made conductive through the deposition of a layer of gold in a vacuum chamber.

Rheological Experiments

The rheological measurements were performed with a constant-rate capillary rheometer (Gottfert Rheograph 2002, Germany); the capillary diameter and its length-to-diameter ratio were 1 mm and 30, respectively. The entrance angle of the die is 180 degrees. Entrance pressure losses were assumed to be negligible for such a long capillary die, and therefore no Bagley correction was applied. The flow properties of these specimens were measured over a range of apparent shear rates of 10–3000 s^{-1} at 250°C.

RESULTS AND DISCUSSION

The irradiation of polyethylene causes chain branching, cross-linking, and oxidative degradation with formation of polar oxidized groups grafted to the polymer chains, whose extent depends on the irradiation conditions, as reported previously.[5,13–14] The oxidation can be controlled by the diffusion of the atmospheric oxygen inside the bulk of the material, depending on the irradiation dose rate and the thickness of the sample.[13] In this study, both powdery UHMWPE (particle size is about 300 μm) and lower gamma irradiation dose rate (1 kGy/h) are favorable to oxidative degradation, and lower gamma irradiation dose rate can avoid undesirable cross-linking of UHMWPE.

Table I. Effect of gamma irradiation on gel content and melt flow rate of UHMWPE

Samples	Gel content (%)	Melt flow rate (g/10 min)
UHMWPE (0 kGy)	0	0
γ-UHMWPE (1 kGy)	0	0
γ-UHMWPE (10 kGy)	0	0
γ-UHMWPE (50 kGy)	0	0.4
γ-UHMWPE (100 kGy)	0	4.8

Table I lists the gel content measurement results and the melt flow index of gamma-ray irradiated UHMWPE powder. It is evident that under the irradiation conditions, the melt flow index of UHMWPE increases with increasing gamma irradiation dose, which reflects the decrease in UHMWPE molecular weight resulting from oxidative degradation. Table I also shows that no gel was detected, indicating the absence of a significant amount of a cross-linked products.

Figure 1 shows FTIR spectra of UHMWPE before and after gamma irradiation. It is apparent that, after irradiation, a new absorption peak appears around 1715 cm^{-1} in FTIR spectra, indicating that the oxygen-containing groups (mainly carbonyl groups) have been introduced onto UHMWPE molecular chains. The intensity of the absorption peak increased with the irradiation dose. In order to trace the introduction rate of oxygen-containing groups onto UHMWPE chains (the rate of oxidation), it is usual to monitor carbonyl (C=O) group formation (I_{CO}) at 1720–1700 cm^{-1} using the following expressions: I_{CO} = absorbance at

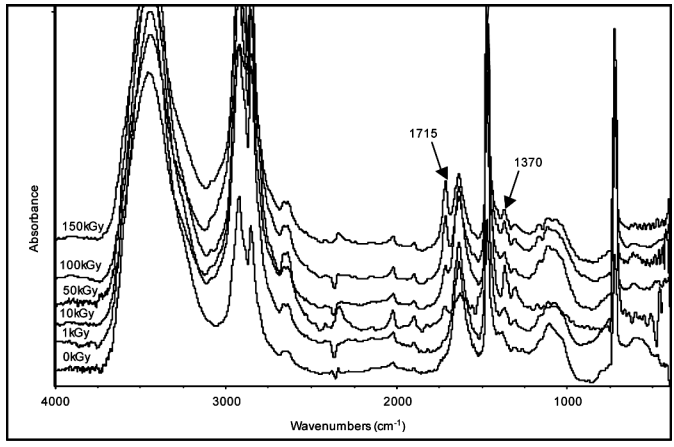


Figure 1. FTIR spectra (4000–400 cm^{-1}) of unirradiated UHMWPE and γ-UHMWPE (dose rate: 1 kGy/h).

1720–1710 cm^{-1}/absorbance of reference peak. Absorbance of a reference peak, which doesn't change with oxidation time, compensates for the changes in film thickness. Here the absorption of hydrocarbon around 1370 cm^{-1} is selected as the reference peak. The effects of γ-ray irradiation dose on the carbonyl group formation are shown in Figure 2, which clearly indicates that the amount of carbonyl content in higher dose irradiation is larger than that in lower dose irradiation.

