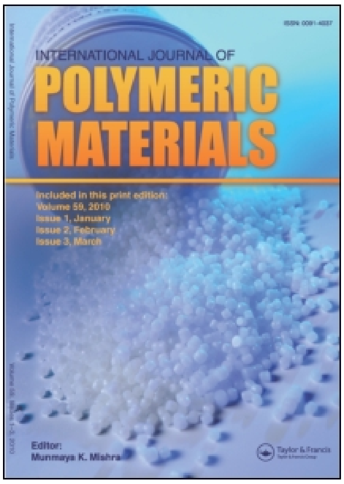

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Chemicals and Energy from Medical Polymer Wastes II. Maleated Pyrolysis Products in IPP/LLDPE Processing

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

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A way for high valorisation of the waxy product resulted from the pyrolysis of disposable syringes it has been proposed. The waxy product has been chemically modified with maleic anhydride and then has been tested in the processing of IPP/LLDPE blends on a Haake-Buchler rheometer or on a Werner and Pfeiderer ZSM-30 corotating twin screw extruder.

The compatibility of components in the binary IPP/LLDPE and ternary IPP/LLDPE/maleated pyrolysis products from the processing characteristics and DSC results has been appreciated.

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

1. INTRODUCTION

High interfacial tensions or poor interfacial adhesion, combined with the high viscosities of the components, are the fundamental barriers to the achievement of the desired degree of dispersion in polymer blends

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and their resulting properties. In such a situation, the blends have an inherent instability which leads to phase separation tendency and stratification during processing. In order to prevent this phenomenon it is necessary to add compatibilizing agents, or to improve the interphase properties by chemical reaction. Maleation of one of the components, or the use of a maleated compatibilizing agent, improves the adhesion of polymers to metals, glass fibers and other polymer and also offers the possibility of a reaction between components (containing functional groups) during processing and thus an essential improvement in the compatibility of the components [1–4].

This paper reports on the maleation of a waxy product resulting from the pyrolysis of used-and-disposable syringes and its role as compatibilizing agent in a blend of 70 wt% isotactic polypropylene (IPP)/30 wt% linear low density polyethylene (LLDPE).

This mixture was chosen because it is an incompatible one [5–7] and it has been shown [8] that the blending of IPP with LLDPE is one of the approaches successfully applied to improve the impact properties of IPP, especially at low temperatures where the mechanical properties are limited by its relatively high Tg as compared to polyethylene. We also expected that our proposed solution is most suitable for the reprocessing of IPP/LLDPE mixtures from the municipal solid waste stream, these two polymers being components of several manufacturing products [7].

2. EXPERIMENTAL

2.1. Materials

2.1.1. Preparation and Characterization of the Maleated Pyrolysis Products

The average composition of the mixture of used-and-disposable syringes was 59 wt% IPP/41 wt%PE [9]. After pyrolysis in an autogenerated atmosphere at 450°C, a waxy paraffinic product was obtained. Low molecular weight fractions (boiling interval below 220°C) were eliminated by distillation. The heavy fraction (molecular weight above 1000, elemental composition: 81 wt% C, 14.7 wt% H; 0.42 wt% N; 3.71 wt% O and an unsaturation degree of about 4%) was subjected to bulk maleation with 10–15 wt% maleic anhydride (MA) (dried on Na_2SO_4) in the presence of 1% benzoyl peroxide based on the pyrolysis product at 120°C or dicumyl peroxide at 170°C. Only the products obtained in the presence of benzoyl peroxide were tested here; the results obtained with the other initiators and products will be presented in a subsequent paper.

Reaction mixtures were made up in glass stoppered vessels in a nitrogen atmosphere. The dissolution of maleic anhydride in the reaction mixture was complete after 10 minutes at reaction temperature and under stirring, later the mixture became hazy, and in time a brown product began to separate. The reaction time was 8 h but it can be considered that the reaction was complete after 1 or 2 hours.

Two kinds of maleated products were obtained: a waxy maleated product (PPCMA) soluble in methyl alcohol and dimethylformamide, and a solid maleated product (PPSMA) insoluble in aromatic hydrocarbons or methyl alcohol but forming a suspension in $CHCl_3$ or CCl_4 at room temperature. It is soluble at 40–50°C in $CHCl_3$ or CCl_4, and also in THF at room temperature. PPCMA was the main product of the maleation; the ratio between quantities of the both products was 10p PPCMA/1p PPSMA.

After separation, the samples were washed with hot water to hydrolyze unreacted anhydride and poly(maleic anhydride) and remove them as water soluble acid and polymer, respectively [10].

FT-IR spectra were recorded on a FT-IR 1760 spectrometer, the specimen being deposited as a thin layer on a germanium disc.

^{1}H-NMR spectra were recorded on deuterated chloroform solutions by means of a JEOL spectrometer at 80 MHz and the shifts were referenced to tetramethylsilane.

In the interpretation of spectroscopic data we had to have in view that our pyrolysis products contained long fragments of both polyethylene and polypropylene with vinyl and vinylidene groups content, as was previously shown, [11] and also that the reaction temperature ($T = 120$°C) was under the ceiling temperature of maleic anhydride ($T_c = 150$–160°C) [12] and at relatively high concentration of maleic anhydride (10–15 wt%). Moreover, recently De Roover, Devaux and Legras [13] proved that the homopolymerization of maleic anhydride can occur during melt functionalization of IPP due to the spontaneous formation of radical species in pure melted IPP at 190°C. They also concluded that the ceiling temperature of maleic anhydride should be higher than that reported previously [12]. In such circumstances it might be anticipated that chain extension took place with the grafting of many maleic anhydride units [14]. By comparing our results with those from the literature, [10, 15–19] the following conclusions can be drawn:

By FT-IR-(Fig. 1) and ^{1}H-NMR spectra (Fig. 2) the presence of the anhydride ring, and additional bands corresponding to a partial hydrolysis in PPCMA, were clearly proved. FT-IR spectra showed characteristic carbonyl absorption bands at 1852 cm^{-1} (shoulder) and 1788 cm^{-1} (strong) due to the appended MA and at 1720 cm^{-1} (very strong) attributable to the ester carbonyl group. Two other additional bands appeared at 990 and 969 cm^{-1} for — CH_2O stretching or — CH=CH— out of plane deformation. In addition to the shoulder at 1852 cm^{-1} and the peak at about 1788 cm^{-1} characteristic of the MA moiety, a third peak was present at about 1695–1576 cm^{-1} in the PPSMA spectrum. This may be attributed to either the carbonyl group resulting from scission of the alkoxy radical formed on cleavage of the hydroperoxide, from the reaction of the polymer radical with oxygen, or unsaturation of some of the grafted MA units due to termination by disproportionation [20]. The IR spectrum of PPSMA differed from of PPCMA by the 1232 cm^{-1} wide band due to — CO — O — CO— stretch vibration, while in the

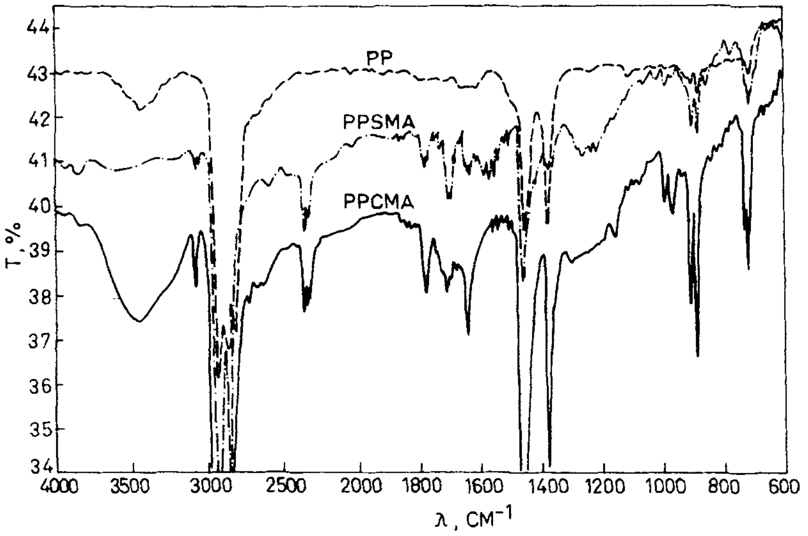


FIGURE 1 FT-IR spectra of the pyrolysis product (PP) and of the two maleated pyrolysis products PPCMA and PPSMA.

