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Development of hardened PVF : PMMA polyblend: effect of gamma and electron irradiation

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Abstract. Specimens of poly(vinyl formal) (PVF) : poly(methyl methacrylate) (PMMA) polyblends with different weight percentage ratios were subjected to gamma irradiation (1 to 50 Mrad) and electron irradiation (1 to 20 Mrad). The effect of irradiation on the strength of the blend specimens was studied by measuring the surface microhardness using a Vickers microhardness tester attached to a Carl Zeiss NU 2 Universal research microscope. Significant changes were observed in the Vickers microhardness number, H_v. The H_v values of gamma irradiated specimens are found to be higher than the unirradiated specimens indicating an occurrence of radiational crosslinking. The maximum value of H_v is obtained at the gamma radiation dose of 15 Mrad. In case of electron irradiation the radiational crosslinking is found to take place for the blend specimens having lower wt% content of PMMA (0 and 1 wt%) in PVF matrix. On the other hand degradation of polymeric system is observed for the blends having PMMA content more than 1 wt%. The maximum value of H_v is obtained for all the blend specimens at the electron irradiation dose of 8 Mrad. The degree of crosslinking in polyblends due to gamma irradiation is found to be more than electron irradiation. The scissioning mechanism is found to predominate in the polyblend system in case of electron irradiation.

Keywords. Polyblend; microhardness; irradiation; crosslinking; degradation.

1. Introduction

The modification of polymers by radiation, either to crosslink or to break molecules, is a significant 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 (Charlesby 1954; Sisman and Bopp 1954; Bopp and Sisman 1955; Bajpai *et al* 1994; Nagesh *et al* 1999). Many widely used polymers suffer main chain scission and a loss in mechanical strength (Hu *et al* 1999); such polymers are known as the degrading polymers. On the other hand, many polymers are found to possess enhanced molecular ordering after being irradiated (McCarthy and Mark 1998). Degradation and crosslinking both could be the consequences of irradiation. Depending on the conditions of irradiation and the chemical structure of the polymer, either crosslinking or degradation occurs and the one which predominates determines the net effect (Bradley *et al* 1984). The size, shape and chemical nature of the polymeric macromolecules also determine the degree of these two phenomena. It is possible to produce fluorocarbon-like low surface energy polymers by the addition of small amounts of selected additives to nonfluorinated polymers such as poly(vinylidene chloride), poly(methyl methacrylate) (PMMA) and polyacrylamide (Jarvis *et al* 1964).

Further, the polymer blends are being studied these days because of the possible improvement in physical properties of the mixture incorporating the individual properties of polymers (Hermes and Higgins 1998; Bajpai *et al* 2002). Polyvinylformal (PVF) is a linear polymer belonging to polyvinyl acetal (PVA) group. Since PVF is a derivative of PVA the blends of PVA can be developed with PVF. PMMA also exhibits miscibility with PVA. Moreover, PMMA is a versatile polymer with wide commercial applications exhibiting good mechanical properties and outdoor weathering. Therefore, the PVF : PMMA polyblends have been developed with various weight proportions of these two polymers. The present paper reports the study on the surface modification of gamma and electron irradiated PVF : PMMA blend system. The tool used for detection is Vickers microhardness technique. This technique is now being widely used for morphological stabilization and plasticization studies on polymers (Gonzalez *et al* 1986; Pandey *et al* 1990; Bajpai *et al* 1992; Mishra *et al* 1994).

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2. Experimental

The solution cast technique (Agrawal *et al* 1996) has been utilized for preparing the blends of PVF and PMMA. Polymer granules of PVF and PMMA of low molecular weight grade (BDH, England) were supplied by M/s Chemical Agencies, Mumbai. The glass transition temperature of both PVF and PMMA is 105°C. The two polymers in selected weight proportions were dissolved in mixture of benzene : ethanol (3 : 2) at 40°C. The solution was poured in glass moulds and solvent was evaporated at 40°C to yield specimens of size 1 × 1 sq cm and 1 mm thickness.

2.1 *Gamma irradiation*

The gamma irradiation of the square shaped, 1 mm thick, specimens was carried out at the University Science Instrumentation Centre (USIC), Nagpur University, Nagpur. "Co 60 Gamma Chamber-900" was used as the irradiation source. Samples were irradiated with various doses ranging from 1 to 50 Mrad (1, 3, 5, 10, 15, 20, 25, 30 and 50 Mrad). The average irradiation dose rate was 0·35 Mrad/h.