Figure 3 shows the variation of contact angle of UHMWPE with distilled water at room temperature. The contact angle of irradiated UHMWPE decreases with the increase of irradiation dose, indicating an increase in hydrophilicity. It is concluded that, after the gamma-ray irradiation, UHMWPE has higher hydrophilicity than unirradiated UHMWPE.

The pictures shown in Figure 4 display the appearance of the four test tubes in which the Molau tests were carried out for the 85/15 PC/UHMWPE(γ-UHMWPE) blends. After the blends were stirred with chloroform and settled for 24 h in a test tube, a transparent solution of PC can be seen in tube (A). An obvious separation of an almost transparent solution of PC from the upper layer of UHMWPE particles can be seen in the PC/unirradiated UHMWPE blend, as shown in test tube (B). It should be noted that the solution in tube (B) is not perfectly clear, probably because a small amount of PC-UHMWPE copolymer may have been produced through macroradical reactions caused by melt blending. Test tubes (C) and (D) demonstrate a strong increase in turbidity of PC/γ-UHMWPE blends. This demonstrates that a larger amount of PC-γ-UHMWPE copolymer is produced.

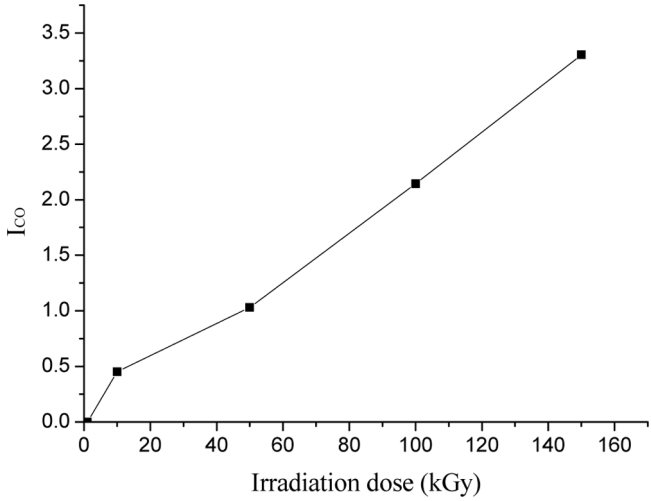


Figure 2. Rate of formation of carbonyl vs. irradiation dose.

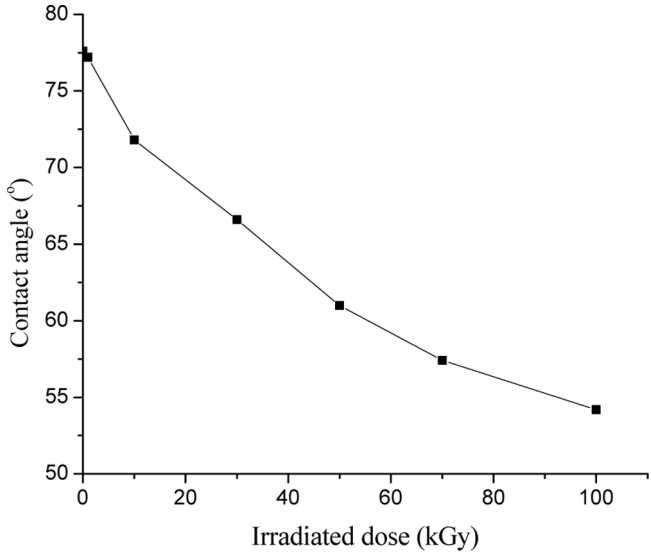


Figure 3. Contact angle of gamma-irradiated UHMWPE vs. irradiation dose.

