RESEARCH ARTICLE | OCTOBER 20 2011

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AIP Conf. Proc. 1391, 176–178 (2011)
https://doi.org/10.1063/1.3646816

Spectroscopic and Thermal Studies on Irradiated Poly (Ethylene Maleic Anhydride)

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Abstract. Radiation effects in Poly (ethylene maleic anhydride) (MANPE) have been investigated by Electron spin resonance (ESR), Fourier transform infrared (FTIR) and Differential scanning calorimeter (DSC) techniques. The ESR spectra of MNAPE under conditions like radiation dose and temperature have been recorded on irradiation. Alkyl group formed in MANPE which abstract oxygen and convert to peroxy radical on increase of radiation dose. More number of chain cleavages occur producing more number of free radicals which resulted increase in intensities of ESR spectrum. With the increase of temperature the free radical formed in MANPE may react with themselves or with other radical, resulting in the decay of ESR signals at high temperature. The FTIR spectra of irradiated MANPE possess absorption bands at 3500-3000cm^{-1} and 1700cm^{-1} positions indicating the presence of OH and C=O groups. The DSC data suggests that on irradiation the melting point slightly increases due to the formation of network structure.

Keywords: Poly (ethylene maleic anhydride), ESR, FTIR and DSC.

PACS: 81.70.Pg

INTRODUCTION

Polyethylene (PE) is one of the industrially important thermoplastic material. Grafting of anhydride groups in PE resulted in thermal stability [1]. The improvement in thermal stability is assigned to the formation of R-OH structures, which prevent the unzipping of polymer chains on thermal degradation. Formation of OH groups in MANPE is reported takes place through the formation of (ROȮ) and alkoxy (RȮ) radicals during thermal degradation [2-3].Though the authors have proposed various mechanisms for the formation of free radicals, no experimental evidence was proved for the existence of ROȮ, RȮ or OH groups in MANPE. In this context the authors have made an attempt to detect the free radicals using ESR and FTIR techniques.

RESULTS AND DISCUSSIONS:

1) ESR Studies:

To prove the existence of ROȮ, RȮ radicals in MANPE, the authors have irradiated the MANPE and recorded to ESR spectra under different conditions. The ESR spectra are basically asymmetric, doublet and characteristic of peroxy radicals. On irradiation MANPE formation of chain radicals might have taken place. The alkyl (macro or chain) radicals abstract atmosphere Oxygen and convert to peroxy radicals. The peroxy radical decompose or react with other radicals to form stable product. Formation of peroxy radicals has been reported in irradiated polyethylene [4], poly (methyl methacrylate) [5] and Nylon homopolymer [6]. In the present studies effect of (i) radiation dose (ii) temperature on free radicals produced in MANPE has been made.

(i) Effect of radiation dose:

Radiation dose dependent changes in ESR spectra of MANPE are as shown on Figure 1. Curves 1, 2, 3 indicate the spectra of MANPE irradiated to 3, 6 and 9 Mrad doses of irradiation. The spectrum at lower doses posses some hyperfine (hf) patterns; whereas at high doses, the hf pattern disappeared and an asymmetric peroxy doublet was observed. Further the intensity of spectra gradually increases with increase of radiation dose as shown in Figure 2. Thus with the increase of

Optics: Phenomena, Materials, Devices, and Characterization
AIP Conf. Proc. 1391, 176-178 (2011); doi: 10.1063/1.3646816

radiation dose more chain cleavages occur resulting production of more number of free radicals.

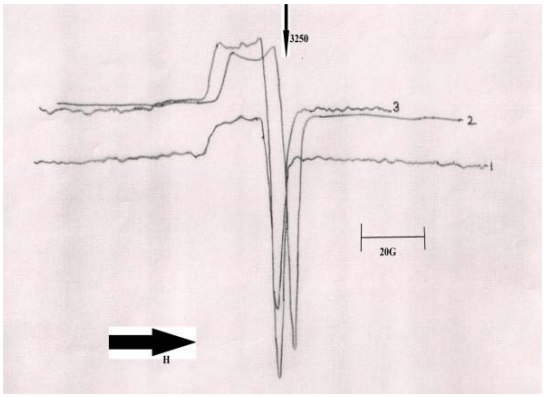

FIGURE 1. Radiation Dose dependent ESR spectra.

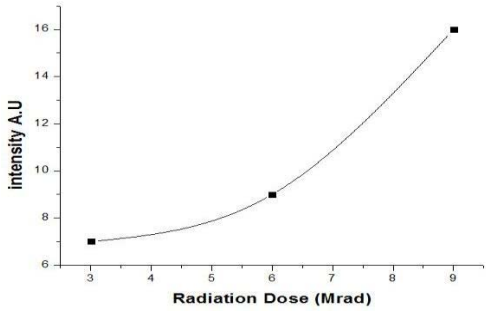

FIGURE 2. Variation of intensity of spectra with different radiation doses.

(ii) Effect of temperature:

Temperature dependent ESR spectra of irradiated MANPE is as shown in Figure 3. Curves 1, 2, 3 and 4 represent the ESR spectra at 300K, 330K, 350K and 370K. Beyond 370K the ESR signal was completely vanished. The spectra observed upto 350K are asymmetric doublet; which arises due to the presence of peroxy radicals. Beyond 350K, the doublet reduced to a singlet at 370K which may be due to alkoxy radicals (RȮ). Disappearance of ESR signal beyond 370K is assigned to be due to recombination of RȮ radical either with themselves or with other groups resulting in formation of stable products. The result is in consequent with the mechanism proposed by Huang et al [2] , who postulated the existence of peroxy, alkoxy and OH terminated products in MANPE. ESR intensity at different temperatures are calculated and a figure plot of ESR intensity against temperature is as shown in Figure 4. The curve is non-linear indicating the complex kinetics of free radical decay. Presence of peroxy, alkoxy and OH groups in MANPE has been confirmed by measuring FTIR spectra of unirradiated and irradiated MANPE.

