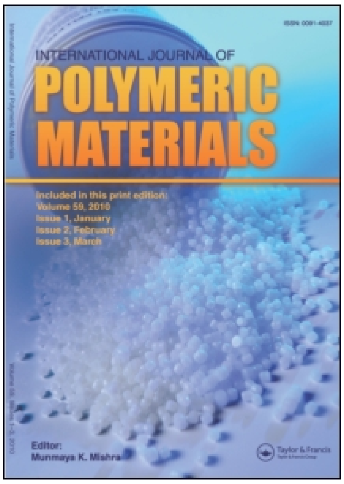

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Modification of Polymer Blends Properties by Plasma/Electron Beam Treatment. I. Plasma Diagnosis and Bulk Properties of Plasma Treated Blends

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Films of isotactic polypropylene/epoxy modified lignin have been plasma and electron beam treated, in order to improve the surface properties and their response to environmental factors. The optimal conditions for the treatment have been established by a detailed plasma diagnosis. The effect of the treatment on the films has been followed by: IR-spectroscopy, X-ray diffraction and differential scanning calorimetry. All results have been comparatively discussed with those corresponding to the untreated samples. It has been established that plasma and electron beam treatments are very efficient in imparting a high polarity and an increased hydrophylicity to the polyolefin-based blends.

Keywords: Plasma; Electron beam; Diagnosis; Isotactic polypropylene; Lignin

1. INTRODUCTION

Polymer blending has become a very suitable method for obtaining materials that can combine the characteristics of both components.

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Most of the time, the properties of the obtained polymer systems are enhanced with respect to those of the blend components. This fact represents an important technical advantage, since polymer blending allows production, at relatively low costs, of new materials by using preexisting ones. In some cases, surface or bulk treatment of the blend is necessary for further enhancement of its properties [1 – 4]. Some of the most frequently used treatment types are plasma exposure and bombardment with charged particle beams.

The energy of the UV photons emitted by the plasma (especially in the case of inert gases) is high enough for breaking the chemical bonds (*e.g.*, C—C, C—H). As a consequence, free radicals are formed, that can undergo inter- and intramolecular transfer recombination, disproportionation, *etc*. As function of the treatment conditions and of the polymer nature, there are also possible: chain scission, formation of double bonds, and crosslinking [5 – 7].

It is well known that the main effects of an electron beam irradiation on polymer systems are [8]: chain scission, oxidation and unsaturation, depending on dose rate, and oxygen content. Under irradiation, polymers generally undergo structural changes. Depending on their chemical structure, some polymers crosslink (polyethylene (PE), polypropylene (PP), polystyrene (PS), phosphazene polymers), while others degrade (polymethacrylates) [9 – 11].

The aim of this paper was to demonstrate the modifications induced in the bulk properties of synthetic polymer/natural polymer blends by plasma/electron beam treatment.

2. EXPERIMENTAL

2.1. Materials

Polypropylene used in the blends was supplied by MIDIA-Romanian Petrochemical Works. It had a melt flow index of 2.46 g/10 min and an intrinsic viscosity in decaline, at 135°C, of 2.11 dl/g. The insoluble fraction in boiling heptane was 99%. Its density, at 23°C, was of 0.909 g/cm^3.

Epoxy-modified lignosulfonates have been obtained by the reaction of ammonium lignosulfonate with epichlorhydrine in the 1/10 ratio, in the presence of 35–40% NaOH solution, at 75°C; reaction time was of 5 hours. Two kinds of products were obtained, varying in molecular weight and solubility. One product is a brown, high viscosity water-soluble liquid resin, while the other is a solid dark-brown, insoluble resin. Their yields were of 80–90 wt% and 20–10 wt%, respectively.

Epoxidized lignin used in this study had an epoxy equivalent of 0.065 and a dynamic viscosity of 17 500 cP, being a low molecular weight lignin, with high solubility in water and in some organic solvents. Its elemental analysis gave the following results: 35.07 wt% C, 7.3 wt% H, 4.61 wt% N, 4.7 wt% S, 5.5 wt% Cl, and 42.9 wt%, O. The ash content was 10.68 wt%.