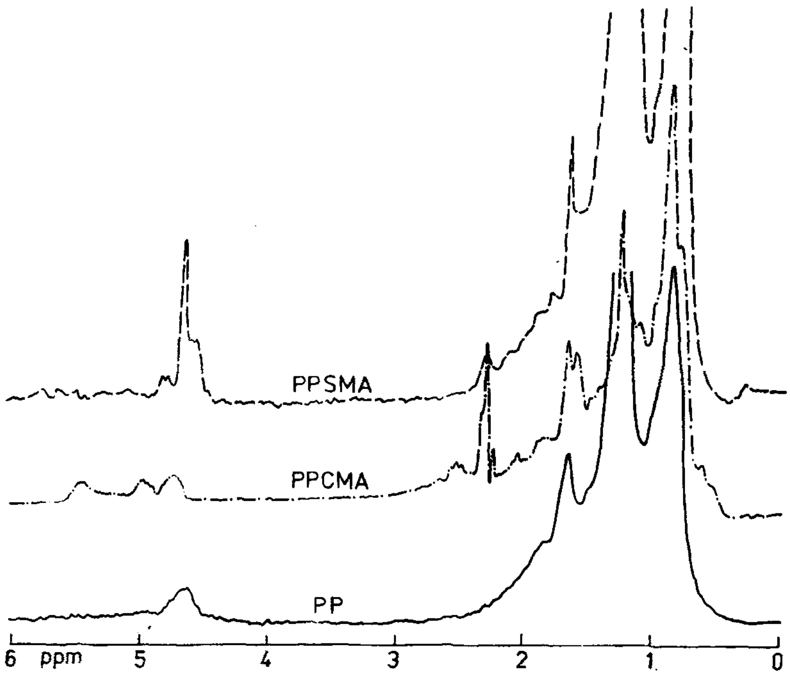


FIGURE 2 ^{1}H-NMR spectra of PP, PPCMA and PPSMA.

PPCMA spectra a wide band was present, at 3426 cm^{-1} due to the partial hydrolysis of the anhydride group.

The shift in the band positions might be due to double bonds present in the products [21]. It is known that maleic anhydride reacts with unsaturated compounds in the α-position [22]. There are also bands corresponding to double bonds 1644–1656 and 2300–2400 cm^{-1}.

Using the ACD/^{1}H-NMR 1.0 from ACD/Labs Demo Verion (1994–1996) program (elaborated by Advanced Chemistry Development Inc., Toronto, Canada) for ^{1}H-NMR spectra evaluation we obtained several ^{1}H-NMR spectra models that were compared with the spectra of the maleated pyrolysis products. It has been concluded that, the most probable mode of the maleic anhydride grafting is on the polypropylene chains having double bonds at the chain ends and grafts had many appended groups. The model spectra showed the shifts of the protons bonded on double bonds and with anhydride rings in proximity in the 4.8–5.8 ppm region with two distinctive groups of lines. The protons on the 4th or 5th anhydride rings appear at 2.6–3.2 ppm region as a strong signal while those belonging to the first and the second anhydride ring at 3.5–4 ppm; these last signals are extremely weak.

The ^{1}H-NMR spectra of the maleated products also showed the shifts characteristic of protons bonded to the double bond substituted with a methyl group in proximity with anhydride ring and a band was also present in the 4–5 ppm region which could be assigned to the shift of protons from double bond by grafting of many anhydride units in α-position to the tertiary carbon of IPP [17, 18]. The weak 3.66/3.56, 3.14 and 2.94 ppm signals associated with single appended anhydride ring were not present in ^{1}H-NMR spectra although such groups might exist in small amount because the doublet from 1.7–1.9 ppm assigned to the — CH_2 group in the α position to the ring of a substituted succinic anhydride appeared in the spectrum (not shown on the figure). In the NMR spectrum of PPSMA there was a very small signal at 7.47 ppm, corresponding to the existence of the unreacted anhydride in small amount. It can be appreciated that the maleic anhydride content was higher in PPSMA than in PPCMA.

A structure with double bond placed at the chain end and graft in α-position to the tertiary carbon is the most probable.

From the elemental analysis results, it has been established that the maleic anhydride content is of 0.183 and 0.594 mole/100 g sample in PPCMA and respectively PPSMA.

The GPC curves were recorded on 1 wt% tetrahydrofuran solutions using a WATERS 712 WISP with triple detector (WATERS 441 Absorbance Detector, VISCOTEK Refractometer/Viscometer Detector Model 250, WATERS 486 Tunable Absorbance Detector) instrument. A column of 7.8 mm ID × 300 mm packed with Styragel HR^2 was used. The flow rate of solvent was 1.0 ml/min and the injection volume 2 ml. The GPC results are given in the Table I.

The GPC results can be correctly interpreted only by the use of this instrument with a triple detector, because one of the products (PPCMA) had low molecular weight, and light scattering measurements were not suitable, and the second (PPSMA) should have a high degree of branching, that could be evidenced only by comparing the results of many investigation methods.

The GPC-light scattering results indicated a high difference between the samples both in the average molecular weight and the molecular

TABLE I GPC Results for Maleated Pyrolysis Products

Characteristic	*PPCMA*	*PPSMA*
Specific Refractive Index, dn/dc (ml/g)	0.082	0.034
Values from Light Scattering Measurements		
M_n (g/mol)	406	246 000
M_w/M_n	35	1.6
Values from Viscosity Measurements		
Average Intrinsic Viscosity (dl/g)	0.031	0.033
M_w (g/mol)	14 140	10 500
Mark-Houwink Values		
log k	–	– 2.8
a	–	0.31

weight distribution. The number average molecular weights were 405 and 245 000 for PPCMA and PPSMA respectively and the polydispersities were 34 and 1.6, the GPC curves of PPCMA being bimodal.

The viscosimetric results showed only an insignificant difference between the two compounds, PPSMA having low viscosity values and high light scattering values; therefore it had a branched chain. Because of the high polydispersity of PPCMA, only the Mark-Houwink values for PPSMA were given.

2.1.2. Polyolefin Blends with Maleated Pyrolysis Products

All of the polymers tested were commercial grades. The polypropylene used was a HIMONT PROFAX 6323 IJ grade as granules with a melt flow rate of 6.2 g/10 min (ASTM D 1238-86, condition 190/2.16 Kg). The melting point determined by DSC was about 171°C. Linear low density polyethylene (LLDPE) manufactured by DOW Chemicals 2535 had a melt flow rate of 6.4 g/10 min and melting point of 122°C.

Two ways were employed for blend preparation. The first one consisted of mixing on a Microprocessor controlled Haake-Buchler Torque Rheometer System 40 at an average temperature of 198–200°C, 32 rpm, 15 minutes. Normally 32.5 g of polymer sample was used per test. Additions were complete in less than a minute. It was established that [23] in this mixing time at approximately same temperature, both polymers did not undergo degradation. Moreover, in each case 1 wt% Irganox 1076, hindered phenol antioxidant, was used be stabilizer so no variation in torque after a 3.5–4 min. mixing time were observed.

