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# Morphological and rheological study of polypropylene blends with a commercial modifier based on hydrogenated oligo (cyclopentadiene)

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**Abstract**

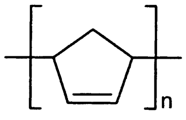
Morphology and rheology of the blends of two commercial polypropylene (PP) grades (designated as MA3 and MM1) with a commercial modifier (EP1) based on hydrogenated oligo (cyclopentadiene) (HOCP) were studied using modulated differential scanning calorimetry (MDSC) and dynamic shear rheometry. Melting and crystallisation points as well as glass-transition temperatures were determined and correlated to blends' compositions. Morphology was additionally studied by hot-stage optical microscopy (HSOM). Molecular characteristics of the materials were determined by gel-permeation chromatography (GPC). Dynamic (oscillatory) shear tests were conducted at different temperatures (190, 210, 230 and 250°C) in a wide frequency range (0.01–300 rad/s) and rheological parameters (such as zero-shear viscosity, activation energy) were also correlated to the composition of the blends. Thermal behaviour of both series of blends suggests phase separation at modifier concentrations above 30%. Dynamic viscosity of MA3/EP1 blends decreased with increasing EP1 concentration, while the rheological behaviour of MM1/EP1 system was more complex, due to changing the molecular weight distribution (MWD) of PP component. © 2001 Published by Elsevier Science Ltd.

*Keywords*: Rheology; Morphology; Blends

## 1. Introduction

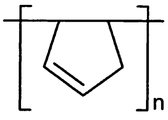
The excellent physico-chemical properties of isotactic polypropylene (iPP) can be further improved by blending it with proper plasticisers, additives, modifiers, etc. Films of iPP blended with hydrogenated oligo (cyclopentadiene) (HOCP) are used in the packaging industry owing to their reduced permeability to oxygen and aromas compared with plain iPP films [1]. These blends deserve attention because of their superior mechanical behaviour [2]. Early studies on crystallisation and thermal behaviour of such blends suggested that their components were miscible in melt [3]. Further analysis by differential scanning calorimetry (DSC) and wide-angle X-ray scattering (WAXS) [4] demonstrated that the presence of HOCP molecules in the film influenced the packing of PP chains, giving rise to the formation of the smectic form at temperatures where pure iPP would normally crystallise in the monoclinic α-form. The phase diagram of the iPP/HOCP system obtained by hot-stage optical microscopy (HSOM) [1] showed the occurrence of both the lower critical solution temperature (LCST) and the upper critical solution temperature (UCST). It indicates that the iPP and HOCP are miscible at temperatures higher than 240°C and lower than 90°C whereas the system undergoes phase separation in the range between these two temperatures.

Dynamic rheological tests performed [5] on the molten iPP/HOCP blends led to the conclusion that the components were miscible in temperature range 190–265°C for HOCP concentration up to 50%. The above study found no change in flow activation energy ($E_a$) and the same semi-circular shape of Cole–Cole plots was obtained. All the research mentioned above was performed using the commercial HOCP produced by Esso Chemical, which is a mixture of *cis*- and *trans*-isomers of the following structures A and B, that have been hydrogenated after the oligomerisation:



A

(1,4- structure)



B

(1,2- structure)

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Table 1
Characteristics of the studied materials

| Grade | Type | MFI[a] | $\eta_0$(190°)[b] | $\eta_0$(250°)[b] | $M_n$[c] | $M_w$[c] | $M_z$[c] | $M_w/M_n$ |
|---|---|---|---|---|---|---|---|---|
| MA3 | iPP | 3.2 | 22060 | 7790 | 48.0 | 385.3 | 1420 | 8.1 |
| MM1 | iPP | 9.0 | 5250 | 1640 | 52.1 | 279.3 | 802 | 5.4 |
| EP1 | iPP/HOCP | 33.0 | 6440 | 1370 | 82.5[d] | 386.6[d] | 1362[d] | 4.7[d] |

[a] g/10 min at 230°C.
[b] Pas.
[c] kg/mol.
[d] Values for PP component only.

The aim of this paper is to develop correlation between morphology and rheology of blends of iPP and a commercial modifier based on HOCP.

## 2. Method

### 2.1. Materials and blend preparation

Two commercial film-blowing PP grades (MA3 and MM1) were blended with a commercial modifier containing 50 wt% of HOCP (EP1) in a Brabender twin-screw extruder at 220°C. The materials characteristics are given in Table 1.