2.2 *Electron irradiation*

The electron irradiation of the specimens was carried out at the Isotope Division of Bhabha Atomic Research Centre (BARC), Mumbai. An Industrial Electron Accelerator (ILU-6-M_3 type), with an electron beam of energy of 2 MeV was used as the radiation source. The average dose delivered was 5 Mrad when 3,250 pulses were given at a pulse rate of 10 pulses/s.

2.3 *Analytical procedure*

The irradiated specimens were indented at room temperature by a mhp-160 microhardness tester with a Vickers diamond pyramid indenter having a square base and 136° pyramid angle, attached to a Carl Zeiss NU 2 Universal research microscope. The indenting load ranged from 60 to 100 g. This was the saturation load range for the blends at the concentration ratios under examination. The diameters of indentation were measured by a micrometer eyepiece with an objective of magnification (12·5 ×). The Vickers hardness number, H_v, was calculated from the relation

$$H_v = 1{\cdot}854\ L/d^2\ (\text{kg/mm}^2),$$

where L is load (kg) and d 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. During the test the specimens were kept strictly horizontal and rigid.

3. Results and discussion

3.1 *Effect of composition*

Figure 1 depicts the variation of Vickers microhardness number, H_v, with various weight percentages of PMMA in the blends of PVF : PMMA at a saturation load of 80 g. It is seen that H_v gradually increases with increasing content of PMMA in the range of 1 to 7 wt%. The value of H_v increases with increasing value of load up to 80 g. The graph is plotted using the load of 80 g as at and beyond this value of load the microhardness of the specimen becomes independent of load and attains a level of saturation. The increasing PMMA content in this polymeric system causes an increase in stiffness, i.e. PMMA up to 7 wt% toughens the blends as depicted by the increase in the value of H_v. All the polyblends studied have higher H_v values than the pure PVF. Further, the blends in pellet form were clear and transparent. This indicates the miscibility of PVF and PMMA in the selected composition ratios. The miscibility of the two polymers in the blend can also be detected from the microhardness measurements, as the value of H_v of blend increases with increase in content of PMMA in the blend up to 7 wt% indicating progressive mixing of PMMA in PVF.

PMMA which has higher mechanical strength as compared to pure PVF, imparts mechanical strength to PVF. The polyblend so formed has increased microhardness and thus hardened PVF : PMMA polyblends are produced. Thus, the two polymers are also mechanically compatible as revealed from microhardness studies up to the blending ratio of 93 : 7 (PVF : PMMA). Addition of PMMA up to 7 wt% develops crosslinks with PVF molecules, thus

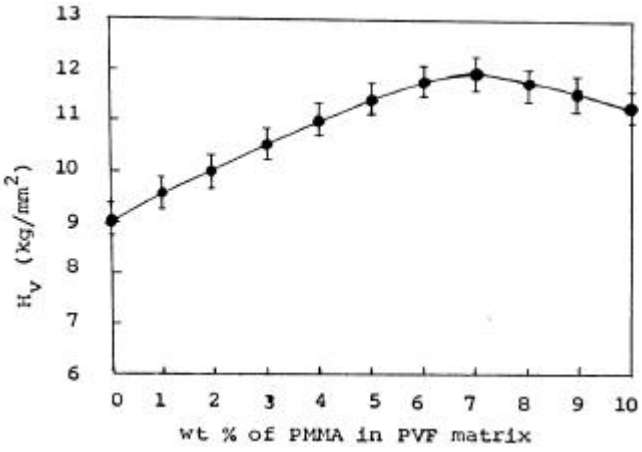

Figure 1. Variation of H_v with different wt% of PMMA in PVF : PMMA polyblend specimens at the saturation load of 80 g.

resulting in hardened blends. Addition of PMMA beyond 7 wt% in the blend tends to slightly decrease the H_v value at different loads. However, this effect tends to get stabilized beyond 8 wt% and up to 10 wt% of PMMA in the blend, thus increasing PMMA beyond 7 wt% slightly softens the blend. This indicates that the miscibility of two polymers above this composition range decreases and slightly phase separated systems are developed exhibiting decreased value of H_v. Moreover, this effect is slightly observed only up to 10 wt% of PMMA in the blend. Hence, the optimum desired ratio of PVF : PMMA for toughened blends is 93 : 7. PMMA acts as hardener to PVF in this composition range.