Binary blend compositions of 100/0, 90/10, 80/20, 70/30 and 60/40 weight/weight IPP/LLDPE were melt mixed and ternary blend composition of 70 IPP/30 LLDPE with 2.5, 5, 7, 10 and 15% weight/weight PPCMA or PPSMA were prepared in the same conditions.

In the second preparation procedure, materials in the ratios 70 wt% IIP/30 wt% LLDPE and 66.5/wt% IPP/28.5 wt% LLDPE/5wt % PPCMA, were also compounded in a Werner and Pfleiderer ZSK-30 corotating intermeshing twin screw extruder with a diameter of 20 mm; L/D of 30/1 for a 25–30% of 90 N.m machine capacity and residence time of 59 sec. at the following conditions: temperatures 184, 193, 203, 201 and 201°C for zones 1, 2, 3, 4 and die respectively; 100 rpm, 130 psi. Before extrusion the mixtures were dried at 80°C in a convection oven. The extrudate was pellitized.

The processing characteristics (according to ASTM D 1238-86, condition E 190/2.16) by means of Haake-Buchler and Tinius-Olsen Extrusion (Piston) Plastometer were tested. The melt index apparatus was operated at isothermal conditions. The land of the piston was 9.4762 mm in diameter and 6.35 mm in length.

The torque rheometer simulates in enough detail some processing conditions of plastic materials and it is also convenient because it requires a small amount of sample and offers a variety of test variables. The torque and polymer melt temperature were recorded as a function of time. The timing started when the sample addition began.

DSC curves were recorded on a Du Pont 200 TA instrument using a heating rate of 10°C/min, temperature range −50 to 200°C, 7–10 mg sample. Two or three runs were performed for each sample.

3. RESULTS AND DISCUSSION

3.1. Processability

The processing characteristics of polymer blends were tested by analyzing the torque rheometer data in conjunction with the extrusion plastometer data [23–25], the melt temperature being approximately constant between 198–200°C.

The analysis of the torque rheometer curves depends on the final purpose. From a processor's viewpoint, there are many potential difficulties caused by the effects of work done on the polymer prior and in transition to the melt state. In the polymer blends another difficulty is related with the work of mixing. It is very important to know how much energy is required to bring a polymer from an initial state to a homogeneous melt, how much time this process requires and whether the polymer will degrade under certain conditions. In the interpretation of the torque rheometer data it is also very important to separate the effect of premelting, undegraded melt viscosity and degraded melt viscosity.

An important parameter to assess in comparing polymer materials or blends behavior is unit work energy defined by the relation:

$$W = 61.59\ S\ TTQ/Vs \qquad (1)$$

and it is the work energy required to process unit volume (in j/cm^3) or unit mass of material. In equation (1) S is rotor speed. TTQ-totalized torque is obtained directly from the rheometer and is the energy required to process a certain material for a certain period of time at given conditions. It is obtained by integrating and totalizing the area under the torque versus time curve. Vs is sample volume charged. Generally, the lower the torque level, the less work will be required in production to process a specific compound.

Taking into account the above-mentioned considerations, we chose two periods of time to evaluate this unit work energy: 0–3.5 minutes (0 means loading time) and 3–5 minutes period. The 0–3.5 minutes period is considered to be very informative for mixing and melting, and 3–5 minutes period is important for melt-viscosity correlations. The data collected during the 3–5 minutes period were used for such correlations, in order to minimize the side effects of partial melting at shorter time and degradation at longer time, especially when PP is the polymer under study. Correlation between torque and melt viscosity is linear during this time period [24]; at shorter time the torque is too high because of incomplete mixing and lack of equilibrium temperature; after this it is too low and can be influenced by degradation. The torque curves, their band width, change in torque level point where melt reaches within 2°C of equilibrium, as ultimate processing time;

level in torque after this point (as stable torque), time of fusion and mixing (which is the time from the loading of the solid material (formulation) into the torque rheometer to the time it melts or fuses and mixes into a plastic mass for a constant speed) have been also compared.

Other values determined were: total shear energy (mechanical energy) that is energy introduced in polymer material by motor drive during processing and is obtained by multiplying torque with rotor speed (S) and $9.087 \cdot 10^{-3}$; specific energy or energy required to process a unit mass of material (this is calculated from total shear energy divided by processed mass); viscosity as ratio between shear stress/shear rate. The torque curve is obviously "viscosity sensitive". If the speed is constant, variation in torque among samples at the same temperature is indicative of viscosity difference, sometimes Torque Rheometer being used as a rotational viscosimeter. Viscosity is proportional to the ratio of the torque (M) and rotor speed (S). The exact relations between them were determined by an appropriate calibration [23–25]. For comparative purposes, we used only M/S ratio, and its variation with composition was compared with that of viscosity obtained by means of an extrusion plastometer. Several values are given in Table II.

The behavior of the mixtures containing PPCMA was different from those containing PPSMA as appeared from the torque rheometer curves presented in Figure 3, even for low amounts (2.5 wt%) of these. The torque rheometer curves of the mixtures containing maleated pyrolysis products showed low torque values but longer mixing time than 70 wt% IPP/30 wt% LLDPE. The PPCMA decreased melt viscosity, while the mixtures containing PPSMA showed high melt viscosity in the 2–4 minutes time period. This change appeared more clear for the mixtures containing 5 wt% PPCMA or PPSMA – Figure 4. The mixtures containing more than 7 wt% PPCMA or PPSMA, showed similar curves with low melt viscosity-Table II, but as will be discussed below, the reasons are different.

The total work energy corresponding to 0–3 minutes processing time was increased in mixing IPP with LLDPE but was very much decreased by incorporation of the maleated pyrolysis products (Fig. 5a). That means that both products facilitated mixing. In the 3–5 minutes time period the 70 wt% IPP/30wt% LLDPE mixtures and the mixtures containing PPCMA showed the same behavior (Fig. 5b); but the mixtures

TABLE II Processing characteristics of IPP/LLDPE/Maleated pyrolysis products

Composition	*Haake Buchler Rheometer*						*Tinius olsen extrusion (piston) plastometer*			
	Processing Time (min)	*Width (min)*	*Total Shear Energy (j)*	*Specific Energy (j/g)*	*Stable torque/ rpm*	*Shear Stress (dynes/ cm^2)*	*Shear Rate (sec^{-1})*	*Viscosity (poises)*	*Flow rate (g/10 min*	*Density (g/cm^3)*
IPP	2.9–4.0	1.01–3.0	412.6	12.89	3.94	47217	16.30	12010	6.68	0.748
90 IPP/10 LLDPE	1.9–2.8	1.0–1.8	306.5	9.43	5.37	64346	16.33	12000	6.75	0.751
80 IPP/20 LLDPE	1.5–2.7	0.6–1.4	277.9	8.55	5.04	60326	17.31	11345	7.34	0.782
70 IPP/30 LLDPE	1.5	0.5–1.5	262.6	8.08	4.03	48246	18.77	10430	8.03	0.783
60 IPP/40 LLDPE	1.9–2.0	1.0–1.9	313.9	9.65	4.35	52273	17.45	11215	7.05	0.753
LLDPE	1.8–3.0	0.4–1.4	193.1	5.94	3.52	42224	16.91	11610	7.10	0.768
68.25 IPP/29.25 LLDPE/2.5 PPCMA	2.2–3.6	1.0–2.3	262.6	8.07	4.03	48246	22.05	8880	9.49	0.786
66.5 IPP/ 28.5 LLDPE/ 5 PPCMA	1.5–2.4	0.9–1.5	185.2	5.69	4.36	52285	23.66	8287	9.65	0.765
63 IPP/27 LLDPE/10 PPCMA	1.0–1.4	0.7–1.0	118.6	3.65	4.03	48246	33.93	5770	13.1	0.700

TABLE II (Continued)

