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Effect of Gamma Irradiation on the Microhardness of Polymer Blends of Poly (Ethyl Methacrylate)(Pema) and Poly (Ethylene Oxide) (Peo)

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***Abstract*—**The effect of gamma irradiation on micro-hardness of polymer blends of poly (ethyl methacrylate)(PEMA) and poly (ethylene oxide) (PEO) has been investigated to detect the radiation induced crosslinking. The blend system comprises a non-crystallizable polymer, PEMA and a crystallizable polymer, PEO. On irradiation, the overall hardness of the blend specimens for different dose levels infers occurrence of a crosslinking process. The radiation-induced crosslinking was greater for blends having lower concentration of PEO. However, increase in radiation dose causes softening of blend system due to radiation induced scissioning of the chains.

***Keywords*—**Microhardness, Radiation induced crosslinking, Solution cast technique, Vicker's hardness number.

I. Introduction

ONE of the goals of material research is to create new materials with properties tailored to a particular application and to understand the physical and chemical mechanisms that determine these properties. One of the important methods to create such materials is blending of two or more polymers having different properties [1]-[11]. Polymers having different sets of physical and chemical properties are usually mixed together to obtain polymer blends which have required set of desired properties. In most cases polymer blends are formed when two polymers are thoroughly mixed in one body. The production of such mixtures makes it possible to improve upon the properties of individual polymers. Commercial polymer blends are utilized for such features for example their strength, stability and wide range of adaptability for various applications in different fields of science and technology. Blending often offers economic benefits also in that it helps in generating high performance materials from low cost polymers. The blending technology offers new type of materials, characterized by controlled chemical constitution and morphology, which can be precisely tailored to specific requirements[10]-[13].

In many applications, the effect of various types of environment, such as thermal, chemical or high energy radiation on the structural and physical properties of polymers is a significant factor. Thus, study of the effect of various types of environment on the structure and properties of polymer is an essential aspect in the development of these materials [10]-[24].

Polymeric materials are profoundly affected by ionizing radiations such as gamma rays, accelerated electrons, α – particles, protons and neutrons, under various conditions [16] –[24]. The effect of such irradiations on the physical and chemical properties of these materials is of considerable importance due to their potential applications in nuclear and space sciences. Many widely used polymers suffer main chain scission or crosslinking, depending upon various physical parameters, when exposed to radiation. Crosslinking and scission are two opposite consequences of irradiation. The radiation induced changes result from disturbance of the distinctive molecular or chemical structure of these materials. The large changes produced by radiation can involve crosslinking, that provides hard and brittle materials, or cleavage which weaken or soften the polymer. Many authors have reported improvement in the mechanical and physical properties of blends exposed to gamma irradiation [21]-[24].

PEMA is a non-crystallizable polymer while PEO is a crystallizable polymer; when these two polymers are blended, the blending yields interesting features regarding plasticization and crystallinity aspects [(6]-[7]. Vicker's microhardness studies of polymer blend specimens shows that PEO acts as a plasticizer for PEMA [6].

The Vicker's microhardness testing has been found to be a non- destructive method and is a very effective tool to study the mechanical properties of polymers [5]-[7],[14]-[19]. In the present work Vicker's microhardness testing was used to study the effect of irradiation on the mechanical properties of this polymer blend.

A. Experimental Materials

The polymers PEMA having average molecular weight of 515000 and PEO with molecular weight of 200000 were

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purchased from Thomas and Bakers, India and used as received. The common solvent, used to dissolve the polymers, was benzene and it was obtained from Hi Media Chemicals, India.

Preparation of blends

The solution casting technique [5]-[7],[21] was used to prepare PEMA/PEO blends. Desired weights of PEMA and PEO were dissolved in benzene at a temperature of 40^0 C. The solution was poured in glass moulds and solvent was evaporated by keeping the glass moulds inside the oven at a 40^0 C temperature for one hour. The oven was then switched off and the solution was allowed to cool in an oven by itself to a room temperature. This yielded blend specimens in form of square sheets of surface area of $6cm^2$ and thickness of 0.4cm.

Irradiation of samples

The square shaped specimens were irradiated with different doses of gamma irradiation and the surface microhardness studies have been carried out on the irradiated specimens.

