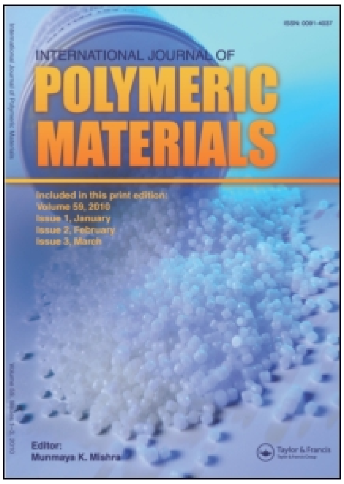

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Chemicals and Energy from Medical Polymer Wastes III. Maleated Pyrolysis Products in IPP/LLDPE Processing. Morphology and Properties

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The changes in the morphology and properties of low density polyethylene/polypropylene blends by incorporation of maleated pyrolysis products of disposable syringes have been studied. The following investigation methods have been employed transmission optical microscopy in polarized light, wide angle X-ray diffraction, mechanical and thermal properties determination.

It has been established that the incorporation of the amorphous maleated pyrolysis products did not decrease the crystallinity of the 70IPP/30LLDPE blend. Moreover for a low content of these (5–10 wt%) an increase in the crystallinity index and also in mechanical properties has been obtained, while the thermal properties remained unchanged.

Keywords: Maleated pyrolysis products; IPP/LLDPE blends; compatibility; morphology; properties

INTRODUCTION

In our previous papers [1, 2], the pyrolysis of disposable syringes followed by chemical modification of the waxy products have been

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*Corresponding author.

presented. It has been established that maleated waxy pyrolysis products (PPMA) can be used as lubricants and/or compatibilizing agents in the processing of isotactic polypropylene (IPP)/linear low density polyethylene (LLDPE) blends.

This paper reports on the morphology and properties of the binary IPP/LLDPE and ternary IPP/LLDPE/PPMA blends, further elucidating and proving the effect of the incorporation of maleated pyrolysis products in polyolefin blends.

EXPERIMENTAL

Materials

The blends preparation and their composition have been given in a previous paper [2]. For the clarity of the results is has to be mentioned that both binary (IPP/LLDPE) and ternary (IPP/LLDPE/PPMA) blends have been studied. In the first case the whole composition range of the blends from 95 IPP/5 LLDPE to 5 IPP/95 LLDPE was tested. In the second case in a binary blend with ratio between IPP/LLDPE of 7/3, various amounts of maleated pyrolysis products varying between 2.5 and 15 wt% have been incorporated. Two maleated waxy products were used, PPCMA and PPSMA, having maleic anhydride contents of 0.183 and 0.594 mole/100 g sample, respectively. Other characteristics were elsewhere given [2].

Methods

The following investigation methods have been used: optical microscopy, X-ray diffraction, thermogravimetry and physico-mechanical indices determination.

The microscopical aspect has been examined by means of a MC-1, IOR-Bucharest microscope in polarized light, magnification 600X.

Wide angle X-ray diffraction (WAXD) studies were conducted using a HZG-4/A diffractometer with filtered CuKα radiation, $\lambda = 1.5405\,\text{Å}$, 30 KV, 25 mA. The instrument is configured with a diffracted beam monochromator and a scintillation detector. Data were collected on blend sheets having a thickness of 0.46 mm.

It is well-known that the morphology of the blends definitely influences the properties of the blends. Thermal and physico-mechanical properties of the blends were measured.

The TG and DTG curves have been recorded on a MOM-Budapest Derivatograph. The heating rate was 12.4°C/min, mass sample 50 mg, air flow 30 ml/min.

Milled samples were converted into sheet by a two-roll-mill-press method in the following conditions: 5 – 10 min mixing on a two roll mill at 170 – 175°C, 10 min pressing at 175 – 180°C and 170 atm. The physico-mechanical indices were determined by means of a dynamometer (VEB Thuringer Industry), at a speed of testing of 100 mm/min.

