Radiational Hardening of Poly(vinylidene fluoride)–Poly(methyl methacrylate)–Polystyrene Ternary Blends

A. K. Mishra, P. Agrawal, R. Bajpai

Department of Postgraduate Studies and Research in Physics, Rani Durgavati University, Jabalpur 482001, India

Received 9 May 2003; accepted 14 October 2003

ABSTRACT: Specimens of poly(vinylidene fluoride) (PVDF)–poly(methyl methacrylate) (PMMA)–polystyrene (PS) polyblends with different weight percentage ratios of the three polymers were prepared with the solution cast technique. The effect of γ irradiation on the Vicker's microhardness was studied. Among the three pure polymers, PVDF, PMMA, and PS, the γ irradiation imparted crosslinking in PVDF, thereby causing radiational hardening. In the cases of PMMA and PS, the effect of irradiation exhibited a predominance of both the scissioning and crosslinking processes in different ranges of doses. Moreover, at a dose of 5 Mrad, in both PMMA and PS, maximum radiational crosslinking was observed. The effect of γ irradiation seemed to stabilize beyond 15 Mrad in PVDF and beyond 20 Mrad in PMMA and PS. Microhardness measurements on ternary blends of PVDF, PMMA, and PS revealed that the blend with low contents of PMMA, that is, up to 5 wt %, yielded softening, whereas increasing the content of PMMA beyond 5 wt % produced a hardened material because of radiational crosslinking, and a higher content of PMMA in the blend facilitated this crosslinking. J Appl Polym Sci 92: 3107–3111, 2004

Key words: blends; polystyrene; hardness; crosslinking

INTRODUCTION

Polymer blends are an important class of materials specifically designed and used for applications that take advantage of the enhanced properties offered by properly fabricated materials. Polymeric materials are profoundly affected by ionizing radiation, including γ rays, accelerated electrons, α particles, protons, and neutrons under different conditions.[1,2] The modification of polymers by radiation is an important industrial process throughout the world. Extensive studies have been undertaken to understand this technology, and the effects of radiation on the most significant classes of polymers are reasonably well catalogued and understood.[3,4] Some widely used polymers suffer main-chain scission and a loss in mechanical strength after irradiation;[5] such polymers are known as *degrading polymers*. However, some polymers possess enhanced molecular ordering after they are inadiated.[6] Both of these phenomena, degradation and crosslinking, can be consequences of irradiation. Either crosslinking or degradation occurs, depending on the conditions of irradiation and the chemical structure of the polymer; the one that predominates determines the net effect.[7] The size, shape, and chemical nature of the polymeric macromolecules also determine the degree of these two phenomena.

Further, polymer blends are now being studied because of the possible improvement in physical properties of mixtures that incorporate the individual properties of each component polymer.[8,9] Studies relating to polymer blends have been reported by various workers.[10] Poly(vinylidene fluoride) (PVDF)–poly(methyl methacrylate) (PMMA)–polystyrene (PS) is one possible ternary blend. PMMA is a versatile polymer with wide commercial applications that exhibits good mechanical properties and outdoor weathering. The use of PMMA is well known because it is a hard and rigid polymer.[11] It is atactic and amorphous and has a high glass-transition temperature (105°C). However, PVDF has good heat resistance and may be used continuously at temperature up to 150°C. It can be melt-processed by the standard techniques of injection molding and extrusion. PS is a hard, rigid, rather brittle material. It has a relatively low softening point and does not withstand the temperature of boiling water. It also has a high refractive index of 1.59, which gives it particular brilliance. It has a low heat distortion temperature of 85°C. We, therefore, considered it important to prepare and characterize a blend by mixing these three polymers. It is well known that microhardness is a very important property as it helps one understand the various physical properties of materials,[12,13] but only a limited work has been carried out as yet on the microhardness of polymers in general and

Correspondence to: R. Bajpai (dr_pk_agrawal@hotmail.com).

Journal of Applied Polymer Science, Vol. 92, 3107–3111 (2004)

those of polymer blends in particular. Earlier, we reported the effects of radiation on the polymer blends of PMMA–PVDF and PS–PMMA.[14,15] In this article, we report the effects of γ irradiation on the microhardness of ternary blends of PMMA, PVDF, and PS.