Polypropylene/epoxidized lignin mixtures were prepared on a Brabender plastograph, at 190°C, 80 rpm, in the presence of diamino diphenylmethane, in the ratios given in Table I.

In the absence of glycidyl methacrylate grafted polypropylene (PP-g-GMA), only 3–4 wt% lignin (sample S6), can be incorporated in PP matrix. This quantity was increased by using PP-g-GMA as a compatibilizing agent. Mixing is easily achieved in the presence of PP-g-GMA-I, with a higher GMA content.

Blends of isotactic polypropylene (IPP)/epoxy modified lignin (LER)/glycidyl methacrylate grafted polypropylene (PP-g-GMA), with different concentrations of LER (Tab. I) have been treated in an anomalous glow discharge in argon, at 10^{-1} Torr, for different discharge tensions (600, 700 V) and various exposure times (1, 5, 10 min). The samples were placed at the limit of the negative glow. In this way, a face of the film was directed towards the cathodic dark space and therefore bombarded with an electron beam, while

TABLE I Composition of IPP/epoxy-modified lignin (LER) blends

Symbol	*PP* (*wt*%)	*Grafted IPP* (*wt*%)	*Type of grafted IPP*	*LER* (*wt*%)	*DDM* (*wt*%)
IPP	100.0	–	–	–	–
S6	96.00	–	–	3.96	0.03
S5	79.07	13.95	PP-g-GMA-II	6.97	0.102
S1	81.71	9.08	PP-g-GMA-I	9.08	0.135
S3	73.66	13.05	PP-g-GMA-I	13.06	0.196
S4	73.70	13.06	PP-g-GMA-II	13.05	0.195

the other side was placed in the negative glow plasma. In order to characterize the plasma in which polymer blends were exposed, Langmuir probe characteristics have been registered, using a plane probe.

2.2. Methods

The experimental device is presented in Figure 1. The glow discharge is produced in a glass tube (cylinder of about 5 cm diameter and 15 cm length), ended by a plane aluminium cathode (K) and a cylindrical stainless steel anode (A). Each electrode is biased with respect to the ground by two d.c. power supplies, as follows: the cathode by about $U_K = 1000$ V and the anode, variable, in the range $U_A = -45$ to $+45$ V. The plane Langmuir probe (S), made of tantalum, plate of about 5 mm in diameter, was biased (U_p) to about floating potential with respect to the ground. Probe characteristics were registered using a recorder, the signal on X being taken over the anode (the anode tension U_a) and the signal on Y was taken from the probe (the probe current intensity I_a). Langmuir probe was placed both in the negative glow (at almost 1 cm from the cathodic dark space) and also at its limit, being directed, respectively, towards the cylindrical anode (S-A),

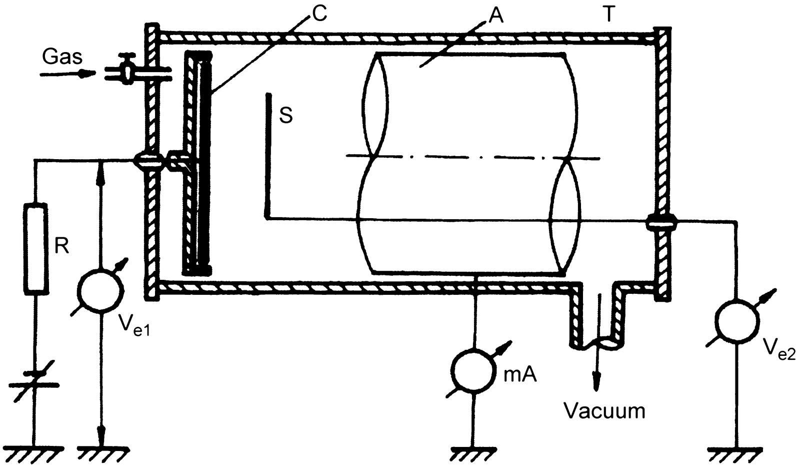

FIGURE 1 Schematic experimental set-up of the device used for plasma treatment.

the plane cathode (S-K) and, also, parallel with the discharge axis (S⊥K).