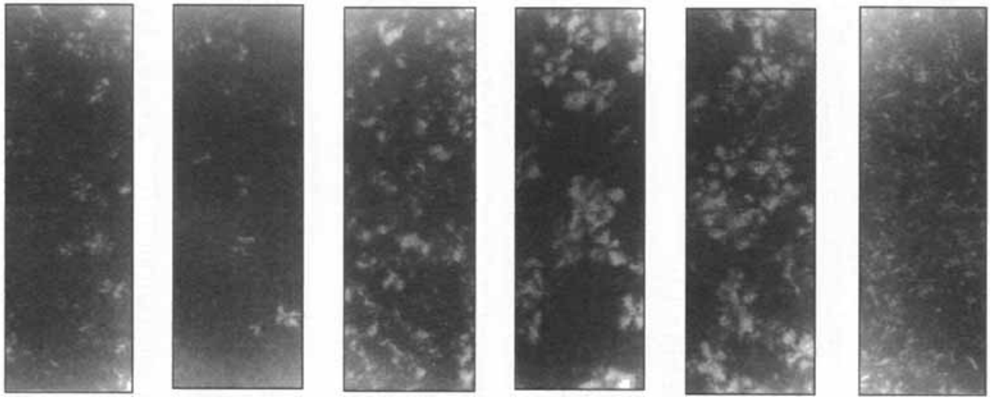
MORPHOLOGY OF THE BLENDS

Microscopy

The optical microscopy in polarized light showed the Maltese crosses, characteristic of the spherulitic crystalline morphology of the blends – Figure 1. This morphology was better developed in the ternary blends containing 5 – 10 wt% maleated pyrolysis products and when the mixing procedure was more efficient than for example, on the corotating twin-screw extrusiometer with respect to the Haake-Buchler rheometer.

X-ray Diffraction Results

The existence of two or three forms of crystalline order in isotactic polypropylene has been amply demonstrated [3 – 8]. Each crystallographic form has its own distinctive diffraction pattern. The γ form (triclinic) is characterized by five X-ray reflections of *d*-spacing in angstroms of 6.37 (vs), 5.29 (vvs), 4.42 (vs), 4.19 (s) and 4.05 (s), four of which lie very close to several reflections of the α form (monoclinic). The α phase spacings in unoriented specimens are at 6.26 (vvs) (110), 5.19 (vs) (040), 4.77 (vs) (130), 4.19 (s) (111), 4.04 (s) (131). Thus the interplanar spacings of α and γ crystallographic forms are very close. The reflection at 4.77 Å of the α form is completely absent in the γ



70.0%IPP/
30.0%LLDPE

68.25%IPP/
29.25%LLDPE/
2.5%PPCMA

66.5%IPP/
28.5%LLDPE/
5.0%PPCMA

63.0%IPP/
27.0%LLDPE/
10.0%PPCMA

63.0%IPP/
27.0%LLDPE/
10.0%PPCMA
extr.

59.5%IPP/
25.5%LLDPE/
15.0%PPCMA

FIGURE 1 Microscopical aspects in polarized light of various IPP/LLDPE/Maleated pyrolysis product blends.

form and a reflection at 4.42 Å was observed instead. The β form (orthorhombic or hexagonal) has a strong single (hk0) (310) peak at a *d*-value of 5.495 Å. The monoclinic α form is the most frequently encountered and it may be accompanied by a lower or higher amount of β modification. This β form will occur with high supercooling and under special crystallization conditions or when selective β-nucleating agents are present [9, 10]. The γ modification may be formed in degraded, low molecular weight *PP* or samples crystallized under high pressure. Quenching the molten polymers leads to an intermediate crystalline order, or paracrystallinity may also develop. Formation of a particular type is solely dependent on a series of crystallization parameters such as melting temperature, rate of cooling, stress, nucleating agents, *etc.*

LLDPE is an ethylene copolymer with a very low crystallinity. In its X-ray diffraction profile there are only two X-ray reflections in the 2θ range of 20–30° which correspond, according to Bragg's law, to *d*-spacings of 4.19 Å (vs) (110) and 3.77 Å (s) (200) [11, 12]. These reflections could correspond to an orthorhombic unit cell according to the literature data, it being applied for both PE and some ethylene copolymers [13, 14]. Other types of crystal structure exist in oriented polyolefins and other particular situations [15].