After extrusion, the blends were cooled with air and pelletised. The composition of the blends (wt/wt) were as follows:

MA3/EP1: 100/0, 90/10, 85/10, 70/30, 50/50, 30/70 and 0/100;
MM1/EP1: 100/0, 90/10, 80/20, 70/30, 50/50, 30/70 and 0/100.

### 2.2. Calorimetric measurements

All modulated differential scanning calorimetry (MDSC) tests were performed using DSC 2920 Modulated DSC manufactured by TA Instruments. Samples for MDSC tests were prepared by cutting the polymer strands into pellets with both flat surfaces and weight of 10–15 mg each. The heating and cooling curves were analysed by TA Universal Analysis Software. The percentage crystallinity ($x_c$) was calculated from

$$x_c(\text{blend}) = 100\%\Delta H^*(\text{blend})/\Delta H_0(\text{iPP}) \qquad (1)$$

where $\Delta H_0$(iPP) is the heat of melting of 100% crystalline iPP and was taken to be 209 J/g.

### 2.3. Optical microscopy

15–20 μm thick films for HSOM were prepared by compression moulding at 220°C in a Wabash compression press. Optical micrographs were taken by Nikon Labophot-2 optical microscope equipped with Mettler FP82HT hot stage.

### 2.4. Gel-permeation chromatography

Gel-permeation chromatography (GPC) analysis was performed at 140°C on a Waters alliance GPCV2000 instrument, equipped with two Styragel HT 6E columns, differential refractometer and viscometer detectors. 1,2,4-Trichlorobenzene (TCB) was used as an eluent, with a flow-rate of 1.0 ml/min. The system was calibrated with 14 narrow polystyrene (PS) standards with molecular weights in the range $1 \times 10^3$–$1 \times 10^7$, by applying universal calibration. Chromatograms were processed by Millennium[32] Software in order to obtain molecular weight distributions (MWD).

### 2.5. Dynamic shear rheology

Samples for dynamic shear measurements were compression moulded in a Wabash press at 220°C and cut into discs of 25 mm in diameter, 1.8 mm thick. Dynamic shear tests were performed on a Rheometrics SR 200 stress-controlled rheometer, equipped with 25 mm parallel plates, at several temperatures (190, 210, 230 and 250°C) in nitrogen atmosphere within a frequency range of 0.01–300 rad/s. The applied strain was in a range 8–15%, which was determined to be in the linear viscoelastic region. Data were collected and analysed using Rhios Rheometrics Software.

## 3. Results and discussion

### 3.1. Differential scanning calorimetry

The same experimental procedure was applied to all the samples: in the first run, the scan rate was 4°C/min from −30 to 200°C. This allowed the determination of both glass-transition ($T_g$) and melting temperatures ($T_m$) to be made. Values of $T_g$ were taken as inflection points of heat-flow curves and confirmed by inflection of corresponding heat capacity curves. Melting temperatures were taken as peak values of endothermic heat-flow curves. The second run for all the samples was cooling from 200 to 40°C with the same scan rate (4°C/min). Crystallisation temperatures were collected as peaks of exothermic heat-flow curves. The influence of EP1 concentration in the blends on $T_m$, $T_c$ and $T_g$ is shown in Fig. 1. From Fig. 1, one can observe that $T_m$