Probe characteristics obtained in these conditions allowed to make a clear distinction between the preponderent effect of the fast electron beam (from the cathodic fall) and that corresponding to the negative glow plasma.

This paper is focused on obtaining the plasma characteristics in which polymer blends have been treated and on bulk properties modification under this type of treatment.

Bulk properties were determined by: IR-spectroscopy, wide angle X-ray diffraction (WAXD), and differential scanning calorimetry (DSC).

IR-spectra have been obtained by means of a Perkine Elmer FT-IR spectrometer, 1760X on films (8 scans), in the region of (200 – 4000) cm $^{-1}$.

WAXD study was carried out using a generator type Rigaku 18 kW, with rotating anode and CuKα filtered radiation, $\lambda = 1.5405$ Å. The instrument is provided with a diffracted monochromator beam (HOPG) and a scintillation detector. Data were collected on blend films at a scanning speed of one degree per minute, at step intervals of 0.01 degrees.

DSC curves have been recorded on a Perkin Elmer DSC 7, at a heating or cooling rate of 10°C/min, in the (100 – 300)°C temperature region (sample mass; 5 – 10 mg), so both melting and crystallization phenomena for plasma/electron beam treated film blends were comparatively studied with the untreated ones.

3. RESULTS AND DISCUSSION

3.1. Plasma Diagnosis

Discharge tension (U_d) represents the sum between the anodic tension (U_A) and the tension applied on the cathode (U_K) ($U_d = U_A + U_k$). During recording of probe characteristics, U_A was varied between -45 V and $+45$ V, the variation of U_A being, in fact, equal with the variation of U_d (ΔU_d) ($U_K = \text{const.} \Rightarrow \Delta U_K = 0$). However, ΔUd didn't lead to a variation of the discharge current intensity higher than

2% during the measurements (the intensity of the current discharge was $\approx 10\,\text{mA}$). This fact indicates that plasma properties can be considered constant during the recording of the probe characteristics and of the sample exposure.

When the probe was directed towards the anode, the fast electrons from the cathodic fall could not hit the probe surface ("shadow" effect) and the probe characteristics are similar to those obtained in the positive column.

In this case the existence of two groups of thermallized electrons, is obvious their temperature being of 6 and 14 eV, respectively. The ratio between the density of the fast electrons and the total density of the plasma electrons was between 0.003 and 0.03, depending on U_A.

On the other hand, when the probe is directed towards the cathode, the obtained characteristic is strongly modified with respect to the first situation. In this case, the floating potential is displaced towards positive values, due to the secondary electron emission at the probe surface, produced by the fast electrons from the negative glow [12, 13]. This time, the preponderent effect is that corresponding to a beam of fast electrons.

3.2. Variation of Bulk Properties

3.2.1. IR-spectroscopy

Changes induced in IPP/LER blends exposed in the negative glow discharge in argon were similar with those induced by photooxidation [14], due to the fact that the main effect of inert gases on the modification of polymer properties is due to UV radiation [5, 15].

From IR spectra of IPP, obtained after the conjugated action of the cold plasma and of the fast electrons, (for an U_d of 600 V and different exposure times ($t = 1, 5, 10\,\text{min}$)) (Fig. 2), several observations could be drawn:

- a splitting and a displacement of the CH_2 vibration modes ($1463\,\text{cm}^{-1}$) towards higher wave numbers, behaviour explained by a possible contraction of the chain, due to IPP crosslinking;
- a new band is present at $1650\,\text{cm}^{-1}$, as a consequence of the formation of double bonds ($C{=}CH_2$);

- a slight increase of the absorbtion bands from 1700 – 1800 cm^{-1}, indicating the introduction of more functional groups (peracids, hydroperoxides, alkoxy radicals), as the treatment time increased;
- an increase of the absorbtion band corresponding to the hydroxyl groups (3100 – 3700 cm^{-1}) with increasing the exposure time, due to the recombination of the free radicals obtained under irradiation with the oxygen from the air.