3.2 *Effect of gamma irradiation*

Figure 2 exhibits the effect of various doses of gamma radiation ranging from 0 to 50 Mrad on the surface microhardness of pure PVF and PVF : PMMA polyblends at the saturation load of 60 g. It is observed that the H_v values for both pure PVF and polyblends are higher than the corresponding H_v values of the unirradiated (0 Mrad) specimens. This clearly indicates an overall hardening of specimens when exposed to gamma irradiation which imparts radiational crosslinking. However, increasing and decreasing nature of H_v with increasing dose beyond 1 Mrad is obtained for all the specimens. These H_v values of the irradiated specimens are still higher than the unirradiated specimens. For pure PVF specimens, the value of H_v increases with dose in the range of 0 to 30 Mrad. This increasing microhardness of pure PVF with gamma irradiation induces crosslinking in PVF which is otherwise soft polymer. The gradual increase in crosslinking with irradiation suggests increase in molecular ordering of PVF. This radiational effect on PVF is maximum at the dose level of 20 Mrad, which then saturates up to 30 Mrad. Beyond 30 Mrad, the value of H_v decreases up to the dose of 50 Mrad. This decrease at a higher dose of irradiation indicates the degradation due to scissioning which destroys crosslinking density. However, the extent of this degradation at 50 Mrad is only with respect to the irradiated PVF specimens and not with respect to the unirradiated pure PVF.

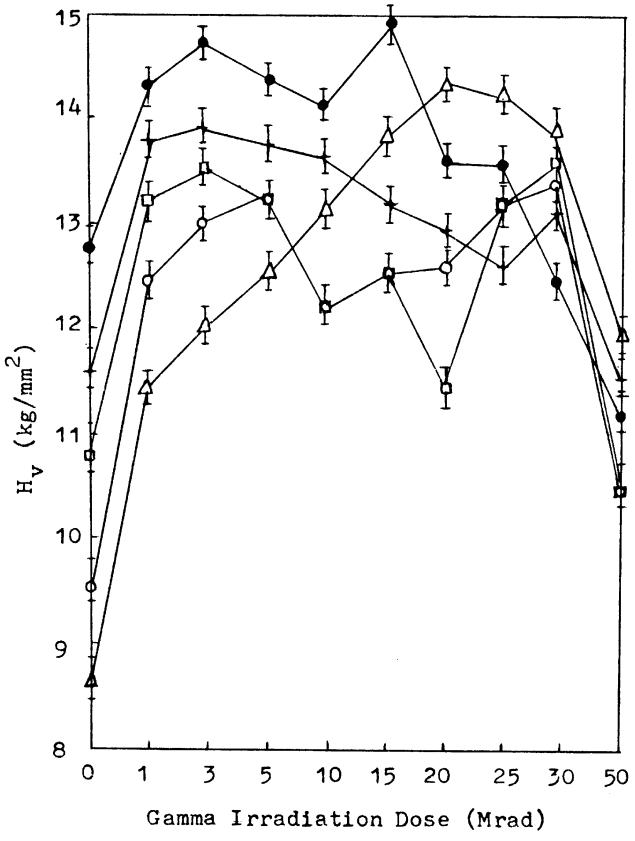

Figure 2. Variation of H_v with various doses of gamma irradiation at a saturation load of 60 g for pure PVF and blend specimens of PVF : PMMA with different weight percentage ratios (Δ, 100 : 0; O, 99 : 1; □, 97 : 3; +, 95 : 5 and •, 93 : 7).

Considering the effect of gamma irradiation on the microhardness of PVF : PMMA polyblends, it is evident that out of the four polyblends (99 : 1, 97 : 3, 95 : 5 and 93 : 7) shown in figure 1 the polyblends with 1 and 3 wt% PMMA exhibit higher H_v values up to the dose of 5 Mrad as compared to pure PVF, whereas polyblends with 5 and 7 wt% PMMA show this increased microhardness level when irradiated up to the dose level of 10 and 15 Mrad, respectively. Analysing the increasing and decreasing profiles of the irradiated polyblends, it can be observed that in all the polyblends, the value of microhardness fluctuates with the varying radiation dosage. This variation of microhardness can be explained with the help of formation of radiational crosslinks and scissioning phenomenon.