An intermediate situation of order type was encountered in the IPP/LLDPE and IPP/LLDPE/PPMA blends, depending on their composition. Comparison of the X-ray diffraction profiles indicated the significant differences between the samples – Figures 2 and 3 and Table I.

It is possible for the γ crystallographic form to be present between the samples in small amounts and in various proportions. This assumptions was made by taking into account that the films were obtained by cooling under pressure and that the IPP employed was a commercial one, *i.e.*, unfractionated. There were also differences in the 2θ region of 20–35°, which could be due to the coexistence of many crystallographic forms and also to the development of paracrystallinity. It is known that paracrystallinity causes broadening of the Bragg reflections in addition to the attenuation of peak intensity and increasing the angle, observed for both IPP and blends.

In the diffractogram of the blends in the 2θ region of 19–30°, the peak position for the ternary blends was shifted with respect to that of

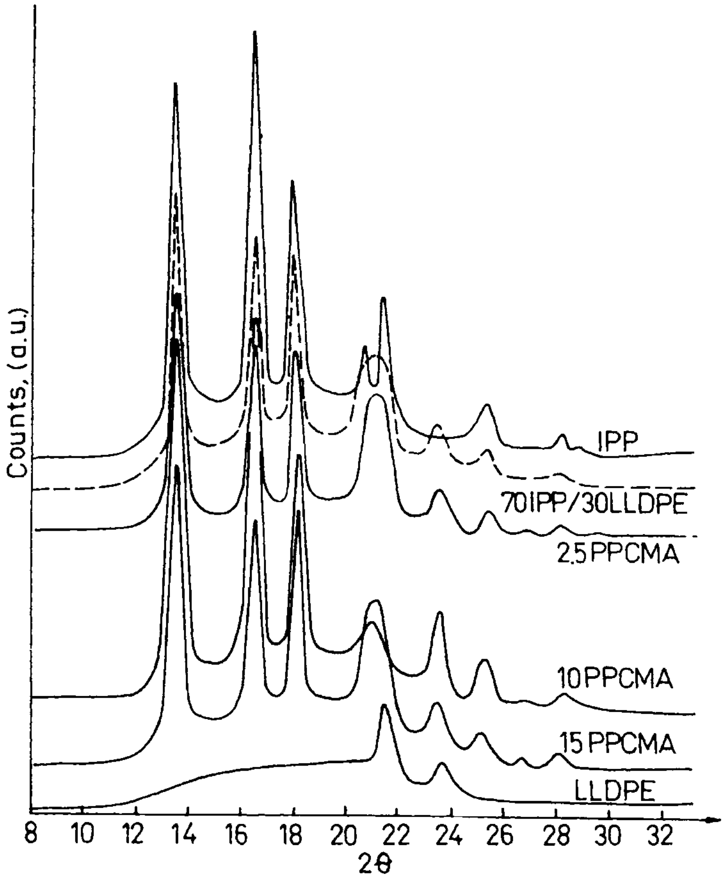


FIGURE 2 X-ray diffraction profiles (WAXD) of binary and ternary IPP/LLDPE/PPCMA blends.

both neat polymers and binary blends. Moreover, the diffractograms of all ternary blends containing PPCMA and ternary mixtures containing 10% PPSMA exhibited a supplementary peak at $2\theta = 27°$. This should indicate a certain change in the crystalline order of the two crystalline components of the blends by PPMA incorporation.