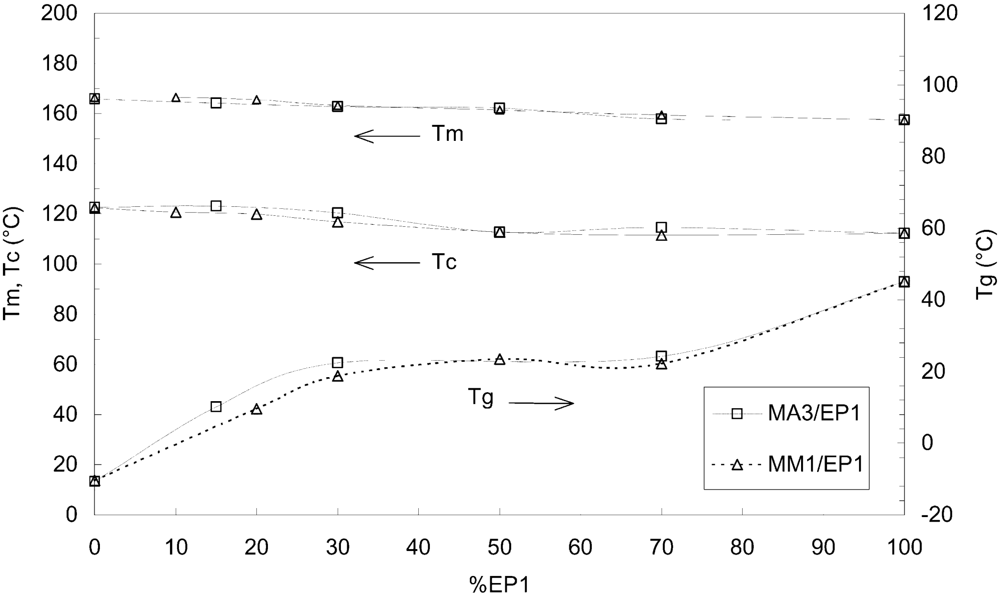


Fig. 1. Melting, crystallisation and glass-transition temperatures of MA3- and MM1-blends with EP1.

and $T_c$ decreased and $T_g$ increased, respectively, with increasing EP1 concentration for both series of blends. In other words, adding EP1 to iPP caused a narrowing of the crystallisation window, measured by $T_c - T_g$. Consequently, blends with higher EP1 content should have less PP in crystalline form, as is confirmed by Fig. 2. The percentage crystallinity was calculated using Eq. (1) and it dropped continually with increasing EP1 concentration.

The shapes of the curves in Fig. 1 slightly differ from the results reported in literature (Cimino et al. [1,4]), where $T_m$ decreased in a linear way and $T_c$ decreased more rapidly. This can be due to difference in materials used and different experimental conditions. It is interesting that both $T_c$ vs %EP1 and $T_m$ vs. %EP1 curves (Fig. 1), for both series of blends, showed inflection points at around 50% of EP1, that corresponds to ≈25% of HOCP. According to the phase diagram of iPP/HOCP system given in the above references, blends with less than 50% of EP1 were miscible in the melt, while in those with ≥50%EP1 phase separation took place. The MDSC runs shown in Figs. 3 and 4 were performed by heating the slowly crystallised sample from 40 to 200°C with 4°C/min scan rate. Multiple endotherms were noticed for both series of blends with EP1 concentration greater than 30%. Many factors can influence such behaviour of PP

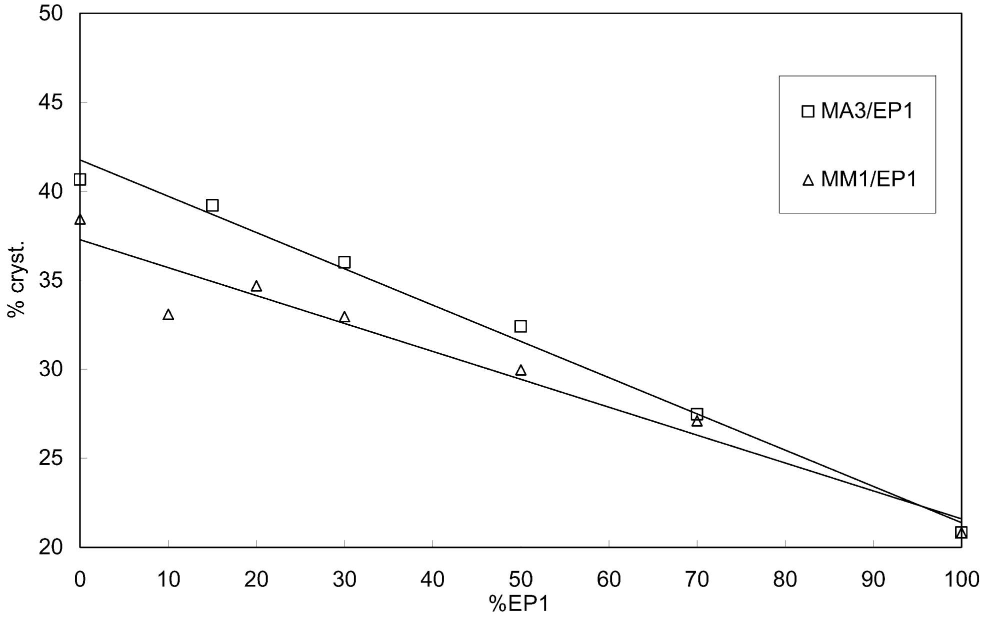


Fig. 2. Percentage crystallinity vs. %EP1 in the blends.