Composition	*Haake Buchler Rheometer*						*Tinius olsen extrusion (piston) plastometer*			
	Processing Time (min)	*Width (min)*	*Total Shear Energy (j)*	*Specific Energy (j/g)*	*Stable torque/rpm*	*Shear Stress (dynes/cm²)*	*Shear Rate (sec⁻¹)*	*Viscosity (poises)*	*Flow rate (g/10 min*	*Density (g/cm³)*
59.5 IPP/ 25.5 LLDPE/ 15 PPCMA	1.5–2.3	1.0–1.5	93.6	2.88	4.23	50677	54.93	3560	19.1	0.639
68.25 IPP/ 29.25 LLDPE 2.5 PPSMA	2.0–3.6	1.4–3.4	206.5	6.35	7.38	88279	18.46	10600	7.63	0.762
66.5 IPP/ 28.5 LLDPE/ 5 PPCSMA	3.2–3.4	2.5–2.8	138.1	4.24	7.03	84150	19.48	9215	8.36	0.745
65.1 IPP/ 27.9 LLDPE/ 7 PPSMA	2.7–3.5	3.1–3.3	65.5	2.01	5.03	60214	21.38	9215	8.37	0.758
63 IPP/27 LLDPE/10 PPSMA	1.3–3.0	0.5–1.0	25.0	0.78		35964	23.06	8470	9.42	0.747
59.5 IPP/ 25.5 LLDPE/15 PPSMA	2.8	2.0–2.7	46.9	1.44	3.00	35964	32.18	6000	14.0	0.795

Processing time or time of fusion was determined by the time from loading to the point when the melt reached within 2°C of equilibrium; Average Shear Stress = 378 M (M torque for 3–5 min period of time), this is a semiempirical relation from ref (23). Shear Stress from the extrusion plastometer data was constant 19587 pa.

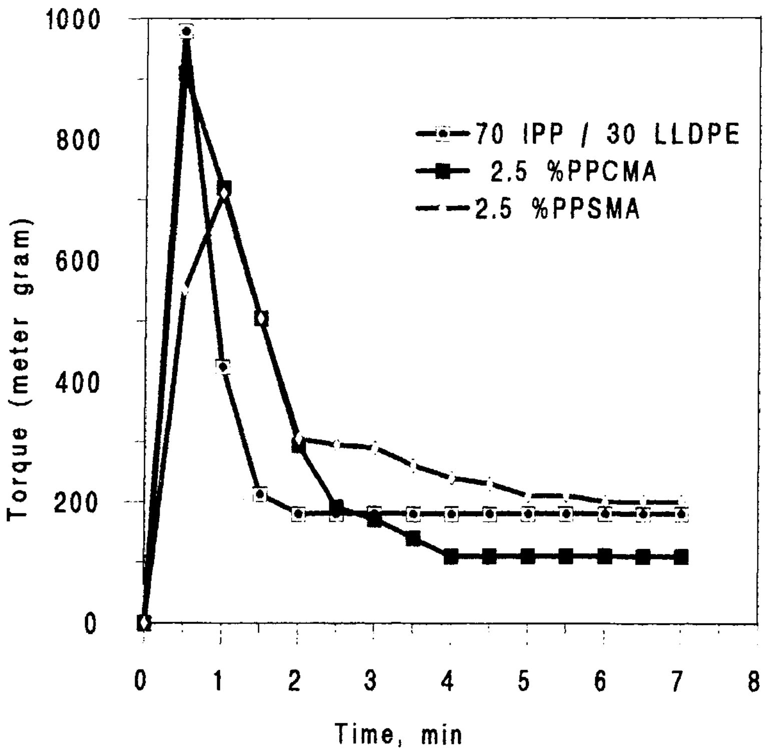


FIGURE 3 Torque-Time Plot for the Binary Mixture 70 wt IPP /30 wt % LLDPE and ternary mixtures containing 2.5 wt % PPCMA or PPSMA.

containing PPSMA in 2.5–7 wt% amount kept high total work energy level values according to the high torque recorded in the torque rheometer curves and variation of torque/rpm versus composition-see Table II.

As was already mentioned, the torque/rpm values are directly proportional to melt viscosity. As can be remarked from the data of the Table II, the average melt viscosity of mixtures containing 2.5–7 wt% PPSMA showed only a slight change, and shear stress had high values, while density remained approximately constant. PPCMA incorporation decreased density values.

Shear rate was approximately constant for binary IPP/LLDPE blends. It was considerably increased by addition of PPCMA; but with PPSMA incorporation, it remained almost constant in the 2.5–7 wt% composition range, then increased. Flow rate presented similar variation.

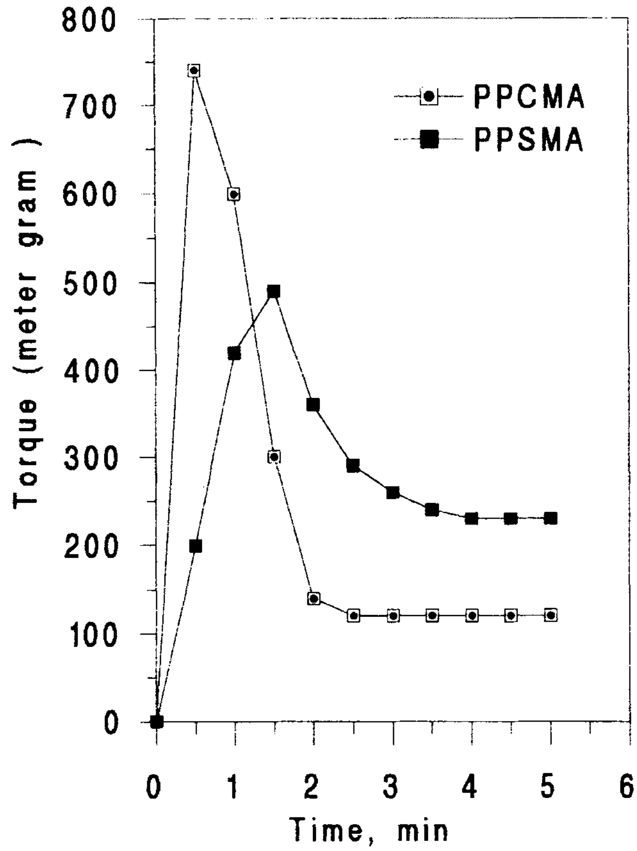


FIGURE 4 Torque-Time Plot for the ternary mixtures containing 5 wt % PPCMA or PPSMA.

The processing time and torque were higher for several mixtures containing PPSMA. The difference between torques, especially the high torque of mixtures containing 2–7 wt% PPSMA, can also be considered as a measure of the crossinking possibly taking place in the system.