It is known that the integral width of the peaks (in rads), corrected for instrument broadening at the half height of the reflection $\beta = \theta_1 - \theta_2$ (in rads), may be approximately related to the dimensions

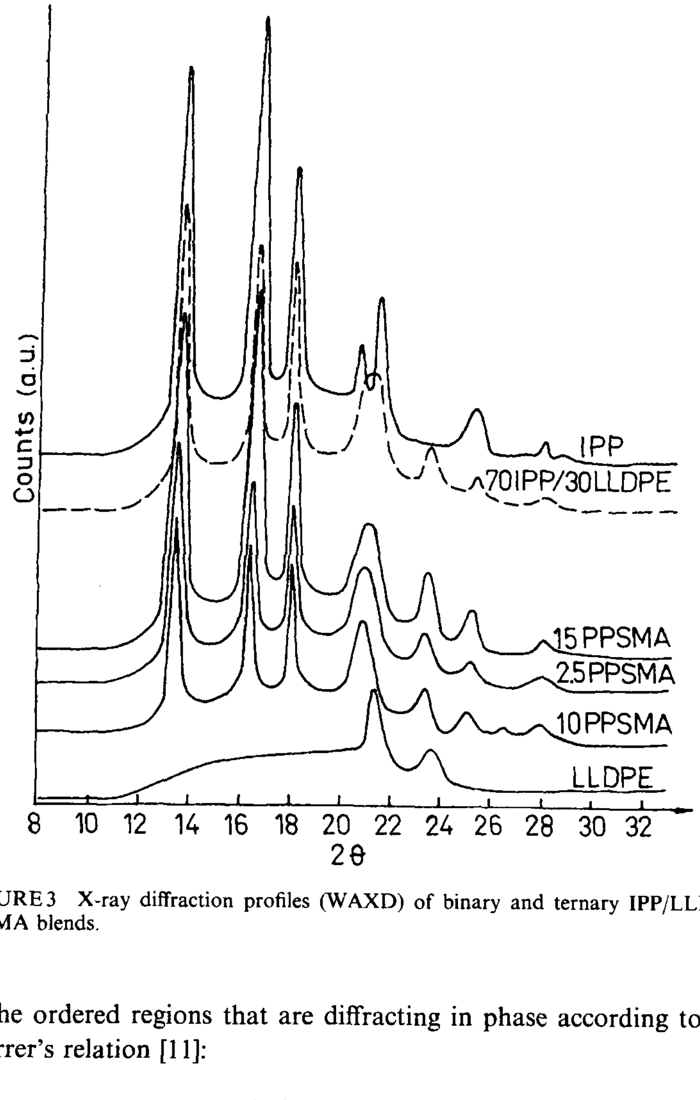


FIGURE 3 X-ray diffraction profiles (WAXD) of binary and ternary IPP/LLDPE/PPSMA blends.

of the ordered regions that are diffracting in phase according to the Sherrer's relation [11]:

$$\delta(2\theta) = 0.89/\beta \cos\theta \tag{1}$$

These values remained almost unchanged, although it seemed that they were higher for ternary blends, achieved by the addition of the maleated pyrolysis products as compatibilizing agent.

In the absence of structure factors and of other corrective information applied, the ratio of the areas (or heights, peak intensities)