The toughening character of PVF : PMMA polyblends with increasing content of PMMA up to 7 wt% due to blending which strengthens the polyblends and also indicated by the value of H_v at 0 Mrad is found to further strengthen with gamma radiation up to the lower dose range of 3 Mrad. This radiational hardening of blends is due to crosslinking between the two polymers. This crosslinking increases with dose up to 3 Mrad as well as with increasing content of PMMA in the blends. PMMA is known to be a typical degradable polymer (Charlesby and Ross 1954) and its main chain suffers random degradation as a result of exposure to irradiation. However, some evidence of crosslinking in the blends of PMMA and some other polymers is available in literature (Wang *et al* 1989; Zhang *et al* 1991). Hence, the above results of PVF : PMMA blends are also suggestive of occurrence of radiation-induced crosslinking. The lower dose level range for this hardening character in the polyblends increases with PMMA content as observed to be 10 and 15 Mrad for 5 and 7 wt% PMMA polyblends, respectively. Ano-

ther remarkable fact observed for the radiational hardening for all the studied PVF : PMMA polyblends is that the maximum microhardness is found at the dose of 15 Mrad. This is the dose level at which density of developed crosslinks in the PVF : PMMA polyblends is the highest. Irradiation of these specimens at higher doses, i.e. beyond 15 Mrad, destroys these crosslinks in the blends as the degradative effect of PMMA starts dominating in the polyblends. This feature also receives support from the fact that the radiational degradation is more prominent in the polyblends with slightly higher PMMA content, i.e. for 5 and 7 wt% specimens. The slight decrease in the value of H_v between the dose range of 3 and 10 Mrad is attributed to loosening of the crosslinks developed at 3 Mrad, hence softening of polyblends. The stronger crosslinks are developed at the dose of 15 Mrad providing hardened blends. The degradative effect beyond 15 Mrad is an outcome of molecular chain scissioning of the polymeric molecules which reduces the average molecular weight of the blended system (Bradley 1984), consequently, H_v decreases. The slight increase in the value of H_v between 20 and 30 Mrad for polyblends with 1 and 3 wt% PMMA seems to be only superficial effect on these specimens.

3.3 *Effect of electron irradiation*

Figure 3 illustrates the variation of H_v with electron irradiation dose at the load of 60 g for pure PVF and different PVF : PMMA blend specimens. For pure PVF specimens (100 : 0), initially, H_v increases with increasing dose of electron irradiation in the lower dose range of 0 to 2 Mrad, indicating a clear evidence of radiational hardening due to crosslinking of PVF chains. Beyond 2 Mrad, H_v value decreases gradually to a small extent up to the dose level of 7 Mrad; however, these values are still higher than the unirradiated PVF specimens (0 Mrad). Finally, the microhardness of PVF specimens again shows an increasing trend beyond 7 Mrad and exhibits maximum H_v value at 8 Mrad. It may, therefore, be concluded from the above observations that, in general, pure PVF specimens exhibit radiational crosslinking when exposed to electron irradiation and gets hardened. The decreasing trend in the value of H_v in the dose range of 2 to 7 Mrad, is attributed to the loosening of crosslinks; however, this effect is still contributory for the hardening of specimens due to radiation when compared to the unirradiated specimens. It is only the degree of crosslinks which varies. The maximum crosslinking is observed at 8 Mrad. Pure PVF is, therefore, a polymer which is conducive for radiational crosslinking in the specified dose of irradiation.

The H_v-dose profile varies with the composition of the blend specimen. Initially, the value of H_v increases with electron irradiation dose up to 2 Mrad for the blend specimens of 1 and 3 wt% of PMMA. The value of H_v for these specimens are greater than those of the unirradiated specimens (0 Mrad). However, H_v decreases with the dose beyond 2 Mrad and this decrease continues up to 7 Mrad for these two blend specimens. Moreover, value of H_v is higher for 1 wt% of PMMA blend specimens as compared to the unirradiated ones. Thus specimens with 1 wt% of PMMA exhibits crosslinking due to electron irradiation at all the doses. However, the degree of crosslinking changes with the dose. Similar profile is obtained for the pure PVF (100 : 0) specimens. However, the value of H_v for these specimens is less as compared to the blend with 1 wt% PMMA. Similarly, radiation crosslinking is also observed for 3 wt% PMMA specimens up to 2 Mrad. However, beyond this dose the degradation effect is observed up to the dose of 7 Mrad. Further, crosslinking predominates at 8 Mrad and thereafter, scissioning is found to occur. Thus the polyblend of PVF : PMMA with 1 wt% PMMA exhibits radiational crosslinking and hardened blends are produced when specimens are exposed to electron radiation. This feature is attainable in the polyblends with 3 wt% PMMA only at 2 and 8 Mrad, at the other doses it is the degradative effect which is observed as the H_v values of irradiated specimens are less than the corresponding unirradiated polyblends.

