

Modification of Isotactic Polypropylene Films (IPP) Through Ar⁸⁺ Ions Induced Grafting of 2-Hydroxyethyl Methacrylate (2-HEMA)

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ABSTRACT

The present work is part of a systematic study that involves grafting of different monomers on different polymeric substrates using low energy ions. Low energy ion irradiated Ar⁸⁺ ion irradiation was explored as a means of forming chemically active sites on the surface of IPP films. The IPP was irradiated by Ar⁸⁺ ions having energy of 1.2 MeV with varying fluence from 1×10^{12} ions/cm² to 5×10^{13} ions/cm². The irradiated IPP was grafted by 2-Hydroxyethyl Methacrylate (HEMA). The grafting yields were determined by weight measurements as a function of ion fluence, grafting time, temperature and monomer concentration. The grafted films were analyzed using FTIR, SEM and AFM. All these measurements suggest that the HEMA was grafted onto Ar⁸⁺ ion irradiated film.

Keywords IPP, graft copolymers, FTIR, AFM, SEM

1. INTRODUCTION

Ion beam technique is widely used as a flexible and powerful tool for different materials surface engineering, including polymers. The increased attention in the ion implantation of polymer materials is due to the possibility of precise control of the technological parameters for fundamental research purposes, and also considering some possible applications to device fabrication. The ion irradiation of polymers causes various processes, such as macro-molecular destruction, cross-linking, free radicals formation, carbonization and oxidation [1-3]. The understanding of certain structural re-arrangements influence on the suitable properties of polymers opens a way to design devices with required parameters, involving such applications as optical filters, absorbers, reflectors, etc [4-5]. The interaction of ions with material is the deciding factor in the ion beam induced material modification. Ion irradiation of polymer can induce irreversible changes in their monotonic properties such as electrical, structural properties and the surface related mechanical property. These changes are responsible to fundamental events like electronic excitation, ionization, chain scission and crosslinks as well as mass loss which take place due to ion beam irradiation.

In the present work, *low energy ion beam* (LEIB) have been used to create free radicals onto IPP [6-7] and thereby grafting hydrophilic monomers onto the IPP film. We have used Ar^{8+} having energy of 1.5 MeV. A method to produce grafted polymers only on the surface, leaving the bulk properties unmodified, is of great interest regarding the number of possible applications and opening the possibility to develop new materials. The advantage of using LEIB to change the superficial properties of polymers is that the projected range and the ion fluence of the implanted layer can be accurately selected. The changes in physico-chemical

properties for a large number of polymers modified by LEIB have been reported [8]. We report a study of grafting of HEMA onto IPP films irradiated with 1.2 MeV Ar^{8+} ions having different fluences ranging from 1×10^{12} to 5×10^{13} ions / cm^2 . The correlation of the grafting yield with ion fluence, monomer concentration, grafting time, temperature was analysed. The evidence of grafting was investigated in detail and the grafting membranes were characterized by using FTIR, SEM and AFM studies.

2. EXPERIMENTAL

2.1 Materials & Method

The films were extensively washed with acetone (Aldrich) and dried in a vacuum oven at 60°C before use. 2-HEMA used in the present work was obtained from Sigma Aldrich and was used without further purification. The other chemicals were all analytical grades and used as received. Double distilled water was used as the reaction medium for graft copolymerization.

2.2 Irradiation of IPP Films with Ar^{8+} Low Energy Ion Beam (L.E.I.B)

IPP film was cut into small strips of size ($4 \times 4 \text{cm}^2$), washed with acetone, dried and weighed. IPP films and irradiated in vacuum at room temperature using ion source at Inter University Accelerator Centre (IUAC), New Delhi. The 1.2 MeV Ar^{8+} beams in the fluence range of 1×10^{11} - 5×10^{13} ions/ cm^2 were used for irradiation. The ion beam current was about 70 particle nA.

2.3 Graft Copolymerization Procedure

Grafting was carried out in Pyrex ampoules having a stop cork. Irradiated IPP films which have been exposed to air were washed with acetone, dried at 50°C in a vacuum

oven, weighed, and then immersed in the mixture of monomer concentration varying from (5-25 V/V%) and solvents in Pyrex ampoules. Ammonium ferrous surface was added to avoid the formation of homopolymer usually formed during grafting. The mixture reaction was deaerated by bubbling nitrogen gas for 10-15 minutes and sealed. The ampoules were heated in a water bath at different temperatures varying in the range of 55⁰C - 85⁰C and for different time periods varying in the range of 1 to 5 hours. After heating, the obtained grafted films were taken out from the monomer solution in the ampoules and washed thoroughly with distilled water to remove the unreacted monomer and the remaining homopolymers that may be occluded in the grafted films and then dried in a vacuum oven at 60⁰C till constant weight was obtained. The percentage of grafting (% Pg) was calculated from increase in weight of the original film.