EXPERIMENTAL

PMMA (BDH, Pode, England), PVDF (Aldrich, Milwaukee, WI), and PS (BDH, England) powders were supplied by M/s Chemical Agencies (Mumbai, India). The quoted values for the molecular weights of PMMA, PVDF, and PS were 500,000, 350,000, and 258,000, respectively; the glass-transition temperatures were 105, 13, and 100°C, respectively. The melting temperatures were 225, 171, and 270°C, respectively.

The solution cast technique was used to prepare blends of the three polymers, PVDF, PMMA, and PS. Selected weight percentages (5, 10, 15, 20, and 25%) of PMMA were added to the PVDF–PS matrix. For every blend, PVDF and PS were taken in equal weight proportions. The known weight proportions of these polymers were dissolved in a common solvent, dimethylformamide, at a temperature of 130°C inside a temperature-controlled electric oven. The solution was constantly stirred during the heating process. After complete mixing, the transparent solution was poured into optically plain glass molds placed inside the oven. The solvent was then allowed to evaporate at a drying temperature of 70°C to obtain pellets of the blend specimens 6 cm^2 in size and 0.04 cm thick. After the perfectly dried samples were obtained, pieces of the appropriate sizes were cut from the pellets.

The blend samples were then mounted on an mhp 160 microhardness tester with a Vicker's diamond pyramidal indenter with a square base and a 136° pyramidal angle attached to Carl Zeiss NU2 universal research microscope (Jena, Germany). A load ranging from 10 to 100 g was applied for 30 s. A micrometer eyepiece was used to measure the diagonals of the indentation. The Vicker's microhardness (H_v) was calculated from the following equation:[16]

$$H_V = 1.854L/d^2 \ (\mathrm{kg/mm^2})$$

where L is load (kg) and d is the diameter of indentation (mm). For each test, the duration of indentation was 30 s. For each load, at least five indentations were made at different points of the specimen, and the average H_v was computed. Usually, the values of H_v were within 5% of the average value. During the test, the specimens were kept strictly horizontal and rigid.

γ irradiation

γ irradiation of the square shaped, 1 mm thick specimens was carried out at the University Science Instrumentation Centre, Nagpur University, Nagpur, India. A Co 60 Gamma Chamber-900 (Bhabha Atomic Research Center, Trombay, Mumbai, India) was used as the irradiation source. Samples were irradiated with various doses ranging from I to 25 Mrad (1, 3, 5, 7, 10, 15, 20 and 25 Mrad). The intensity of the γ rays was kept at 88,332.5 Curie, and the average radiation dose rate was 153.6 krad/h.

RESULTS AND DISCUSSION

Figure 1 illustrates the variation of H_v with the γ irradiation dose ranging from 1 to 25 Mrad at a load of 80 g for the pure PVDF, PMMA, and PS specimens. For pure PVDF, H_v increased with dose up to 10 Mrad, except for a slight decrease at 7 Mrad, and thereafter, it decreased in the dose range of 10–15 Mrad. Beyond 15 Mrad, the value of H_v again increased. The peak value of H_v was obtained at a dose level of 10 Mrad, suggesting radiation hardening due to the crosslinking of chains in PVDF. Moreover, it was interesting to observe that the H_v values of irradiated PVDF specimens at all doses of radiation were higher than the unirradiated PVDF specimens. Thus, in PVDF, there was an overall predominance of the crosslinking effect induced by γ irradiation. However, the degree of radiational crosslinking varied in the studied irradiation dose range. PVDF, which is a semicrystalline polymer, underwent crosslinking and increased its crystallinity under γ irradiation. This effect was at a maximum at a dose of 10 Mrad.