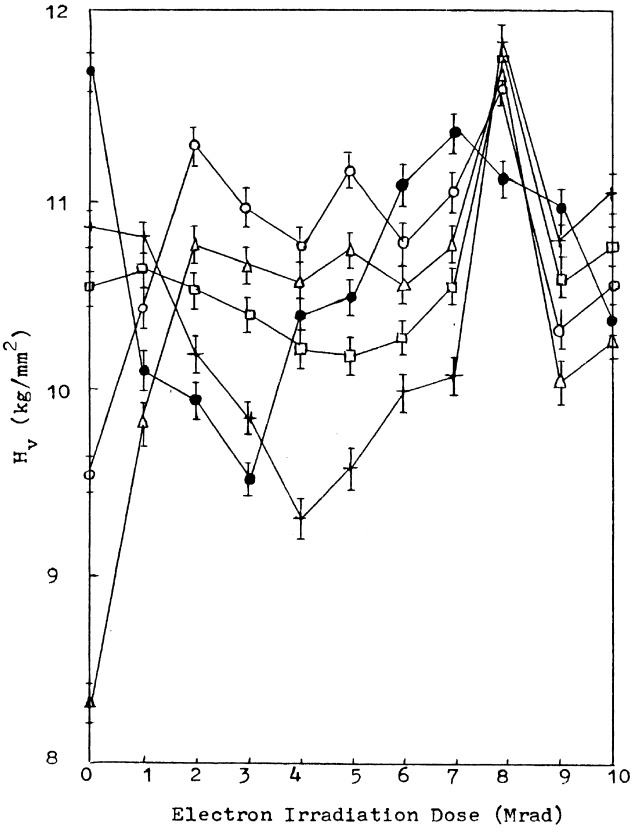

Figure 3. Variation of H_v with various doses of electron irradiation at a saturation load of 60 g for pure PVF and blend specimens of PVF : PMMA with different weight percentage ratios (Δ, 100 : 0; O, 99 : 1; □, 97 : 3; +, 95 : 5 and •, 93 : 7).

In polyblend specimens with 5 and 7 wt% of PMMA, the effect of electron irradiation is degradative up to the dose of 7 Mrad. These blend specimens get softened with irradiation as the scissioning process predominates in the polyblend system. However, slight increasing trend in the value of H_v beyond 4 Mrad and maximum at 8 Mrad for the blends with 5 wt% PMMA specimen indicates progressive crosslinking and radiational crosslinking is achievable at the dose of 8 Mrad as the value of H_v at this dose is higher than the unirradiated polyblends. For 7 wt% PMMA blend specimens also the increasing value of H_v beyond 3 Mrad and up to 8 Mrad reveals slight crosslinking; however, these values are still smaller than the unirradiated ones and hence the electron radiation imparts overall softening effect to these polyblend specimens. Hence, the electron irradiation has deleterious effect on 93 : 7 polyblends. PMMA exhibits crosslinking with PVF when exposed to electron radiation at lower concentration, i.e. 1 wt% PMMA at the dose range of 0 to 8 Mrad only at the higher dose of 8 Mrad for 3 and 5 wt% PMMA polyblends. This also seems true from the fact that PMMA is a degradative polymer (Charlesby and Ross 1954) and when this polymer is added to PVF in moderately higher concentration, i.e. 5 and 7 wt%, then the polyblend so developed reverses its effect from radiational crosslinking observed for the lower content (1 and 3 wt%) PMMA blends to radiational softening.

The degree of crosslinking in PVF : PMMA polyblends under gamma radiation seems to be more than under electron radiation as the level of radiational hardening observed is more in the case of gamma radiation. Further, the increasing trend of H_v values with increasing content of PMMA in the polyblend up to 7 wt% observed for the unirradiated (0 Mrad) specimens normally seems to be unaltered with gamma radiation dose up to 10 Mrad. This feature, however, gets reversed with electron radiation, where H_v values of the blends decrease with increasing content of PMMA. In the present investigation the electron irradiation is faster and its effect is, therefore, quicker and hence the degradation process predominates in PVF : PMMA polyblends whereas gamma irradiation provides sufficient time for crosslinking process to predominate.

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