The percentage of grafting was calculated by $(\%Pg) = \frac{W_g - W_0}{W_0} \times 100$

Where W_g and W_0 are the weight of the IPP samples before and after grafting, respectively.

2.4 Characterization

2.4.1 FTIR Spectroscopy

FTIR spectra of pristine IPP film and grafted films IPP-g-HEMA, were recorded on a Thermo 5700 FTIR RX1 (4000-500 cm⁻¹) spectrophotometer (Norwalk, CT).

2.4.2 AFM Analysis

Surface topography of pristine IPP film and grafted films IPP-g-HEMA were performed on a multimode Nanoscope IIIa SPM under Tapping Mode. The samples have been analyzed by tapping mode with a tapping silicon nitride probes mounted on cantilevers in the tapping mode to avoid surface damage and a low force constant.

2.4.3 SEM Analysis

Surface topology and homogeneity of pristine IPP film and grafted films IPP-g-HEMA were performed on a LEO VP 435 instrument. The membranes were coated by means of double-sided electric adhesive tapes. A thin layer of gold was sputtered on the sample surface under reduce pressure to prevent the charging in the specimen and prior to the SEM measurement. The electrons beam parameters are kept constant while analyzing all the samples. The micrographs of the samples with 10-40 kV EHT and 25 pA beam current are recorded by camera attached on the high-resolution recording unit.

3 RESULTS AND DISCUSSION

3.1 Mechanism of Grafting

Ionizing radiations have sufficient energy for generation of free radicals. The free radicals generated on polymeric backbone provide active sites where monomer can be grafted. A plausible mechanism of grafting has been proposed. The swift Ar^{8+} ions abstract hydrogen atoms from IPP during their passage through the IPP film. When the IPP radicals are in contact with air, they react with oxygen and lead to the formation of oxidized compounds such as peroxide and hydroperoxides as shown in scheme 1. The peroxides/hydroperoxide groups on IPP undergoes a redox reaction with the ferrous ion of Mohr's salt to form an oxyl polymer radical capable of initiating graft copolymerization with a minimum of homopolymerization. Due to the low ion range, the grafted polymer extends only to a depth of a few hundred nanometers and then induce a change on the physico-chemical properties of the surface leaving the bulk.

Scheme 2 Grafting process of HEMA onto IPP

Grafting is performed by treating irradiated IPP with HEMA. This grafting process consists of initiation, propagation, and termination. Scheme 2 is suggested for the grafting of HEMA onto IPP film.

3.2 Parameters Affecting Grafted Membranes

3.2.1 Effect of Ion Fluence

It is found from figure 1 that the grafting percentages of HEMA on Ar⁸⁺ ion irradiated IPP film were determined at different fluences. The percentage of grafting increases with increasing the fluence. It induce the creation of high density active sites onto base polymer with increasing ion fluence. It is found to be maximum at a fluence of 5×10^{13} . No effort was made to grafting the films beyond this fluence because the mechanical strength of the film started deteriorating with increasing ion fluence.