The SEM micrographs of the fractured surface of PC/UHMWPE blends are shown in Figure 5. The PC/unirradiated UHMWPE blend in Figure 5(b) shows a spherical dispersion of the UHMWPE phase in

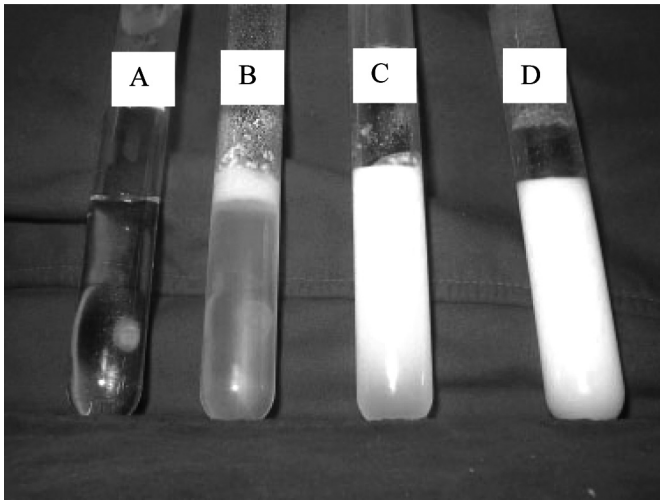
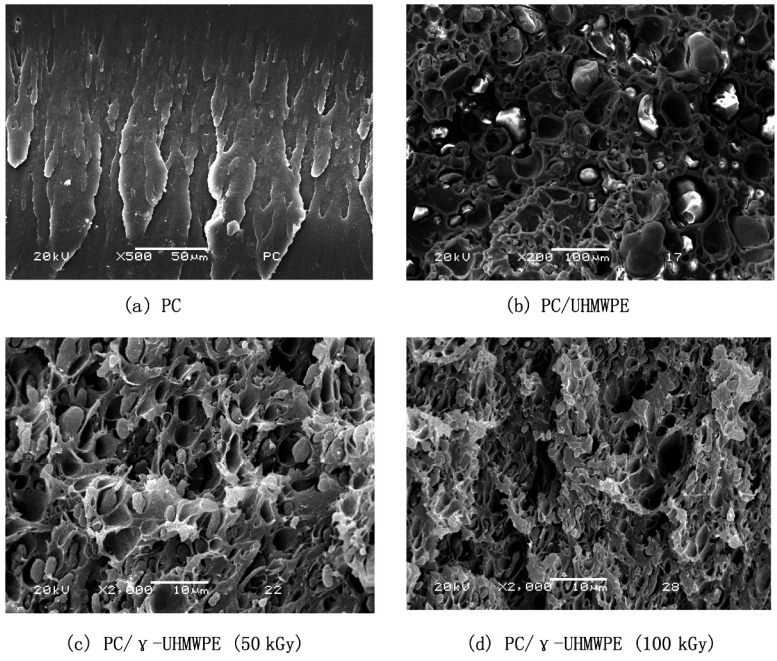


Figure 4. Molau test of PC, PC/UHMWPE (85/15), PC/γ-UHMWPE (85/15): (A) PC, (B) PC/UHMWPE, (C) PC/γ-UHMWPE (50 kGy), (D) PC/γ-UHMWPE (100 kGy).

the PC matrix. No interfacial action between PC and UHMWPE is observed from SEM micrographs, which resulted from the fact that there was almost no interfacial adhesive between UHMWPE spheres and PC matrix, and the majority of UHMWPE spheres were pulled out and the voids remained. However, irradiated UHMWPE made the morphology undergo a considerable change in the dimension of the dispersion phase and the interfacial behavior. Finer UHMWPE particles and a dim phase are observed (notice the higher magnification of the relevant micrograph in Figure 5(c), (d). The increasing irradiation dose on UHMWPE brings about a considerably further improvement of compatibility. In fact, when the irradiation dose of UHMWPE was up to 100 kGy, the two phases of PC/γ-UHMWPE blend became practically indistinguishable. It is then reasonable to assume that in PC/γ-UHMWPE blend the carboxylic acids formed during gamma irradiation on γ-UHMWPE main chains could chemically react with the –OH terminal groups or ester groups of PC to produce the graft copolymers during melt processing.