IR spectra of plasma exposed IPP/LER blends show that the oxidation proceeds differently as function of LER content (Fig. 3). Thus, for a LER content up to 6.97 wt%, the absorbtion band at

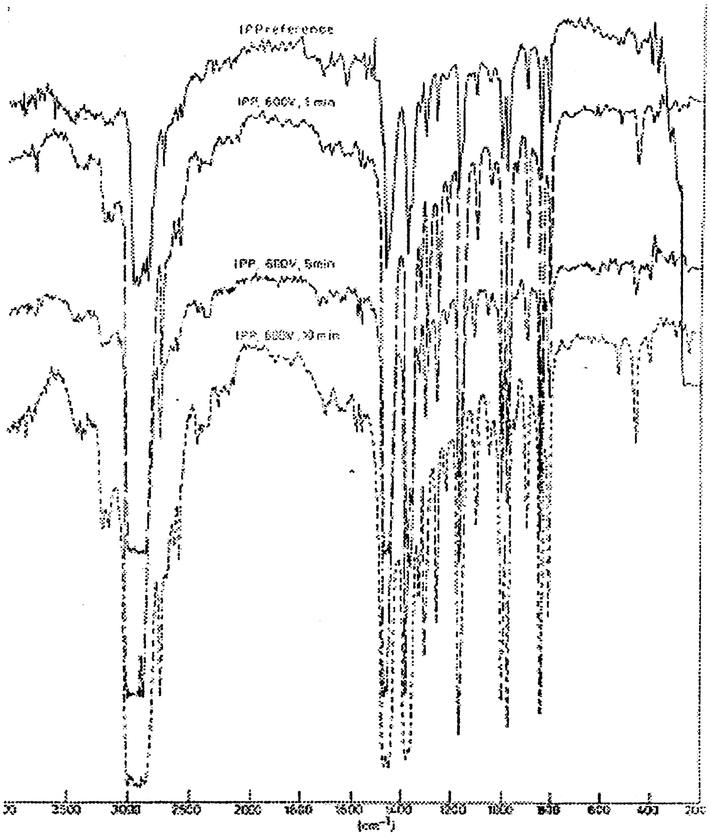

FIGURE 2 IR spectra of IPP sample unexposed and exposed in the negative glow plasma ($U_d = 600$ V; $t = 1, 5, 10$ min).