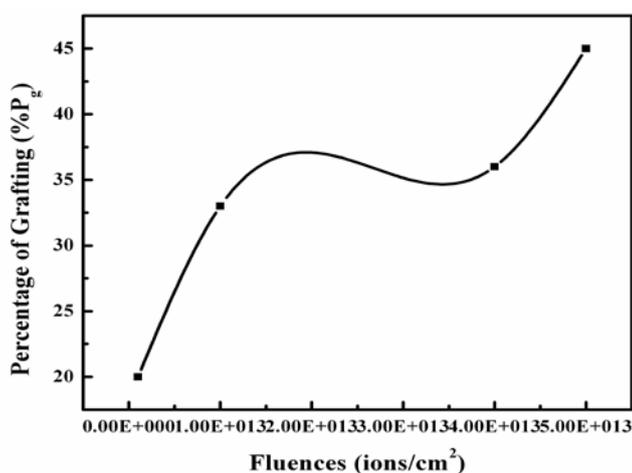


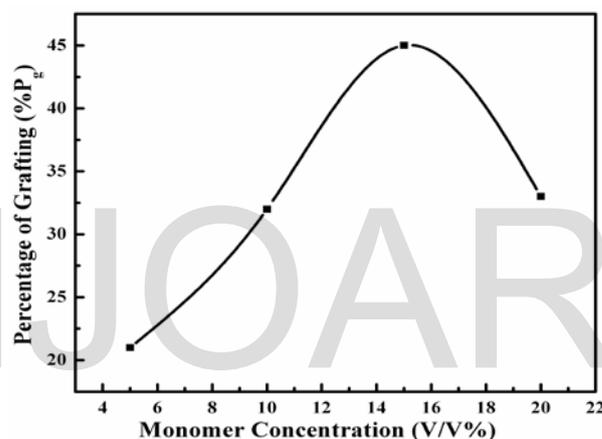
Figure 1- Effect of Fluence on Percentage Grafting; [Temperature] =75 °C; [Time] = 5 Hours; [Monomer Concentration] =15 V/V%.

3.3 Effect of Monomer Concentration

It can be observed from figure 2 that the grafting percentage increases smoothly with

increasing monomer concentration giving maximum percentage of 45% at 15% V/V concentration of HEMA and then decreases with further increase in the concentration of the monomer [9]. The initial increase in grafting may be due to the reason that most of the monomer is utilized by the available free radical sites on the IPP backbone. The monomer solution could access the reactive sites by diffusion on the surface of the irradiated film. Moreover at the lower concentration, the extent of homopolymerization of the monomer is smaller. The grafting reaches a maximum value and thereafter decreases. This is because the number of free radical sites available on the IPP backbone becomes a limiting

factor. The grafting monomer formation when the an



decrease in percentage of grafting beyond optimum concentration is due to the preferential homopolymer formation. This result was found when the grafting was performed at optimum condition of

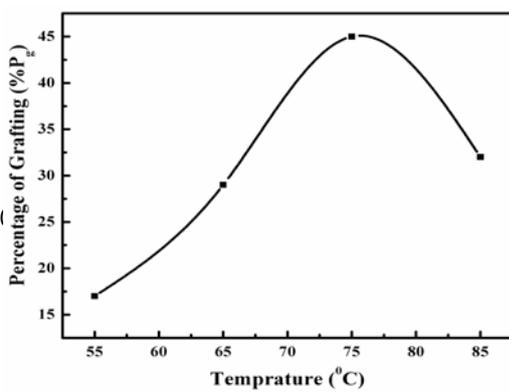
temperature at 75°C for 5 hours.

Figure 2-Effect of Monomer Concentration on Percentage Grafting; [Temperature]

=75°C; [Time] = 5 Hours; [Fluence] = 5×10^{13} ions/cm².

3.4 Effect of Temperature

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effect of reaction temperature on graft polymerization was studied

at temperature varying from 55⁰C to 85⁰C. The results are shown in figure 3. It can be seen that an increase of temperature up to 75⁰C increases the percentage of grafting. This may be due to the increase of the initiation and propagation rates of graft copolymerization. Increase in the percentage grafting with increasing temperature is also due to increase in the decomposition of the initiator leading to the formation of more free radicals. But beyond 75⁰C, the grafting rate decreases. Because at higher temperatures, higher combination rates of monomer are obtained increasing homopolymerization reactions, which results in a decreased grafting rate.

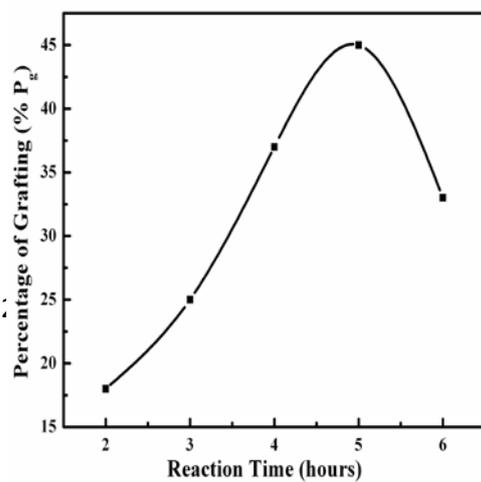
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Figure 3- Effect of Temperature on Percentage Grafting; [Monomer Concentration] = (15 V/V %); [Time] =5 Hour; [Fluence] = 5×10^{13} ions/cm².