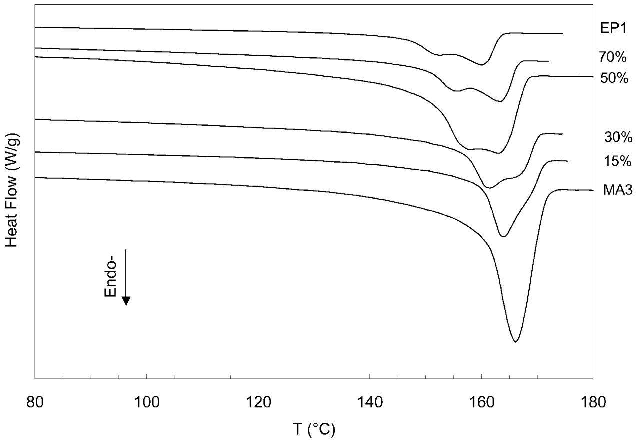


Fig. 3. Multiple endotherms for MA3/EP1 blends.

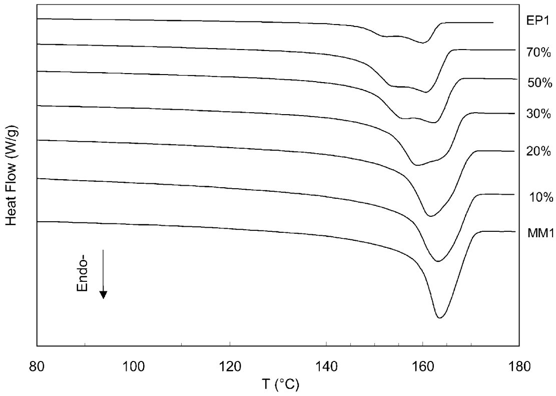


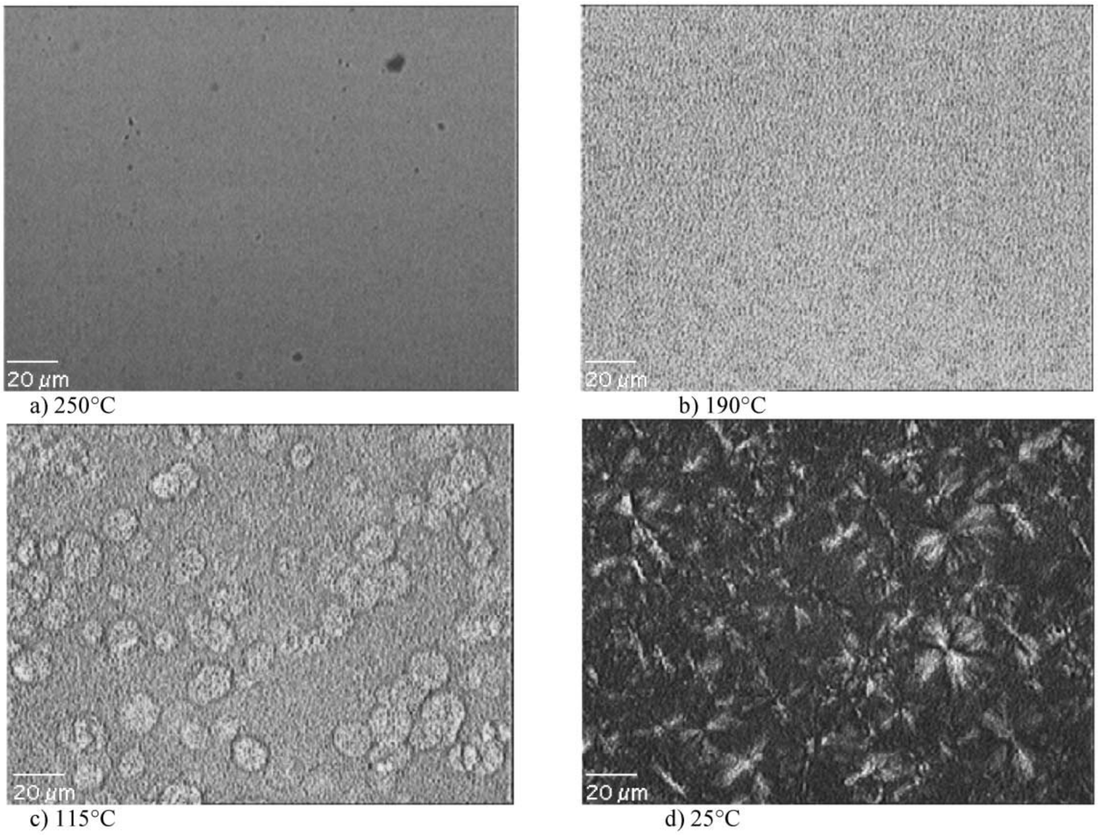
Fig. 4. Multiple endotherms for MM1/EP1 blends.