The gamma irradiation of square shaped, 0.4 cm thick specimens, were carried out at the University Instrumentation Centre (USIC), Nagpur University, Nagpur, Maharashtra (India). Co60 Gamma Chamber-900 was used as the irradiation source. Samples were irradiated with various doses ranging from 200 Krad to 25 Mrad (200, 400 and 800 Krad, 1, 5, 10, 15, 20 and 25 Mrad). The average irradiation dose rate was 0.35 Mrad/hour.

The irradiated specimens were indented at room temperature by Vicker's diamond pyramidal indenter having a square base and 1300 pyramidal angle attached to a Carl Zeiss NU2 universal research microscope (USA) at the Department of Physics, R.D. University, Jabalpur (India) and the Vicker's hardness number (HV) was determined with mhp 60 microhardness testers. The indenting load chosen was 40g. For each test duration of indentation was kept 30 seconds. At least five indentations were made at different points of the specimen and the hardness number HV was calculated for each specimen from the measured diagonal of the indentation by the relation:

$$H_v = \frac{1.854 \times L}{d^2} Kg/mm^2$$

Where L is the load in kg and d is diagonal of indentation in mm.

II. Results and Discussion

Fig. 1 shows the effect of various doses from 0 to 1 Mrad on surface micro- hardness of pure PEO, pure PEMA and polyblends of PEO and PEMA at a load of 40g. Fig. 2 shows the effect of various doses from 1 to 25 Mrad on surface microhardness of pure PEO, pure PEMA and poly blends of PEO and PEMA at a load of 40g. The H_V values for all the unirradiated sample(0 Mrad) are also plotted in Fig. 1.

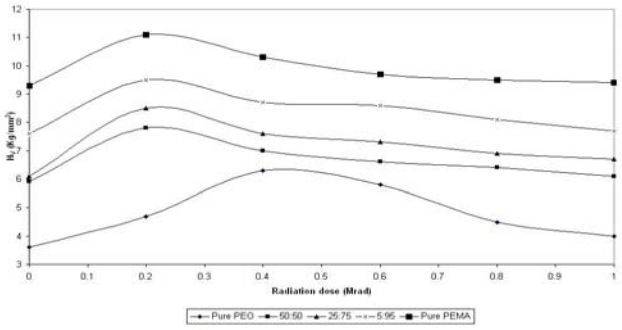

Fig. 1 Variation of HV with radiation dose for low range of the radiation dose from 0 to 1Mrad for pure PEO, PEMA and polyblend specimens having different percentage ratio of the two polymers

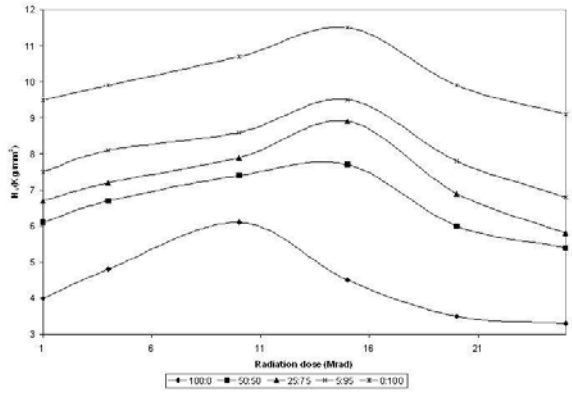

Fig. 2 Variation of HV with radiation dose for high range of radiation dose from 1 to 25 Mrad for pure PEO, pure PEMA and polyblend specimens having different weight percentage ratio of the two polymers

For pure PEO, in the low range of radiation dose (Fig.1) the H_V increases with the dose upto 400 Krad and thereafter it decreases from the peak value in the dose range of 400 Krad to 1 Mrad. However the H_V values are still higher than that of unirradiated sample(0 Mrad). Thus for lower radiation dose overall hardening occurs; however, the effect of doses of radiation exhibits both increasing and decreasing trend of H_V values [22]-[26]. Hardening in the dose range from 0 to 400 Krad is attributed to radiation induced crosslinking of chains in PEO. The density of crosslinking decreases beyond 400 Krad which results into decrease in microhardness of the specimen. Gamma-radiation-induced crosslinking in PEO has been reported. The crystallinity of semicrystalline polymer like PEO is severely affected by radiation and at extremely high radiation dose, PEO will be amorphortized; as reported in literature[25].

For higher radiation doses from 1 to 25 Mrad (Fig. 2), microhardness of pure PEO increases sharply upto dose of 10 Mrad. Beyond 10 Mrad, the H_V decreases and thereafter beyond 15 Mrad, the H_V values are less than that of unirradiated specimen (0 Mrad). The decrease in microhardness beyond 10 Mrad is due to radiational

scissioning of chains of PEO. This cleavage of main chain of PEO, ultimately causes softening of the polymer.