The results of the rheological measurements carried out on the blends are shown in Figure 6. It was found that the viscosity of the blends with



(a) PC (b) PC/UHMWPE

(c) PC/γ-UHMWPE (50 kGy) (d) PC/γ-UHMWPE (100 kGy)

Figure 5. SEM morphology of fractured surface of the PC, PC/UHMWPE (85/15), and PC/γ-UHMWPE (85/15).

irradiated UHMWPE (50 kGy) was higher than that of the blends with unirradiated UHMWPE at the same PC concentration, especially at low shear rate. The melt viscosity of the blends with irradiated UHMWPE (100 kGy) exhibits a reduction in comparison with blends with unirradiated UHMWPE. The rheological behavior of polymer blend is generally a reflection of the change in molecular weight and the interaction among the components. Usually, the decrease of molecular weight causes a lowering of the melt viscosity, and the increase of the interaction among the components causes an increase in the melt viscosity. As shown in Table I, γ-ray irradiation causes slight degradation of UHMWPE and a decrease in molecular weight. Thus, the rheological behavior of PC/UHMWPE (50 kGy) blend should obviously be attributed to the oxidized groups of UHMWPE, which developed the interaction between UHMWPE and PC interface. The rheological behavior of PC/UHMWPE (100 kGy) blend is mainly due to a decrease in molecular weight.

The yield strength and the notched Charpy impact strength of PC/γ-UHMWPE blend were measured and are summarized in Table II. Compared with the PC/UHMWPE (85/15) blend, the yield and notched impact strength of PC/γ-UHMWPE (50 kGy) (85/15) increase from 39.7 MPa and 9.9 kJ/m^2 to 49.2 MPa and 24.9 kJ/m^2. The yield strength and impact strength of PC/γ-irradiated UHMWPE blends increased with irradiation dose because a higher dose produced higher content of oxygen-containing groups, which is advantageous for the improvement of compatibility between PC and γ-UHMWPE.

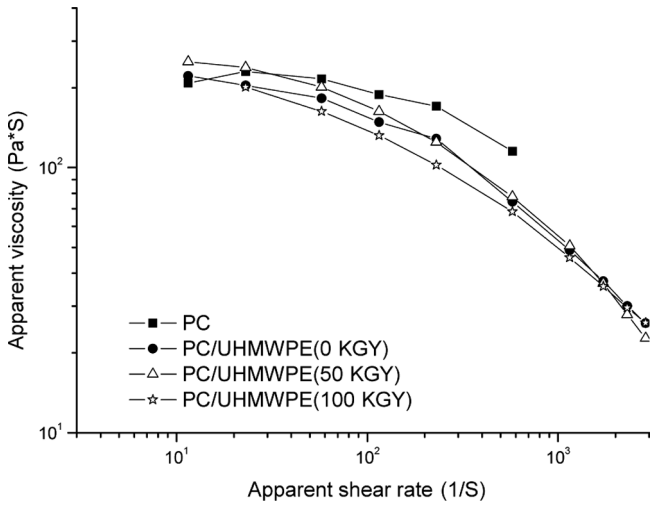


Figure 6. Apparent viscosity of PC/UHMWPE (85/15) blend vs. Apparent sheer rate (250°C).

Table II. Mechanical properties of PC/γ-UHMWPE (85/15)

Irradiation dose (kGy)	Yield strength (MPa)	Notched Charpy impact strength (kJ/m^2)
0	39.7 ± 0.2	9.9 ± 1.9
10	44.2 ± 0.3	9.5 ± 1.6
50	47.9 ± 0.9	23.6 ± 2.6
100	49.2 ± 0.2	24.9 ± 3.0

CONCLUSIONS

Gamma-ray irradiation treatment of ultrahigh molecular weight polyethylene in air at room temperature was successfully used to realize the functionalization of UHMWPE with the absence of cross-linked products. The melt flow index, amount of carbonyl content, and surface hydrophilicity of UHMWPE increase with irradiation dose. The morphological observation of polycarbonate/γ-UHMWPE blends shows that the particle size of the dispersed phase is reduced and the interfacial adhesion between polycarbonate and γ-UHMWPE is improved. Gamma-ray irradiated UHMWPE can greatly increase the tensile strength and impact strength of PC/UHMWPE blends because of enhancement of interfacial adhesion and the compatibility of the blends.

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