Very interesting correlations appeared between melt flow rate and viscosity (Fig. 6) and stable torque/rpm and melt flow rate (Fig. 7). The first was linear. The second showed approximately constant values for binary IPP/LLDPE and ternary IPP/LLDPE/PPCMA blends; while ternary IPP/LLDPE/PPSMA blends showed various behavior depending on composition, namely a region at low PPSMA

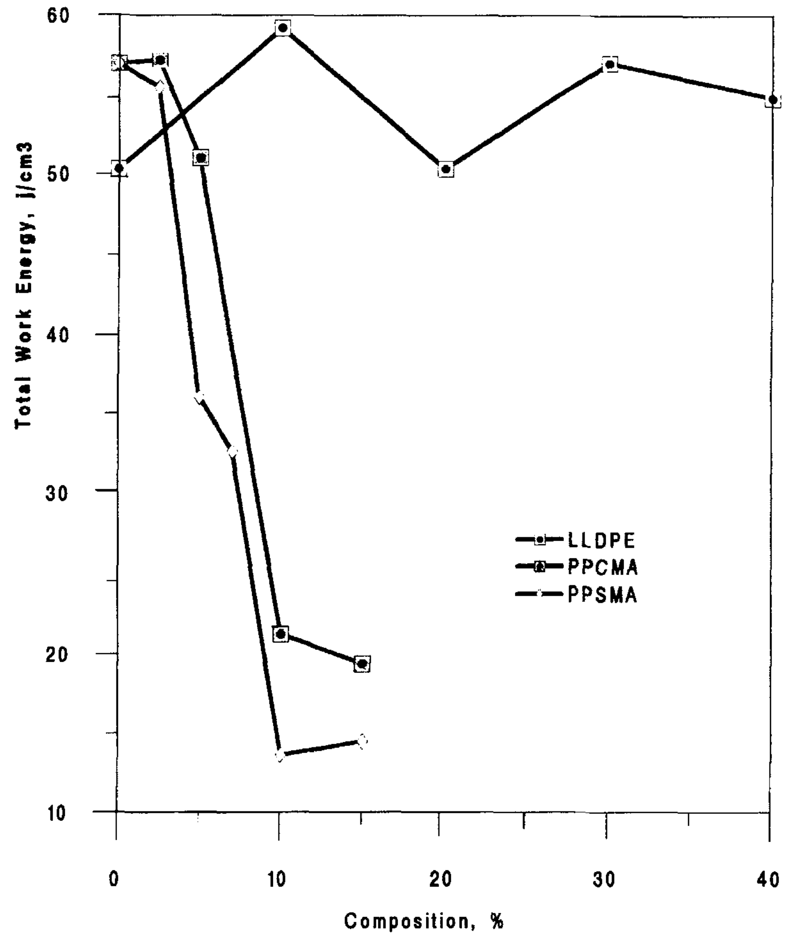


FIGURE 5a Total Work Energy versus Composition for the 0–3 minutes processing time.

content with high torque level, and a second region corresponding to high PPSMA content, the last blends having the lowest values for torque/rpm.

The processing temperature used in these experiments was 190°C. That is probably close to the ceiling temperature of maleic anhydride. At this temperature, it is possible that several side chains, containing more that a single unit of maleic anhydride, underwent depolymerization, and excited maleic anhydride units existed in the system. They

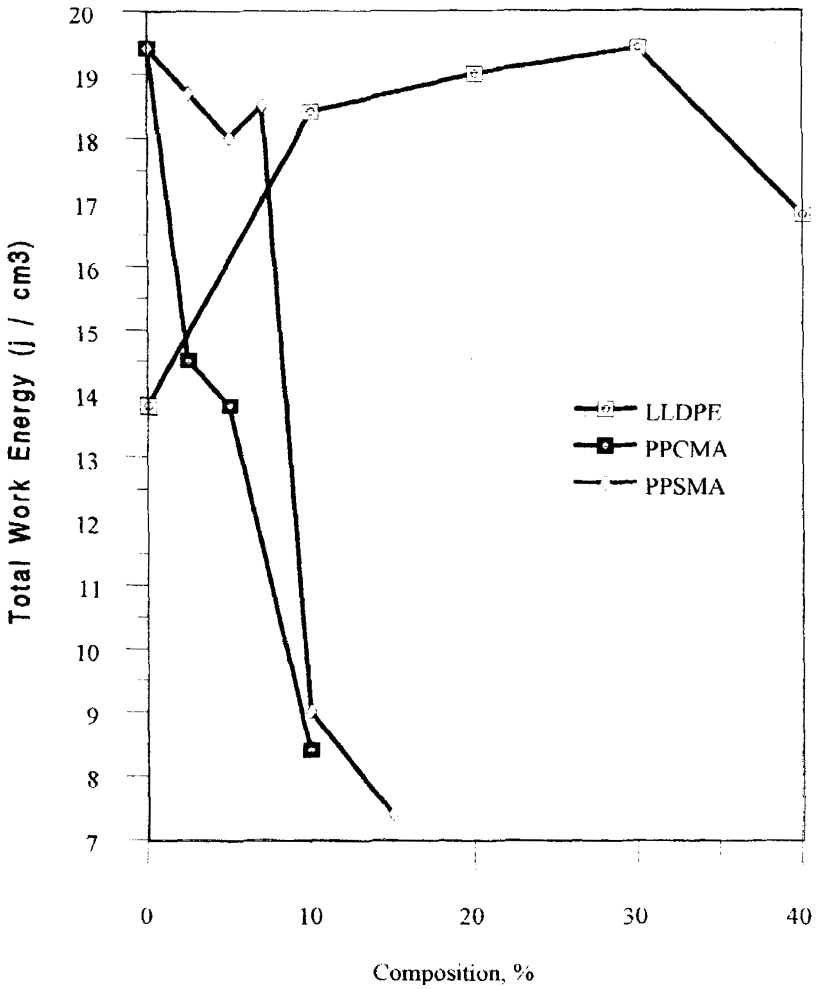


FIGURE 5b Total work energy versus Composition for 3–5 minutes processing time.

could initiate further maleation and the crosslinking of polyethylene chains [15, 23–28] and concomitantly IPP degradation [20]. The first phenomena were prevalent at low concentration of PPSMA, while the IPP degradation was predominant at high PPSMA content.

The PPCMA having low maleic anhydride content did not lead to such pronounced modifications. It should be mentioned that for 2.5 wt% PPCMA or PPSMA no decrease of torque during processing

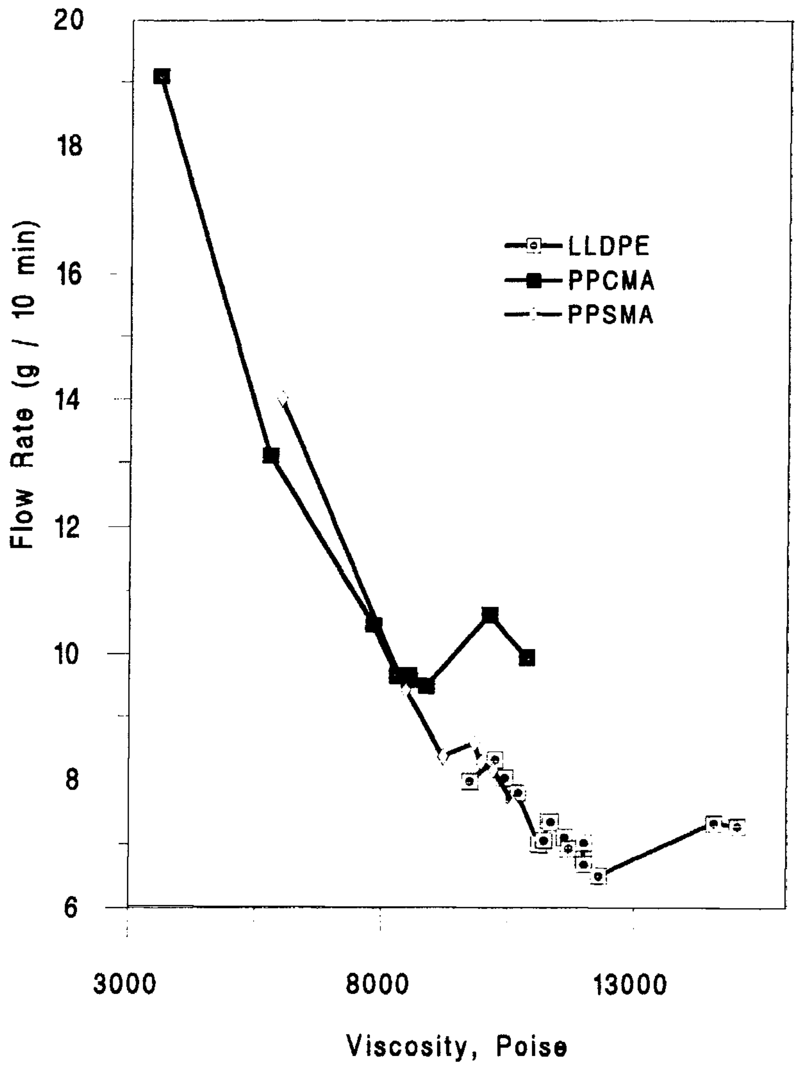


FIGURE 6 Melt flow rate versus Viscosity.

time or torque/rpm was observed. Moreover the PPCMA did not decrease the torque/rpm values for all concentrations employed; therefore no degradation occurred. The viscosity decrease could be due to the low viscosity of PPCMA, variation in the density, and this suggests a very weak interaction in polymer blends. Very low torque values for high concentration of PPSMA could also be due to PP degradation in the presence of this compound accompanied by remaleation and crosslinking of PE.