TABLE I X-rays diffraction data for IPP/LLDPE/PPMAs blends

Sample	d_{hkl} (Å)	Crystallite size (Å) (Å) experimental	Crystallite size (Å) Average	$(1-2d_{hkl}\beta)/(1-d_{hkl}\beta)^*$	$A_{crystalline}/A_{total}$ (%) experimental	$A_{crystalline}/A_{total}$ (%) additive	X_H IPP	X_H LLDPE	$X_{k=1}$	$X_{k=4}$ experimental	$X_{k=4}$ additive
	6.458	173		0.945							
IPP	5.304	159	172	0.951	45.12	–	34.2	–	0.45	0.17	–
	4.897	185		0.962							
	4.149	93.5	79.8	–	11.48	–	–	33.5	0.11	0.03	–
LLDPE	3.767	66.2									
70IPP/30	6.505	199		0.952			29.3	22.9	0.39	0.14	
LLDPE	5.336	159	166	0.9571	39.09	35.03					0.13
	4.897	139		0.949							
	6.505	199		0.952			35.9	26.9	0.58		
2.5	5.368	194	195	0.960	57.88	34.15				0.26	0.13
PPCMA	4.897	194		0.964							
	6.505	176		0.946							
10	5.400	177	170	0.956	52.66	31.52	36.4	15.2	0.53	0.22	0.12
PPCMA	4.897	156		0.913							
	6.504	189		0.950							
15	5.368	165	164	0.953	37.71	29.77	35.4	26.1	0.38	0.13	0.11
PPCMA	4.897	137		0.953							
2.5	6.505	199		0.952							
PPSMA	5.368	137	160	0.942	42.33	34.15	28.3	20.9	0.42	0.15	0.13
	4.897	144		0.951							
10	6.505	194		0.951							
PPSMA	5.368	142	167	0.945	40.74	31.52	–	–	0.41	0.15	0.12
	4.897	166		0.957							
15	6.505	164		0.942							
PPSMA	5.336	166	158	0.953	42.57	29.26	35.0	16.9	0.43	0.16	0.11
	4.897	144		0.951			2				

*d_{hkl} – interplanar spacing, β – integral width of diffraction peak, X – crystallinity index, X_H – crystallinity index from DSC curves.

of the peaks was taken as indicative of the ratios between the two (crystalline and amorphous) phases.

The crystallinity index was determined by the peak resolution method:

$$X_c = A_c/(A_c + kA_a) = 1/(1 + kA_a/A_c) \tag{2}$$

where A_c and A_a are the relative areas (integrated intensity) of the "crystalline" and "amorphous" peaks, respectively; and k is a constant. For comparative purposes, k may be set to unity. If the crystallinity index should have a value approximating absolute crystallinity, k must be determined. For polypropylene, the typical value for k is 4 [6]. The k value takes into account the disorder in the crystalline regions associated with thermal motion and the first and the second type of disorder (paracrystallinity). Two values for k were used in X_c evaluation, $k = 1$ and $k = 4$. Generally, in polymer blends containing one crystallizable component, the crystallinity is not changed, if the components are incompatible. The amorphous components decrease crystallinity; the peak intensity decreases with the increasing amorphous component content, due to dilution [7]. In the studied case –Table I– the crystallinity index for the binary 70 IPP/30 LLDPE blend was smaller or approximately equal to the additive values. For the other samples, the experimental crystallinity index was higher than the additive one. The amorphous component, PPMA, did not decrease crystallinity.

The variation of the crystallinity index evaluated from X-ray diffraction with the blend composition was similar with the variation of similar values obtained from DSC curves with respect to melting range of both IPP or of LLDPE, as the ratio [16]:

$$X_H = \Delta H_{\exp}/\Delta H_m \cdot 100 \tag{3}$$

where $\Delta H_{\exp}$ and ΔH_m are the fusion enthalpies of the sample and of pure crystal, respectively, both referred to the same basis (J/g).

It has been shown [6] that a two-phases crystalline structure must exist if the degree of crystallinity satisfies an inequality that may be expressed as:

$$X_c < (1 - 2d_{hkl}\beta)/(1 - d_{hkl}\beta) \qquad (4)$$

where d_{hkl} is the interplanar spacing corresponding to a given reflection. This value was evaluated for the three main diffraction peaks with the interplanar spacing: 6.27, 5.25 and 4.76 Å. The results of Table I indicate that the degree of crystallinity of the binary and ternary blends satisfied this inequality. Therefore two crystalline phases existed in these systems.

MELTING POINT DEPRESSION

An attempt was made to establish the maximum level of interaction between the blend components using the melting point depression by diluent, evaluated from the DSC curves presented in the previous paper [2].