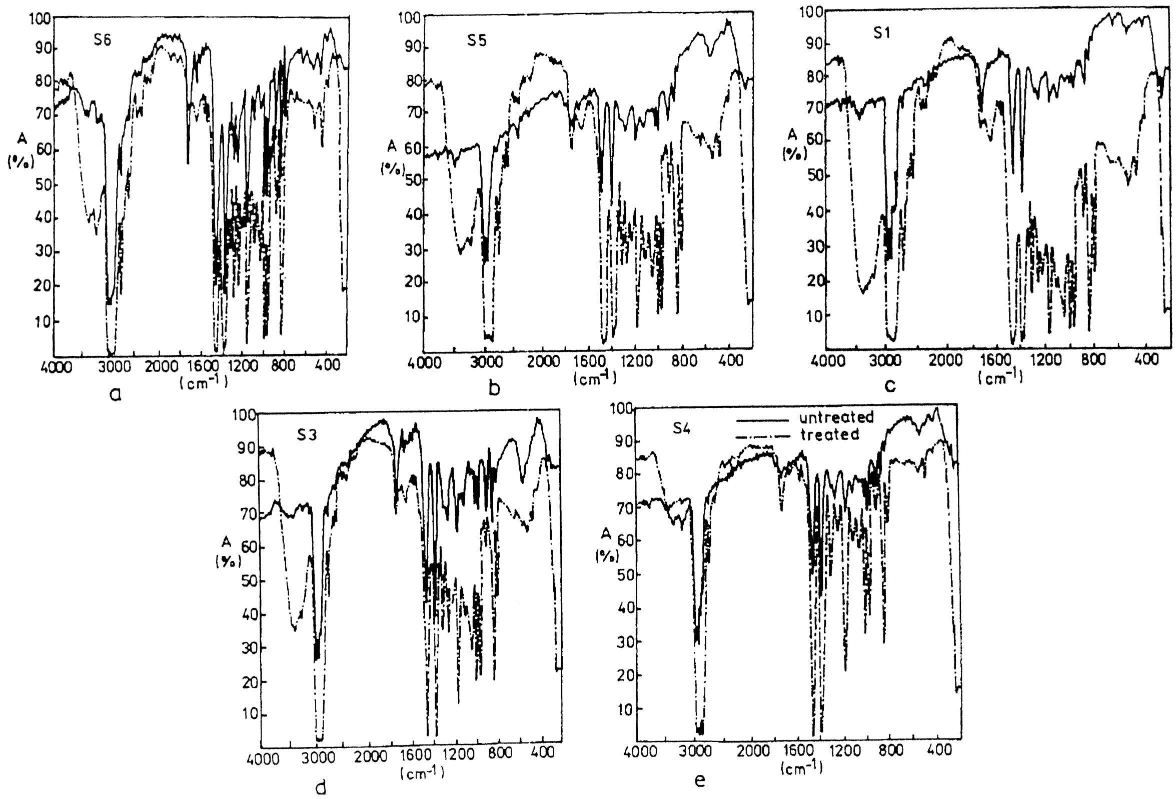

FIGURE 3 IR spectra for untreated and electron beam/plasma treated IPP/LER blends with a LER content of: (a) 3.96 wt%; (b) 6.97 wt%; (c) 9.08 wt%; (d) 13.06 wt%; (e) 13.05 wt%.

$1700-1800\,cm^{-1}$ doesn't change under the treatment. Therefore, it could be said that incorporated in small amounts in IPP matrix, LER acts like a stabilizer, while for a higher LER content ($>$ 9 wt%), this absorbtion band significantly increases. In this latest case, LER initiates radicalic reactions and leads to the oxidative degradation of IPP.

The increase of the crystallinity level was also obvious for all IPP/LER blends treated in the mentioned conditions (Tab. II).

3.2.2. Wide Angle X-ray Diffraction

X-ray diffraction spectra, registered for the studied samples, present a fairly good symmetry, showing a somehow regular texture in the film plane. Moreover, the relative high broadening of the diffraction peaks also shows a partially ordered phase (Fig. 4).

An increase of the crystallinity degree after the applied treatment was observed in the X-ray diffraction results (Tab. III), in accordance with the above mentioned IR results. In the same time, from the X-ray diffractograms an increase of the peak corresponding to β crystal form (for an interplanar distance of 5.495 Å) was observed after the irradiation of polymer blends. (Fig. 4). An increase was also observed for the relative proportion (H) of α (monoclinic crystal form) and β (orthorombic or hexagonal form) in the treated samples with respect to the reference ones (Tab. III).

TABLE II Crystallinity degree (X_C) evaluated from IR-spectra for IPP and IPP/LER blends before (untreated) and after (treated) plasma exposure ($U_d = 600\,V$; $t = 5\,min$)

Sample	*LER content*	X_C
IPP, untreated	0	0.515
IPP, treated		0.472
S6, untreated	3.96	0.483
S6, treated		0.547
S5, untreated	6.97	0.494
S5, treated		0.589
S1, untreated	9.08	0.517
S1, treated		0.617
S3, untreated	13.06	0.327
S3, treated		0.554
S4, untreated	13.05	0.384
S4, treated		0.497