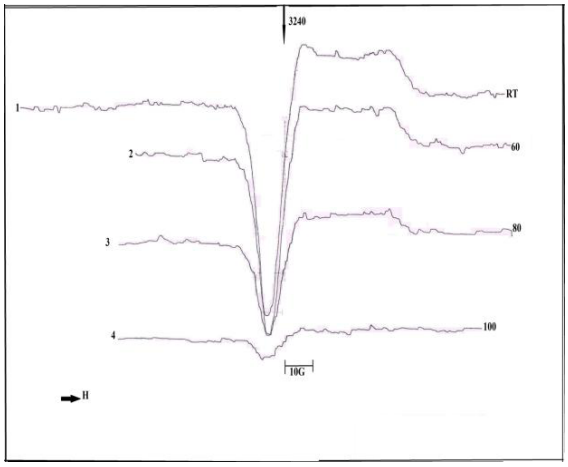

FIGURE 3. Temperature dependent ESR spectra

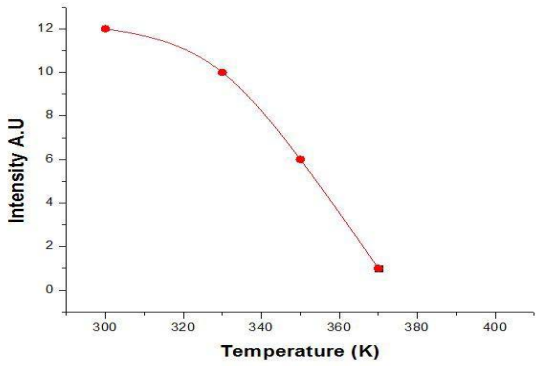

FIGURE 4. Variation of intensity of spectra with different temperatures.

2) FTIR Studies:

FTIR spectra of unirradiated and irradiated MANPE are recorded. The MANPE has shown an absorption band around 1700cm^{-1} position, which characteristic the C=O vibration of anhydride group. On irradiation the intensity of 1700cm^{-1} group increased and in addition another function group at 3500-3000cm^{-1} position is present. This group is assigned due to the formation of OH groups in MANPE. Formation of OH groups by the dissociation of ROȮ radical is postulated by various authors.

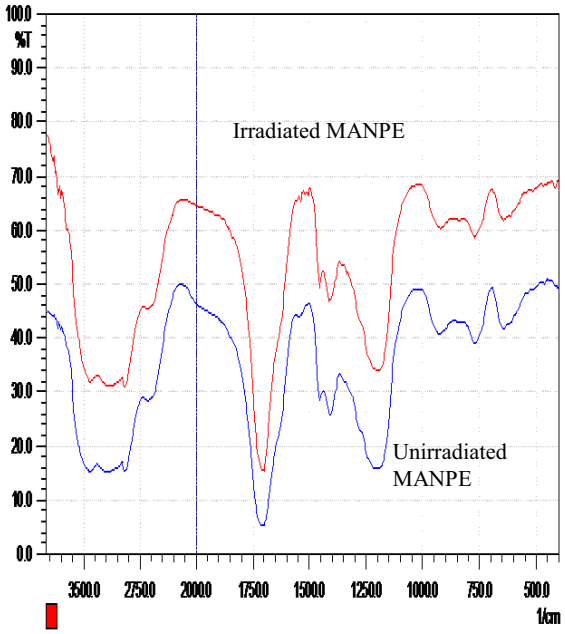

FIGURE 5. FTIR spectra of Irradiated and Unirradiated MANPE

3) DSC STUDIES:

Differential scanning calorimeter is used to study the effect in transition temperature with radiation dose. The MANPE has exhibited an exothermic peak around 140^{o}C, assigned to the melting point of polymer. On irradiation formation of crosslinks , the stability of polymer increases, as has been observed in case of irradiated MANPE, which has shown melting around 145^{o}C. Therefore an increase in melting point of 5^{o}C is observed due to irradiation.

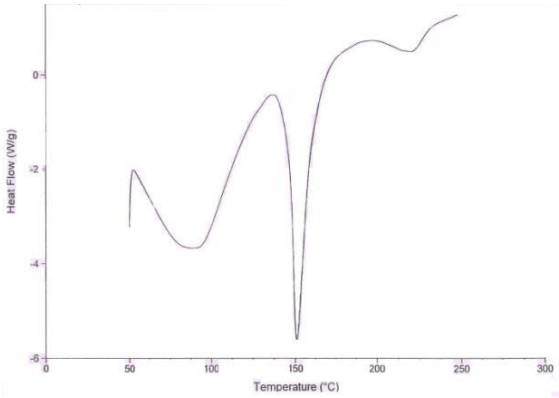

FIGURE 6. Thermogram of irradiated MANPE

CONCLUSION:

Irradiation of MANPE results in formation of alkyl radicals, which abstract oxygen and convert to peroxy radicals. The peroxy radicals are characterized by asymmetric doublet spectrum as observed in the present studies. With the increase of temperature the peroxy radicals convert to alkoxy radicals which give ESR singlet spectrum, which is observed at 370K. the alkoxy radical further undergo decomposition resulting in stable product like OH terminated groups.

AKNOWLEDGEMENT:

The authors wish to acknowledge the help of Ms. Vrinda Viswanathan SAIF, IIT Mumbai for recording ESR spectra.

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