Nishi and Wang [17] demonstrated that the melting point of the crystals (Tm) can be related to that of the neat polymer (Tm^0) by the relation:

$$Tm^0 - Tm = -(BV_{2u}/\Delta H_{2u})\,Tm^0\,v_1^2 \qquad (5)$$

at $T = Tm^0$, where the subscripts 2 and 1 indicate polymer and diluent respectively, subscript u designated the value per mole of structural units, Tm^0 is melting point in the absence of diluent [18], Tm is melting point of the blend. $\Delta H_{2u}/V_{2u}$ is the heat of melting per unit vloume of crystalline material; v_1^2 is the volume fraction of the amorphous component (*i.e.*, maleated pyrolysis product) and

$$B = \chi_{12}RT/V_{1u} \approx (\delta_1 - \delta_2)^2 \qquad (6)$$

B and χ_{12} characterize the interaction between the molecules *i.e.*, it is a parameter of interaction energy of components; V_1 is the molar volume of diluent.

These equations are frequently used to evaluate miscibility in crystalline polymer blends [19]. These relations are valid as long as the crystals are at equilibrium; the melting is conducted under close to equilibrium conditions; the second component does not undergo a phase transition within the investigated range of variables [20].

Unfortunately, these conditions are rarely considered and seldom met. That is why the interpretation of the measured data must be done with utmost care. The main difficulty lies with the need to work with crystals which have the same lamella size and crystal perfection at a maximum experimental melting temperature. The influence of composition on the *Tm* of both components is quite strong. The change in the crystal system of a polymer from monoclinic to smectic on addition of the other polymer makes the Eqs. (5) and (6) inapplicable. It has been established [21] that the presence of LLDPE in blends with IPP has a disruptive effect on the regularity of the crystalline structure of the latter polymer. Only crystallographic analysis provides information on the true reason for the observed variation of melting point with composition. From the thermodynamic point of view, crystallization lowers the total free energy of the systems. The free energy change on crystallization is proportional with the degree of supercooling. Five patterns of crystallinity could be developed upon addition of a crystallizable diluent: the diluent does not affect crystallization; the diluent prevents crystallization at its high loading; the diluent accelerates crystallization and the diluent provides enough thermal mobility to cause crystallization of normally non-crystalline polymer.

Analyzing all these conditions, on the X-ray diffraction results and knowing that the possibility of interaction of components is higher for ternary blends containing PPSMA, we conclude that the relations (5) and (6) are applicable only for ternary blends containing low amounts of PPCMA, because both IR spectra and X-ray diffraction pattern exhibit only insignificant changes with respect to those of the 70 wt% IPP/30 wt% LLDPE binary blend. From the plot of $Tm - v_1^2$ – Figure 4 – we have evaluated that a value of B ranging from 13.94 to 16.225 J/cm^3 and χ_{12} ranging from 0.212–0.246 that describe favorable interaction between the polymers, according with the literature data [22].

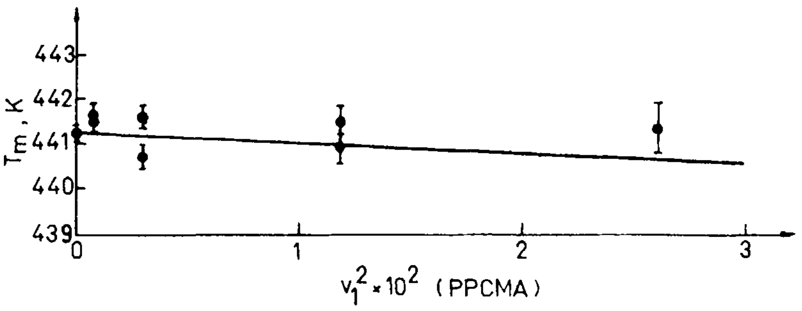


FIGURE 4 Melting point as a function of the square of the PPCMA volume fraction.

PROPERTIES

Physico-mechanical Indices

The microscopical and X-ray diffraction results are in very good accordance with physico-mechanical indices variation presented in Figure 5. Whereas the binary IPP/LLDPE blends showed a sudden decrease of tensile strength on the incorporation of LLDPE in IPP, the tensile strength of the ternary blends increased for 5 – 10 wt% of maleated pyrolysis products incorporated in binary blend, then decreases due to the incompatibility increase of components. Elongation at break remained in the range of 10 – 15% while for the extrusion prepared blends, elongation values higher than 20 – 25% were obtained.