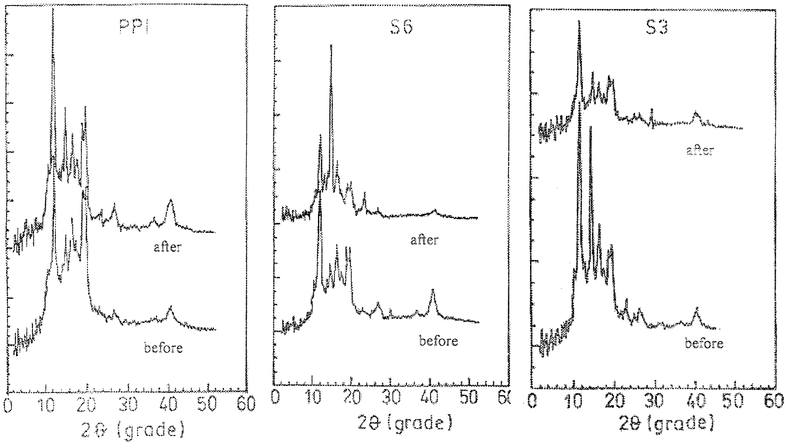

FIGURE 4 X-ray diffractograms for the untreated samples ("before") and plasma exposed ("after") for: IPP, S6, and S3 ($U_d = 600\,V$, $t = 5\,min$).

TABLE III Relative proportion (H) of α and β crystal forms in the treated samples with respect to the untreated ones

Sample	$H_{untreated}$	$H_{treated}$
IPP	0.049	0.066
S6	0.076	0.088
S3	0.000	0.075

Changes in crystallinity and in crystal forms might have several explanations, such as: LER action as a β nucleating agent, phase separation, chemcrystallization process, or local heating during plasma exposure.

3.2.3. Differential Scanning Calorimetry

From DSC curves, it can be remarked that both treated IPP and IPP/LER blends exhibit additional melting peaks accompanying the main melting peak of the base polymer (Fig. 5). The additional peak appears at high temperature for treated IPP and at low temperature for the treated blends. This behaviour is in accordance with X-ray results that demonstrated the development, in the presence of LER,

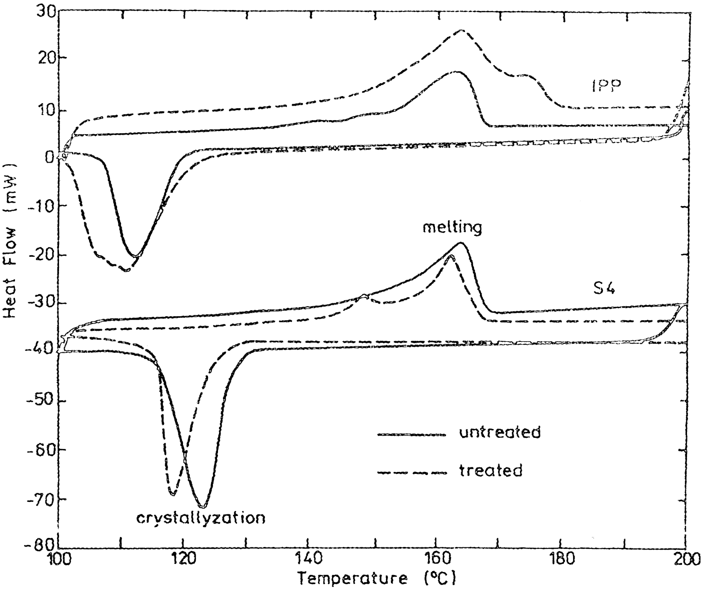

FIGURE 5 DSC curves for IPP and S4 film blend, untreated and electron beam/plasma treated.

of the β-'crystal form, less thermally stable [16]. The presence of the peak at high temperature could be due to the chemcrystallization that takes place after the treatment, due to the introduction of polar groups and to the densification of the material, as the IR spectra results also proved (Fig. 2).

4. CONCLUSIONS

Bulk analysis shows that by choosing an appropriate content of the natural polymer in blends based on synthetic polymers and by applying adequate treatment conditions, materials with controllable properties could be obtained.

The influence of these two different treatment types (plasma exposure and electron beam bombardment) on the polymer blends is clearly shown by the variation of the surface properties, which will be discussed in detail in a future paper.

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