The effect of various doses of γ irradiation on the pure PMMA specimen was initially to increase the value of H_v up to a dose level of 5 Mrad and, thereafter, to decrease the value of H_v. However, beyond 15 Mrad, the microhardness of PMMA specimens again increased. The values of H_v for irradiated PMMA specimens when compared with those of the corresponding unirradiated ones both decreased and increased in various ranges of irradiation dose. Initially, at the lower range of 1 and 3 Mrad, the predominance of the scissioning effect was observed as the H_v values were less than those of the unirradiated ones. However, at 5 Mrad, the effect of irradiation reversed, and crosslinking dominated, which increased the H_v values of PMMA specimens. Radiational crosslinking in PMMA was observed at 5 Mrad. This effect seemed to continue up to a dose level of 10 Mrad; however, the degree of crosslinking decreased. In the dose range 10–15 Mrad, the scissioning effect again appeared to predominate as H_v values in this range were lower than those of the unirradiated specimens. Further, beyond 15 Mrad, the crosslinking of chains in PMMA probably induced hardening as H_v values increased and became almost similar to those of the unirradiated PMMA specimens at 25 Mrad. Thus, finally, the effect of γ irradiation seemed to have stabilized beyond 20

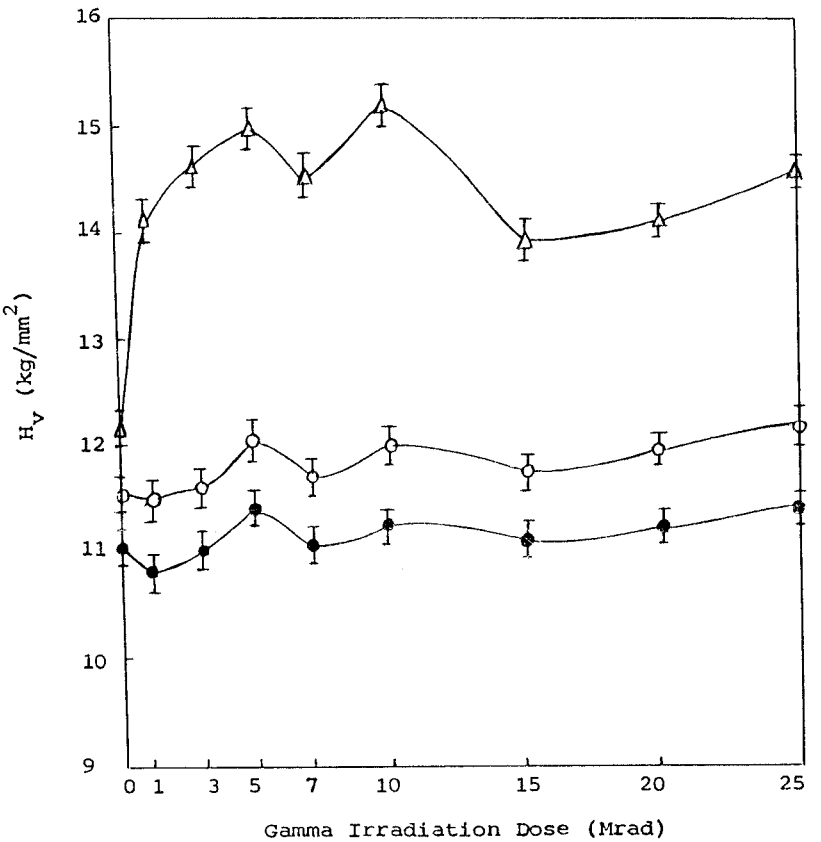

Figure 1 Variation of H_v with various doses of γ irradiation at 80 g for pure (△) PVDF, (●) PMMA, and (○) PS specimens.

Mrad. Hence, PMMA, which is a typical degradable polymer and whose main chain suffers random degradation as a result of exposure to γ irradiation, degraded at small dose levels of 1 and 3 Mrad and up to some extent at 15 Mrad. However, PMMA was crosslinked under irradiation at a dose of 5 Mrad.