3.5 Effect of Reaction Time

The effect of reaction time on the graft polymerization was studied. It can be seen from figure 4 that the percentage of grafting increases sharply with increase in the reaction time from 1 hour to 5 hours. After 5 hours, it decreases smoothly. The decrease

optimum



in grafting percentage after time can be due to the induced decomposition of the monomer

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leading to decreases in active radicals required to generate active sites on polymeric back bone.

Figure 4- Effect of Reaction Time on Percentage Grafting; [Monomer Concentration] =15 V/V%; [Temperature] =75°C; [Fluence] = 5×10^{13} ions/cm².

4. CHARACTERIZATION

4.1 FTIR Spectroscopy

The presence of grafting onto IPP film was confirmed through FTIR analysis. The FTIR spectrum of pristine and grafted IPP films having different different grafting yield and fluence varying from 1×10^{12} ions/cm² to 5×10^{13} ions/cm² has been studied. The characteristics bands for IPP film appears at 841 cm^{-1} and 1141 cm^{-1} are due to the (-CH(CH₃)-C-). In the spectra, absorbance in the region $2950\text{-}2850 \text{ cm}^{-1}$ corresponds to CH₃, CH₂, CH stretching (The appearance of these band at this region may be caused by the out-of plane stretching vibration and symmetric stretching vibration of the CH₃, CH₂ respectively) while the peak in the region $1455\text{-}1377 \text{ cm}^{-1}$ may be caused by the CH₃ out of plane bending vibrations and the symmetric bending vibration of CH₂, respectively. The peak observed near 1170 cm^{-1} , $999\text{-}977 \text{ cm}^{-1}$ confirms the isotactic category of

polypropylene used in this study. However, the peaks at 973, 1377 and 1456 cm^{-1} represent segments residing predominantly in the amorphous region. It also shows a C=C stretching peak at 1639 cm^{-1} due to the presence of vinyl unsaturation in HEMA. A comparison of this spectrum has shown a broad peak at 3292 cm^{-1} coming from the merge of -OH groups of HEMA. The group found at about 3450 cm^{-1} (ester carboxyl group) is due to the bond breakage leads to the formation of tertiary IPP macroradicals, which, on spontaneous oxidation in air, generate hydroperoxide groups on IPP. Figure 5 shows that in the spectra of IPP-g-HEMA a new band appears at 1725 cm^{-1} corresponding to -C=O stretching vibration and caused by the stretching vibration of carbonyl group of HEMA, indicating that carbonyl has been grafted onto IPP. This band is absent in the spectra of pristine IPP. These results indicate that the grafting of HEMA onto the IPP film is clearly achieved.

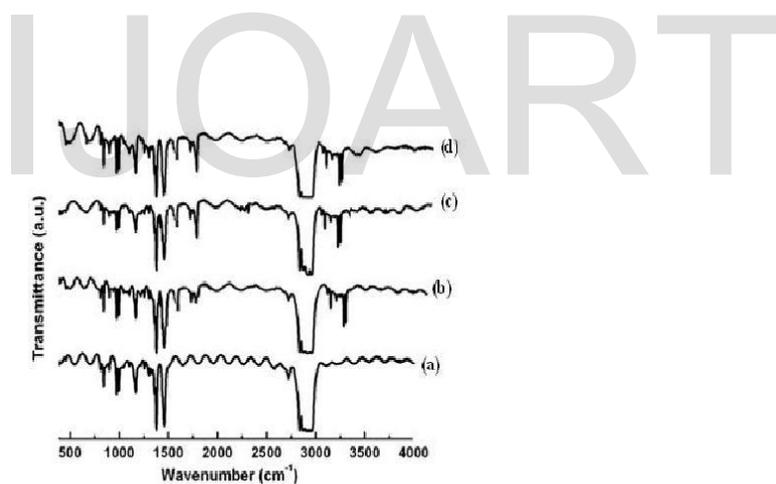


Figure 5- FTIR Spectra of (a) Pristine IPP (b) IPP-g-HEMA (1×10^{12} ions/ cm^2) (c) IPP-g-HEMA (1×10^{13} ions/ cm^2) (d) IPP-g-HEMA (5×10^{13} ions/ cm^2).