Thermal Properties

Thermal properties remained almost unchanged up to 5 wt% maleated pyrolysis product in the IPP/LLDPE blends. Then the maximum rate decomposition temperature decreased and all DTG curves shifted towards lower temperatures – Figure 6. For the content of 15 wt% PPMA the inflection at 315°C became more evident.

An appreciation of the thermal behavior can also be made from the data presented in Table II, presenting characteristic temperatures, overall activation energies evaluated both by integral methods (Coats and Redfern [23] – subscript CR and Reich and Levi [24] – subscript RL) and the differential method (Swaminathan and Modhavan [25] –

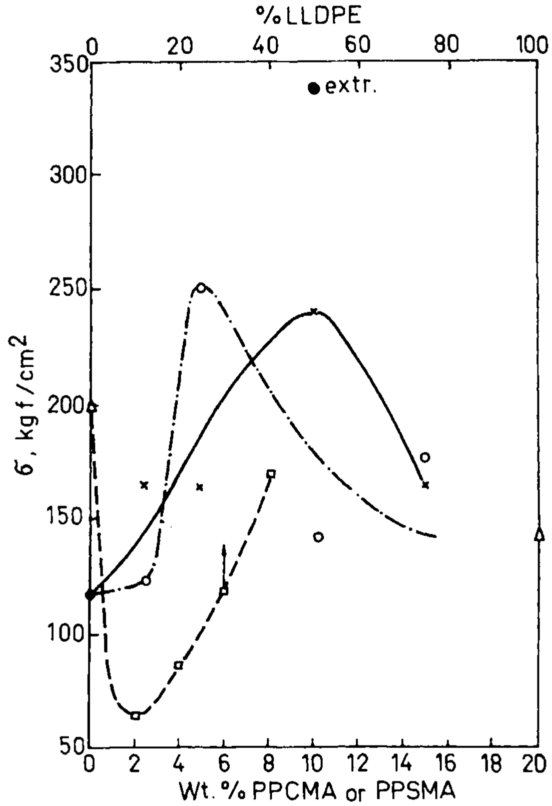


FIGURE 5 Tensile strength *versus* composition of the blends (□) binary blends IPP/LLDPE; (○) ternary blends IPP/LLDPE/PPSMA; (x) ternary blends IPP/LLDPE/PPCMA.

subscript SM). The following observations can be mentioned: characteristic temperatures were changed only for 15 wt% PPMA. The weight loss was about 95% for all samples. Overall activation energy for the ternary blends was lower than the additive value, and correspondance between the values obtained by integral and differential methods was evident for the samples which did not present the variation of activation energy with conversion degree (α) – Figure 7.

For the second step, separate in the case of ternary blends containing 5 and 15 wt% PPSMA and 15% PPCMA, only values

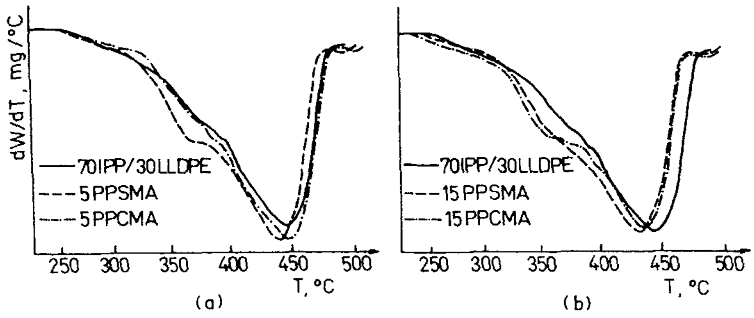


FIGURE 6 DTG curves of the binary 70IPP/30LLDPE and ternary blends containing 5 wt% (a) and 15 wt% (b) maleated pyrolysis products.