The pure PEMA also exhibit trend similar to pure PEO, however in this case maxima in lower range occurs at 200 Krad and in higher range occurs at 15 Mrad. The decreasing trends in the value of H_V in the dose range of 400 Krad to 1 Mrad for pure PEO and 200 Krad to 1 Mrad for pure PEMA is attributed to the loosening of the crosslinks; however this effect is still contributory for the hardening of specimens due to radiation when compared to the unirradiated specimens. The densities of developed crosslinks are maximum at 10 and 15 Mrad respectively for PEO and PEMA. Therefore, PEO and PEMA are the polymers which are conductive for the radiational crosslinking in the specified dose range of radiation.

The polyblends specimens also exhibit identical trends for both low as well as high radiation doses. The H_V versus radiation dose profile varies with the composition of the blend specimen. Among all the samples, the H_V versus radiation dose profile for pure PEMA (which is amorphous) is highest while that for pure PEO is lowest.

For pure PEMA as well as for the polyblend samples, in lower range of radiation dose from 0 to 1 Mrad, H_V increases upto 200 Krad. Beyond 200 Krad, the H_V decreases in the range from 200 to 1 Mrad, however the H_V values are still higher than those for unirradiated specimens. Hence the study reveals that radiation imparts hardening to the pure PEMA and pure PEO as well as to the polyblend samples. The hardening in the polyblends is due to radiation induced crosslinking between the two polymers. The density of crosslinking, decreases in the dose range from 200 Krad to 1 Mrad. The density of crosslinking is more for blend having lower wt %(weight percentage) of PEO. The density of crosslinking decreases with increasing weight percentage of PEO. Thus in the dose range from 0 to 1 Mrad, among the blends the degree of radiation induced hardening is maximum for the polyblend having 5 wt% of PEO and is minimum for the polyblend having 50 wt% of PEO.

In the higher range of doses from 1 to 25 Mrad, the pure samples as well as polyblends exhibits similar trend. The microhardness again increases and rises sharply to the maxima at 15 Mrad. Beyond 15 Mrad, the H_V of all the samples decreases and falls below the values for the unirradiated samples.

The decrease in H_V with radiation dose indicates radiational scissioning effects, which results softening of the samples. The gradual increase in crosslinking with irradiation suggests increase in molecular ordering of the samples [26]-[27], thereby developing dense crosslinks. In the lower radiation range this effect is maximum at the dose level of 200 Krad, which then reduces and saturates upto 1 Mrad. Beyond 1 Mrad , the H_V values increases and reaches maximum at 15 Mrad. After 15 Mrad, the decrease in H_V indicates the degradation due to scissioning which destroys the crosslink density. PEMA is known to be typical degradative polymer and its mainly suffers random degradation when exposed to high energy radiation. The results obtained confirm the fact.

The figures reveal that radiation induced hardening is more for the blends having lower concentration of PEO .Thus we conclude that PEMA and PEO can be crosslinked under irradiation and the degree of crosslinking is related to the miscibility of PEO and PEMA in the blend [6]-[7]-[10]. As the miscibility decreases rapidly when the wt% of PEO is increased beyond 25% the radiation induced hardening decreases and is minimum for the blend having 50 wt% of PEO. Thus the PEMA which is typical degradative polymer when this polymer is blended with PEO in moderately higher concentration of above 50 wt% then the irradiation produces hardening which decreases with decreasing concentration of PEMA.

The softening character of the blend of PEO with PEMA with increasing content of PEO has been reported [6]-[7]. However radiation induces hardening in the blends. This hardening is due to developed crosslinking between two polymers. Irradiation of PEMA, PEO as well as the polyblend specimens at higher doses destroys the crosslinks and chain scissioning occurs which reduces average molecular weight of the blended system.

III. Conclusion

The study reveals that pure PEO, pure PEMA as well as their blends exhibit hardening due to radiational crosslinking. At higher radiation dose the degree of crosslinking increases but as the radiation dose is increased beyond 15 Mrad, the softening of blend specimens occurs due to scissioning which destroys developed crosslinks. The radiation induced hardening is more for blends having lower wt% of PEO. Thus the developed plasticized blends having good value of crystallinity can further be hardened by irradiation.

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