For pure PS specimens, the effect of γ irradiation was again both to decrease and to increase the microhardness at varying dose levels. The H_v–dose profile was similar to that obtained for pure PMMA. If the value of H_v for the irradiated PS specimens were compared with unirradiated ones, one observes that except for at 1 and 15 Mrad, the level of microhardness increased compared to that of the unirradiated PS specimens. Thus, the chains in PS exhibited a slight predominance of the scissioning effect only at limited dose level, and an overall predominance of crosslinking at a majority of the dose levels was clearly indicated. This radiational crosslinking was at a maximum at 5 Mrad. The effect of γ radiation seemed to have stabilized beyond 20 Mrad, as there was no appreciable change in the H_v values of the irradiated and unirradiated PS specimens beyond this dose.

We, therefore, concluded that among the three pure polymers, PVDF, PMMA, and PS, the effect of γ irradiation was to impart crosslinking in PVDF, thereby causing radiational hardening. However, in PMMA and PS, the effect of irradiation exhibited predominance of both scissioning and crosslinking in different ranges of doses. Moreover, at a dose of 5 Mrad, in both PMMA and PS, maximum radiational crosslinking was observed. The effect of γ irradiation seemed to stabilize beyond 15 Mrad in PVDF and beyond 20 Mrad in PMMA and PS.

As shown in Figure 2, the H_v values for ternary blends varied significantly both with the change in γ irradiation dose and with the varying weight percentage of PMMA in the blend. The H_v–dose profiles for all of the ternary blend specimens were similar. Initially, up to 5 Mrad, H_v increased with dose; this was followed by a decrease at 7 Mrad. Beyond 7 Mrad, it again increased at 10 Mrad. Thereafter, the trend of H_v reversed at 15 Mrad. Finally, beyond 15 Mrad, the effect of dose on H_v seemed to stabilize. The peak value of H_v was obtained at a dose of 5 Mrad for all of the specimens.

In case of the ternary blend with 5 wt % PMMA, the H_v values at all doses of irradiation were less than those of the corresponding unirradiated specimens; therefore, the γ irradiation to these specimens imparted a scissioning effect, leading to the

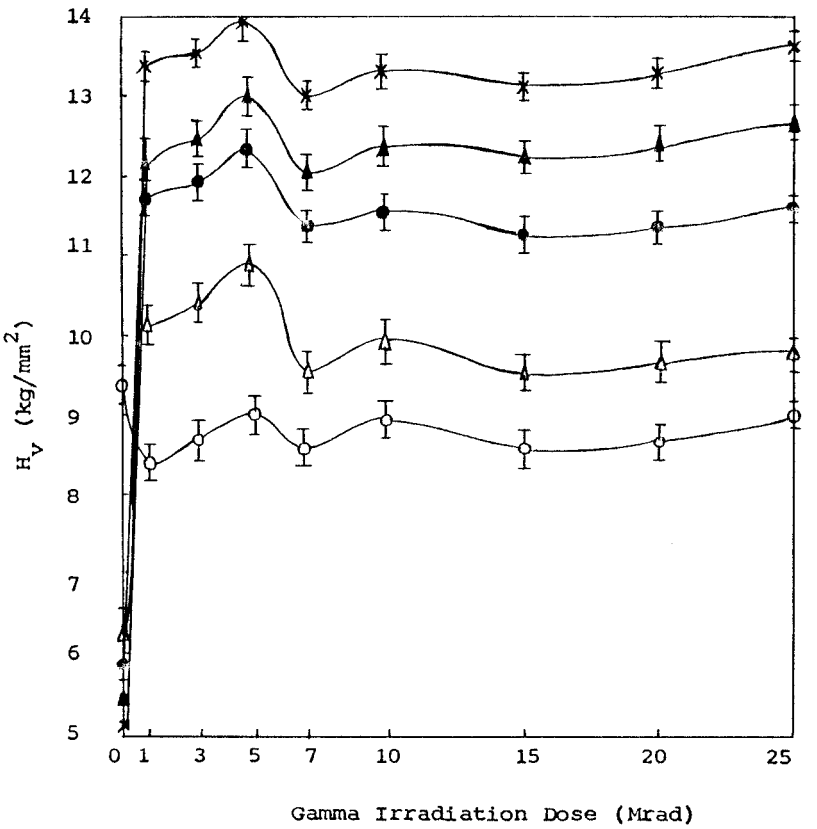

Figure 2 Variation of H_v with various doses of γ irradiation at 80 g for ternary blend specimens of PVDF–PMMA–PS with different weight percentages of PMMA: (○) 5, (△) 10, (●) 15, (▲) 20, and (×) 25 wt % PMMA.