From the processing data we may conclude that the maleated pyrolysis products acted also as lubricants because they significantly affected the processability. They promoted proper flow of the plastic melt and minimized frictional heat generation, but they also influenced polymer-polymer interactions. PPCMA could be considered as an internal lubricant because it reduced melt viscosity, while PPSMA acted as an external lubricant reducing the friction between the melt and the hot metal parts of the processing equipment and preventing sticking, controlling the fusion of the material. The higher the level of external lubricants, the longer the fusion time will be. The increase of processing time with PPSMA content is a proof of its role as an external lubricant, being known that the excessive lubrication appeared as a slow temperature rise and long fusion time.

The optimum amount of lubricant is a must for the improvement of processing and for good quality products. In our case, it appeared that the optimum quantity of PPCMA should be 5–10 wt% while that of PPSMA must be very small, 2.5 wt%, to prevent IPP degradation [20]. This very low level was found for other maleated polyolefins used as coupling or compatibilizing agents [29]. Low quantities are recommended because the compatibility was improved (see DSC results), without degradation of the polymers. The prevention of IPP degradation in the presence of the initiators [30] was also achieved by the maleation of pyrolysis products prior to the IPP/LLDPE processing, although online maleation or reactive processing could be possible.

During the extrusion compounding it was observed that there was continuity of operation for the mixture containing PPCMA, that was not achieved in its absence. All values obtained lie on the same curves with those obtained for blends prepared on Haake Buchler Rheometer see Figures 11 and 12.

3.2. DSC Results

DSC curves of the binary IPP/LLDPE blends are given in Figure 8. They are typical for incompatible components, melting regions being

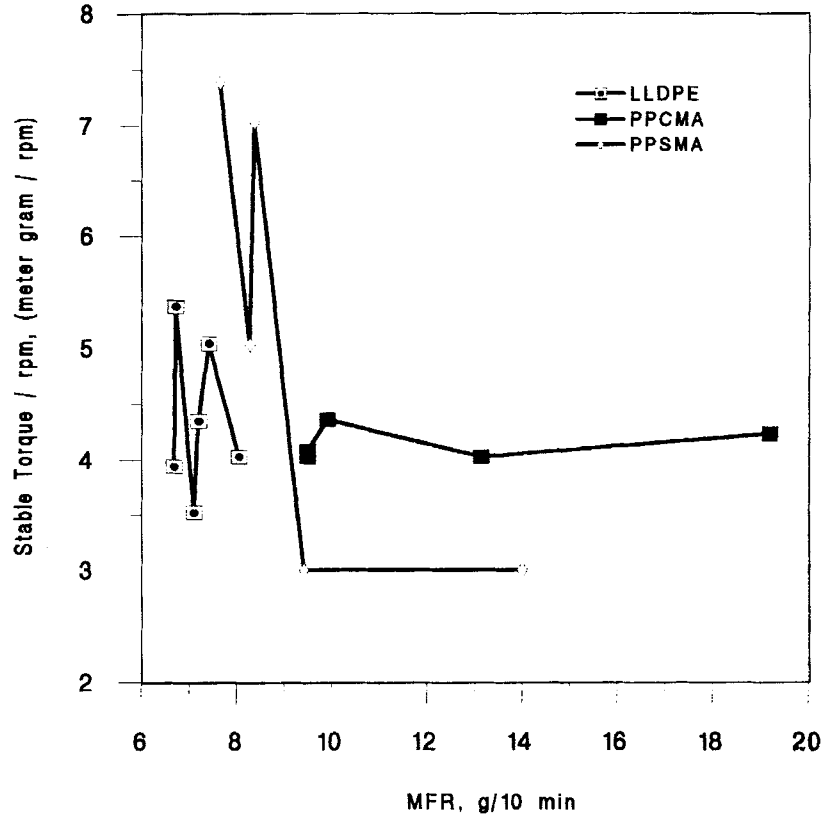


FIGURE 7 Stable Torque/rpm versus Melt Flow Rate.

quite separate, the melting temperatures of the components in the mixtures being unchanged. An exception was 90% IPP/10% LLDPE mixture, that showed an increase in Tm corresponding to IPP melting. Only for this ratio, the components presented a certain degree of compatibility, according to the literature data [30].

The ternary blends containing maleated products had characteristic DSC curves (Figs. 9 and 10). The melting peaks were broader and peak temperatures shifted toward lower values. An exception was the blends containing 5 and 7 wt% PPSMA which had higher Tm values corresponding to LLDPE melting in DSC curves, this being a proof for a probable partial crosslinking in these blends.

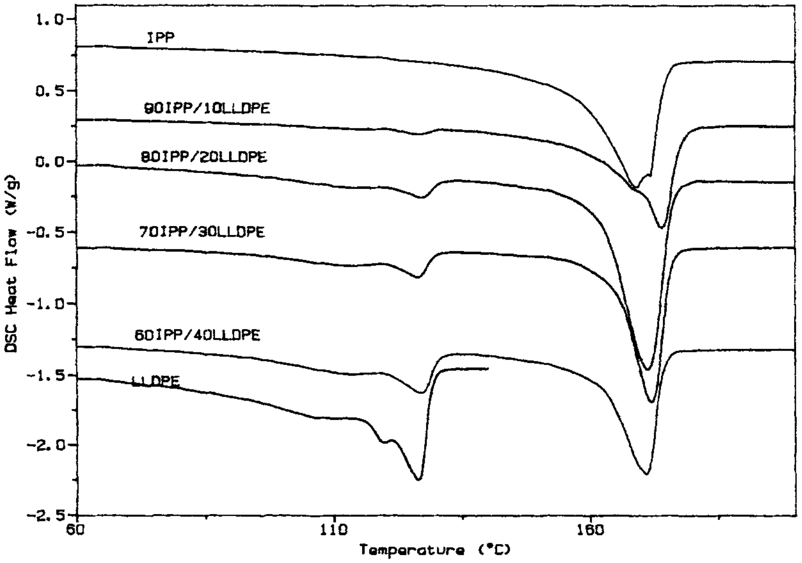


FIGURE 8 DSC-curves of the Binary IPP/LLDPE Blends.