4.2 AFM Analysis

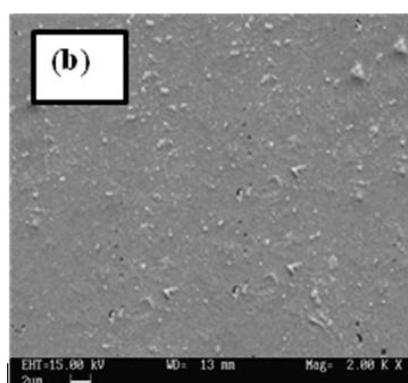
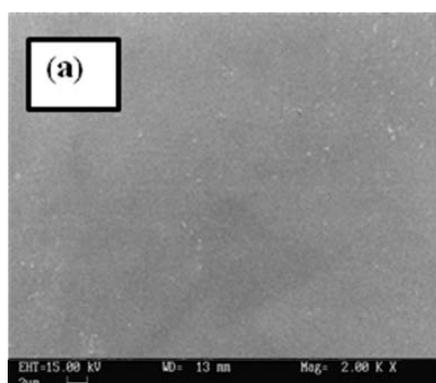
Figure 6 shows the surface roughness changes under the grafting reactions by AFM analysis. As it is evident from the figure that the surface roughness increases from values 5nm from pristine to 68 nm for IPP-g-HEMA at varying grafting yield and fluence. Surface roughness of the samples with increases with increasing the grafting

yield as well as with increasing the fluence as given in table 1. It is found to be maximum at the grafting yield of 45% having fluence 5×10^3 ions/cm². The reason for the maximum roughness observed at his value is mainly due to the HEMA chains form their own domains and morphology at the surface which gives a characteristic structure. It can be clearly seen that after surface modification, large quantity of HEMA is grafted on the membrane surface.

Figure 6- AFM Images of (a) Pristine IPP (b) IPP-g-HEMA (1×10^{12} ions/cm²) (c) IPP-g-HEMA (1×10^{13} ions/cm²) (d) IPP-g-HEMA (5×10^{13} ions/cm²).

4.3 SEM Analysis

It can be seen from the figure 7 that the pristine IPP shows the flat surface and the



grafted film shows the rough surface because of

the diffusion of HEMA monomer through the irradiated zones to encounter a reactive IPP macroradical.

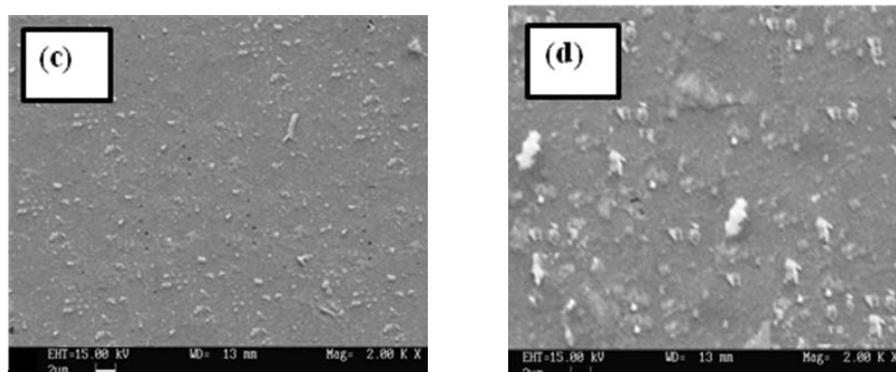


Figure 7- SEM Images of (a) Pristine IPP (b) IPP-g-HEMA (1×10^{12} ions/cm²) (c) IPP-g-HEMA (1×10^{13} ions/cm²) (d) IPP-g-HEMA (5×10^{13} ions/cm²).

5. CONCLUSIONS

The IPP films were implanted with low energy ion beam of Argon ions having energy 1.2 MeV. The generation of the free radicals by LEIB allowed the grafting of HEMA onto IPP surface. The grafting yield as a function of the ion fluence, monomer concentration, reaction time, reaction temperature was investigated. The maximum percentage of grafting (45 %) was obtained at an optimum condition of fluence 5×10^{13} ions/cm² with a monomer concentration of 15 V/V% at a temperature of 75⁰C for 5 hours. The structures of grafted membrane were characterized by FTIR, AFM, and SEM which indicates that HEMA have been grafted onto IPP. Low energy Ar ions can be used as initiators for grafting the surface of these polymeric films to modify the surface layer without affecting the bulk.

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