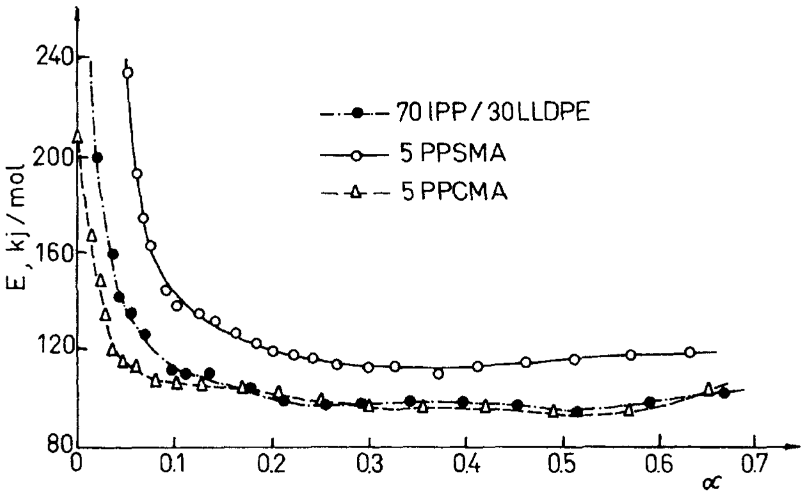


FIGURE 7 Activation energy evaluated by Reich and Levi method with conversion degree.

obtained by differential methods seemed to be correct, because the change of E with α was significant, so that the integration of the temperature integral was not possible [26].

Finally, an examination of the k values indicates that the change in thermal stability was not important for the first step of decomposition and in the studied composition range of the binary and ternary polymer blends.

TABLE II Thermogravimetric data and global kinetic parameters for thermoxidative decomposition of the binary and ternary IPP/LLDPE/PPMA blends

Sample	*Characteristic temperatures*				*Weight loss*(%)	E_{CR} (*KJ/mol*)	n_{CR}	$E_{RL,\ \alpha<0.15}$ (*KJ/mol*)	E_{SM} (*KJ/mol*)	lnA_{SM}	n_{SM}	$k(sec^{-1})$ 10^4
	Ti (°*C*)	*Tinfl* (°*C*)	*Tm* (°*C*)	*Tf* (°*C*)								
IPP	250	–	414	446	96.5	84.09	0.8	94	80.14	13.0	0.6	3.6
LLDPE	311	–	468	510	94.5	104.92	0.3	128	112.2	16.9	0.4	0.21
70 wt%IPP/30 wt%-LLDPE	258	335	444	487	96.2	82.45	0.7	97	71.9	10.8	0.7	2.3
5 wt% PPCMA	258	321	447	490	95	79.32	0.6	98	74.7	11.2	0.6	1.9
5 wt% PPSMA	255	315	440	481	25	95.3	0.5	115	83.1	14.4	0.1	7.9
					70	–	–	–	85.4	13.3	0.6	1.6
15 wt% PPCMA	232	317	438	475	22	86.2	0.3	110	93.9	16.7	0.0	8.2
					73	–	–	–	110.9	16.99	0.0	0.28
15 wt% PPSMA	245	314	430	472	22.5	88.7	0.3	120	77	13.4	0.0	10.5
					72	–	–	–	120	20.6	0.0	1.7

T_i, $T_{infl}T_m$, T_f, are temperatures of onset of peak, corresponding to the inflexion of DTG curves and to the maximum rate of weight loss and, final temperature respectively, E – overall activation energy, n – reaction order, A – pre-exponential factor, k – rate constant.

CONCLUSION

The crystallinity, mechanical and thermal properties of the 70IPP/30LLDPE blends are improved by incorporation of maleated pyrolysis products of disposable syringes. These maleated products act as compatibilizing agents.

The results are in good accordance with those presented in the previous paper related to the good processability and compatibility of ternary blends comparatively with binary ones.

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