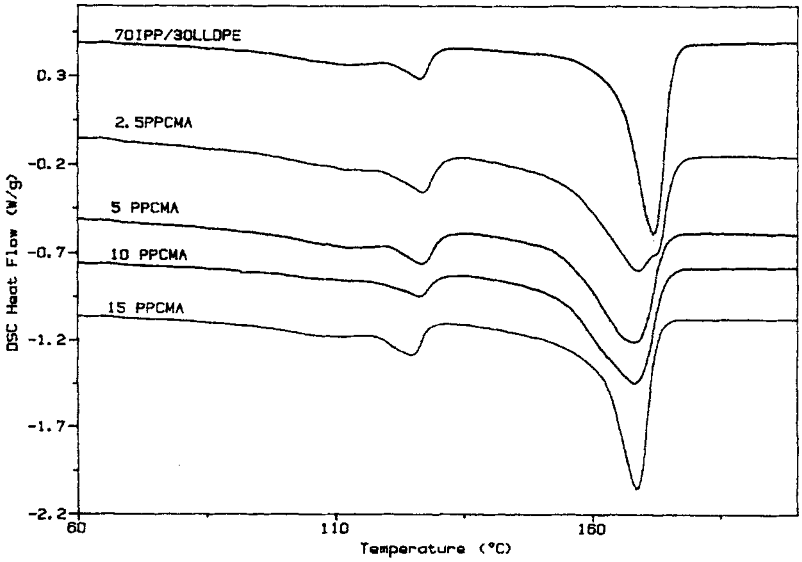


FIGURE 9 DSC-curves of the Ternary IPP/LLDPE/PPCMA Blends.

The same conclusion can be drawn from the variation of the melting heat versus composition (Figs. 11 and 12). Again we can observe the high variation for the 90 IPP/10 LLDPE blend in the ΔHm values. Other values lay close to the additive ones. The variation corresponding to the mixtures containing PPSMA showed smaller values. Probably the crystallinity was reduced or a degradation/decomposition and even cross-linking took place in the same temperature range. The higher PPSMA quantity decreased melting heats and hence the crystallinity too. It is known that there is a direct correlation between crystallinity and physical and mechanical properties. It is expected that, for a low ΔH, the tensile strength and modulus would have very low values (results will be given in a subsequent paper). PPCMA did not decrease these values for IPP melting; therefore the crystallinity was not modified to the same extent.

The role of the compatibilizing agent clearly appeared in the modification of the DSC curves. The peak corresponding to IPP melting became broader, even at only 2.5 wt% PPCMA or PPSMA, both melting temperatures decreasing. This modification appeared until a

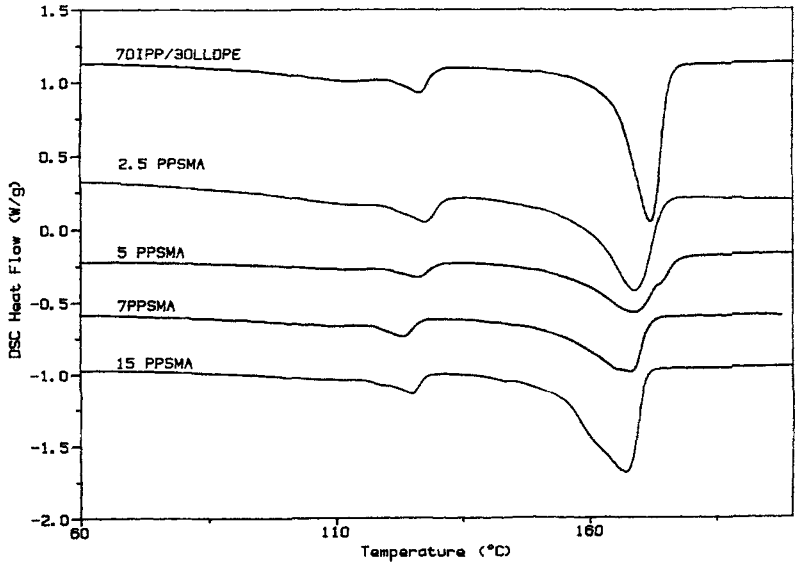


FIGURE 10 DSC-curves of the Ternary IPP/LLDPE/PPSMA Blends.

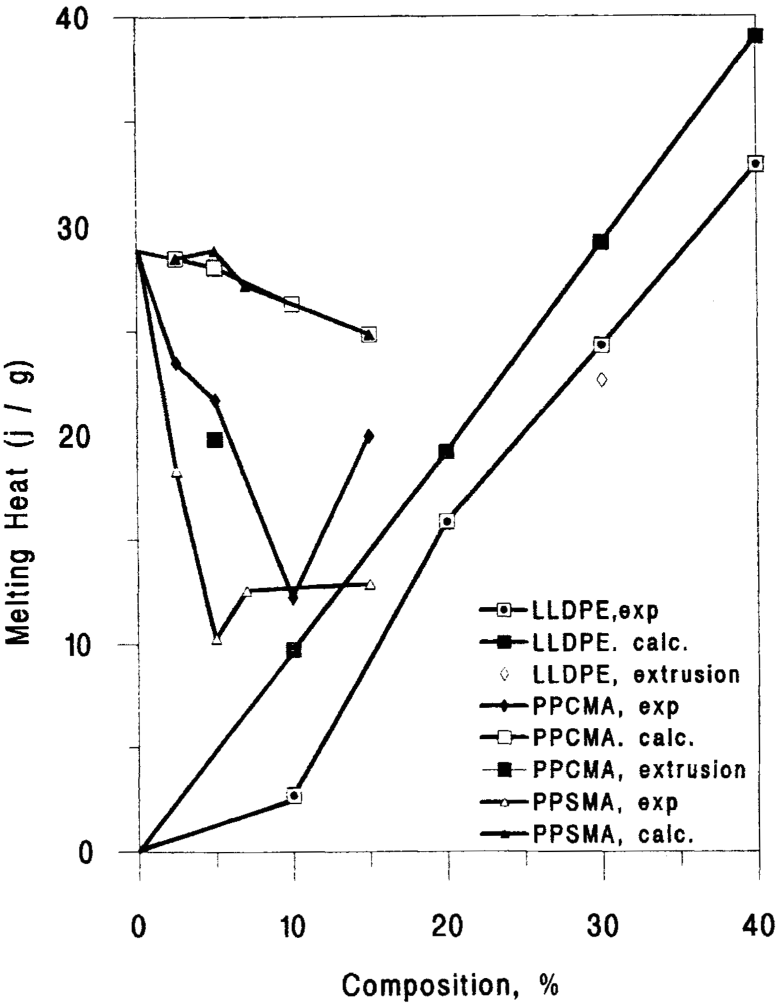


FIGURE 11 Melting Heat corresponding to the LLDPE Melting versus Composition of the Binary and Ternary Blends.

content of 10 wt% maleated pyrolysis product; then the peaks became similar to those of 70 wt% IPP/30 wt% LLDPE.

A possible explanation is either the formation of a mixed phase, or a change in polymer crystallite size and distribution which caused broadening enlargement of the peaks. The first hypothesis is supported by the decrease in the heat of melting, more important for those corresponding

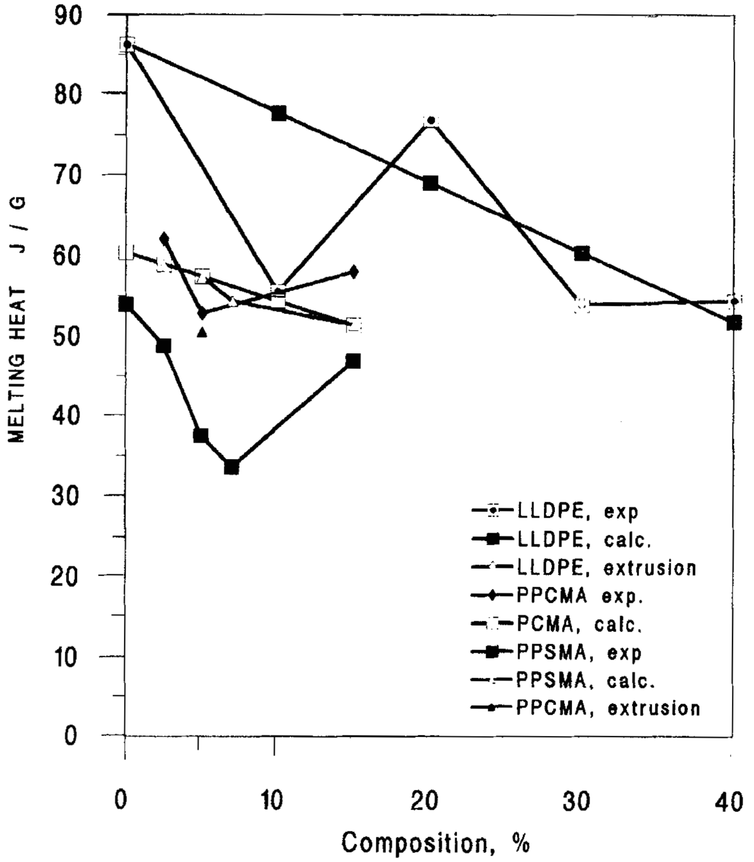


FIGURE 12 Melting Heat corresponding to the IPP Melting versus Composition of the Binary and Ternary Blends.