softening of the specimens and a decrease in the strength. Also, the H_v values of these blend specimens were less than those of the pure irradiated PVDF, PMMA, and PS specimens. Irradiation had a deleterious effect on the blend specimens with 5 wt % PMMA. The effect of γ irradiation on the ternary blend specimens with 10 wt % of PMMA just reversed. The microhardness values of these blend specimens were higher than those of the corresponding unirradiated specimens. Moreover, the H_v values of these specimens were higher than those of the blend specimens with 5 wt % PMMA. The irradiation induced crosslinking of the chains of various polymers in the ternary PVDF–PMMA–PS blend. Thus, PMMA was crosslinked in the PVDF–PS matrix after irradiation. In the ternary blend that exhibited a two-phase system, PMMA acted as a hardener[17] and enhanced the strength of the blend because of radiational crosslinking. This effect was further strengthened because of irradiation as the content of PMMA in the blend increased to 15, 20, and 25 wt %. Thus, increasing the PMMA content in the blend system facilitated greater crosslinking and, thereby, imparted more hardening to the specimens. The density of radiational crosslinking increased with increasing PMMA in the blend. Maximum crosslinking for all of the specimens was observed at a dose of 5 Mrad. The degree of crosslinking decreased beyond 5 Mrad and stabilized beyond 15 Mrad.

We, therefore, concluded that microhardness measurements on ternary PVDF–PMMA–PS blends revealed that the blends with a low content of PMMA, that is, up to 5 wt %, yielded softening, whereas increasing the content of PMMA beyond 5 wt % produced a hardened material because of radiational crosslinking, and a higher content of PMMA in the blend facilitated this crosslinking.

The authors thank V. K. Vatsal, technical officer of the Department of Physics, Rani Durgavati University, Jabalpur, for help and support in maintaining the Carl Zeiss NU 2 universal research microscope.

References

1. Wang, L. H.; Huang, Z.; Hong, T.; Porter, R. S. J Macromol Sci Phys 1990, 29, 155.
2. Lizymol, P. P.; Thomas, S. Polym Degrad Stab 1993, 41, 59.
3. Vaughan, A. S.; Stevens, G. C. Polymer 1995, 36, 1541.

4. Vaughan, A. S.; Stevens, G. C. Polymer 2001, 42, 8891.
5. Hu, J.; Schulze, U.; Pionteck, J. Polymer 1999, 40, 5279.
6. McCarthy, D. W.; Mark, J. E. Rubber Chem Technol 1988, 71, 941.
7. Bradley, R. Radiation Technology Handbook; Marcel Dekker: New York, 1984; p 74.
8. Cabral, J. T.; Gerard, H.; Clarke, N.; Higgins, J. S. Phys B: Condens Matter 2000, 276–278, 408.
9. Bajpai, R.; Mishra, V.; Agrawal, P.; Datt, S. C. Bull Mater Sci 2002, 25, 21.
10. Hermes, H. E.; Higgins, J. S. Polym Eng Sci 1998, 38, 847.
11. Agrawal, P.; Bajpai, R.; Datt, S. C. Indian J Pure Appl Phys 1996, 34, 780.
12. Balt́ Calleja, F. J.; Fakirov, S. Trends Polym Sci 1997, 5, 246.
13. Bajpai, R.; Agrawal, K.; Agrawal, P.; Datt, S. C. J Polym Mater 1998, 15, 329.
14. Bajpai, R.; Mishra, V.; Datt, S. C. Polym Test 1994, 13, 435.
15. Bajpai, R.; Kotare, R.; Datt, S. C. Polym Test 1994, 13, 107.
16. Lopez, J. Polym Test 1993, 12, 437.
17. Bajpai, R.; Dhagat, N. B.; Katare, R.; Agrawal, P.; Datt, S. C. Bull Mater Sci 2003, 26, 401.