to LLDPE melting and for PPSMA containing blends. The results are in accordance with those from the literature. The excess of maleated PP, as has been also shown by O'Donnell and Baird [31] changes the morphology from larger elongated structures to smaller structures that can lead to reduced tensile moduli (and other mechanical properties). Maleated products lowered the interfacial tension for all compatibilized blends. For thermoplastic blends, a compatibilizer creates a droplet morphology which lower tensile properties, but it improves the adhesion between phases.

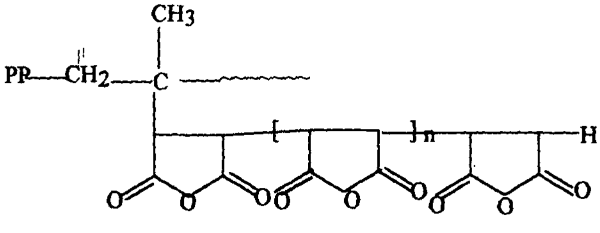
Therefore, if the IPP/LLDPE system showed a pronounced incompatibility, and the 90 wt% IPP/10 wt% LLDPE only offered slight compatibility, then by using maleated pyrolysis products, it was possible to enlarge the compatibility window to incorporate 30–40 wt% LLDPE in IPP. This was possible mainly by change in interfacial properties and by the probable partial cross-linking in the system containing PPSMA. Both situations could be of practical interest.

A general reaction scheme was suggested by the mechanism proposed by Gaylord *et al.* [15, 20, 26–28, 33] which could be more probable in our case in the reaction conditions and with two kinds of chain fragments in the maleation step and the second step of IPP/LLDPE blends processing should include the following sequence of reactions, where O is polyolefin fragment:

I. Maleation Step

1. $\mathrm{O} \xrightarrow{\mathrm{ROOH}} \mathrm{O}^*$ (at secondary carbon in ethylene oligomers; at tertiary carbon in propylene oligomers or in $\alpha-$ (or $\beta-$) position in respect to the double bonds)
2. $\mathrm{O}^* + \mathrm{MA} \longrightarrow \mathrm{O-MA}^*$
3. $2\mathrm{MA} \xrightarrow{\mathrm{ROOH}} [^*\mathrm{MA}^{+-}\mathrm{MA}^*]$ the maleic excimer
4. $\mathrm{O} + [^*\mathrm{MA}^{+-}\mathrm{MA}^*] \longrightarrow \mathrm{O}^* + [\mathrm{MA}^{+-}\mathrm{MA}^*]$
5. $\mathrm{O}^* + [^*\mathrm{MA}^{+-}\mathrm{MA}^*] \longrightarrow \mathrm{O} - \mathrm{MA}^{+-}\mathrm{MA}^*$
6. $\mathrm{O} - {}^*\mathrm{MA}^{+-}\mathrm{MA}^* \longrightarrow \mathrm{O} - \mathrm{MA}^* + [^*\mathrm{MA}^*]^*$
7. $\mathrm{O} - \mathrm{MA}^* + \mathrm{O} - \mathrm{MA}^* \xrightarrow{\text{disproportionation}} \mathrm{O} - \underset{\text{saturated}}{\mathrm{MA}} + \mathrm{O} - \underset{\text{unsaturated}}{\mathrm{MA}}$
8. $[^*\mathrm{MA}^*]^* + \mathrm{MA} \longrightarrow [^*\mathrm{MA}^{+-}\mathrm{MA}^*]$
9. $[^*\mathrm{MA}^{+-}\mathrm{MA}^*] \longrightarrow \mathrm{MA} - \mathrm{MA}^* \xrightarrow{\mathrm{MA}} [^*\mathrm{MA}^{+-}\mathrm{MA}^*] \longrightarrow \mathrm{MA} - \mathrm{MA}^{+-}\mathrm{MA}^* \longrightarrow \mathrm{MA} - \mathrm{MA} - \mathrm{MA}^*$ Polymerization of maleic anhydride
10. $\mathrm{O} - \mathrm{MA}^* + \mathrm{MA} \longrightarrow$ reaction 6 $\xrightarrow{n\,\mathrm{MA}} \mathrm{O} - (\mathrm{MA})_n$
11. $\mathrm{O} - \mathrm{MA}^* + \mathrm{O} \longrightarrow \mathrm{O} - \mathrm{MA} + \mathrm{O}^*$
12. $\mathrm{O}^* + n\,\mathrm{MA} \longrightarrow \mathrm{O} - (\mathrm{MA})_n$

For example the structure of IPP–g–MA established by Gaylord [20] was:



with termination by disproportionation or recombination

13. O − MA* + O* ——→ O − MA − O less possible

14. O* + O* ——→ O − O chain extension or crosslinking, more probable with PE chains.

O is oligomer from polyethylene or polypropylene pyrolysis. In the reaction 14, only ethylene oligomers can participate in a crosslinking reaction.

Probably the maleation occurs easily with pyrolysis products containing vinyl and vinylidene double bounds (see NMR spectra from Fig. 2) because the reaction at one α-methylene or methine group takes place even without initiator [22] and the main product is always accompanied by resinous material (PPSMA in our case).

II. Processing step

Liu, Baker and Russell [34] showed that maleic anhydride was successfully grafted to PE in air without addition of free radical initiator, when temperature was raised to 155°C. Therefore, the polymer chain can be considered thermally activated at processing temperature of 190°C, especially if a depolymerization step is possible for side chains containing more than a maleic anhydride unit.

$$\mathrm{O}-(\mathrm{MA})_n \xrightarrow{T>150^\circ\mathrm{C}} \mathrm{O}-(\mathrm{MA})_{n-1}+\mathrm{MA}^*$$

Excited MA* increases radical generation on polymer sites on secondary — CH_2— moieties or on tertiary — CH— moieties. The crosslinking at low concentration of MA* in the system may be attributed to the preferential generation of secondary polymer radicals (especially on LLDPE chains) by excited MA and therefore an increase in their coupling and crosslinking. It has been shown [26] that the various oxygen containing compounds including the antioxidants (as that used in these experiments) had little or no effect on the extent of crosslinking. They act only in preventing degradation.

At high MA concentration, the tertiary moieties on the polypropylene backbone are excited and tertiary radicals undergo disproportionation resulting in degradation rather than cross-linking according to all steps presented in the scheme, but O is now polymer LLDPE or IPP.

The pendant succinic anhydride groups can interact with both LLDPE and IPP matrix leading to the cross-linking or degradation as a function of temperature and concentration of MA in system.

CONCLUSION

Pyrolysis and maleation avoid some steps as size reduction, cleaning and refining proposed in other papers for processing of commigled plastics [35].

Maleated pyrolysis products improved the mixing of IPP with LLDPE acting both as lubricants and compatibilizing agents. They may be used both in processing of such blends from the virgin materials or in the reprocessing of mixed polymer wastes. This study offers a solution to create a closed loop between secondary and tertiary recycling of polymer wastes.

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