[6,7]. Since all the test samples were treated in the same manner, the different behaviour of the blends with different %EP1 can be caused by the difference in their morphology. This can lead to the conclusion that the molten blends were phase separated at concentrations greater than 30%EP1.

### 3.2. Hot-stage optical microscopy (HSOM)

Thin films prepared from the blends by compression moulding were heated to 260°C in a hot-stage (the temperature where all the melts were expected to be miscible) and then cooled to 40°C with the same cooling rate as used for MDSC tests (4°C/min). The phase separation and crystallisation behaviour was monitored using 100× magnification and recorded on videotape. The photos presented in this paper were taken by capturing the video-images using a Macintosh Power PC computer.

As expected, EP1 melt was homogenous at temperatures higher than 240°C. During cooling, phase separation took place (Fig. 5a and b). At lower temperatures, PP crystallised from immiscible melt (Fig. 5c). After standing at room



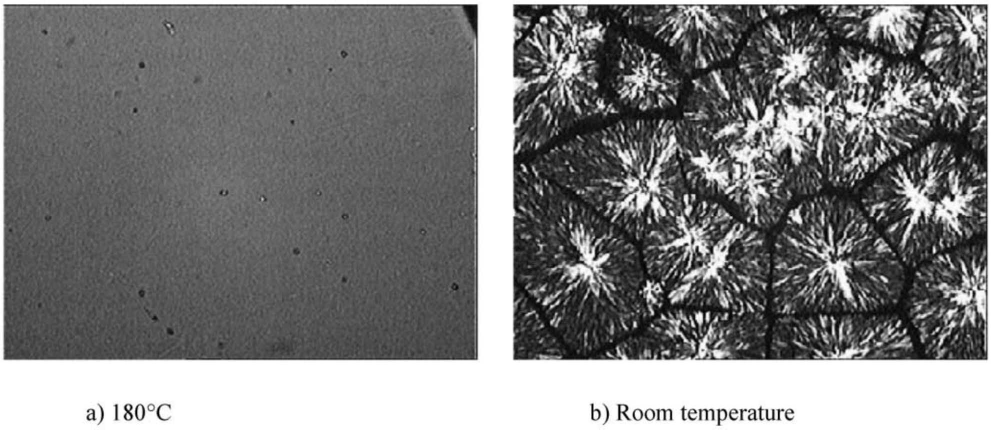
a) 250°C

b) 190°C

c) 115°C

d) 25°C

Fig. 5. (a–d) Optical micrographs of EP1 film under cooling from 260°C to room temperature.



a) 180°C

b) Room temperature

Fig. 6. Optical micrographs of MA3/EP1-85/15 blends under cooling: (a) melt at 180°C; (b) after standing at room temperature for 1 h.

temperature, EP1 film consisted of PP spherulites surrounded by amorphous regions (Fig. 5d). The melts of the blends with less than 50% of EP1 were homogeneous at all temperatures. PP crystallised from the miscible melt, as shown for MA3/EP1 85/15 (Fig. 6a and b) and MM1/EP1 80/20 (Fig. 7a–c). The observed melt morphology was in agreement with MDSC results and revealed PP crystallisation behaviour during cooling. The presence of HOCP in miscible melts diluted the crystallisable PP chains, slowing down the process and leading to smaller crystals (as more nuclei could form during the initial phase of crystallisation). It seems that phase separation did not affect this behaviour, which agreed with percentage crystallinity data from MDSC, i.e. PP crystallised from both PP-rich and HOCP-rich phase, with a crystallisation rate that depends on available PP concentration.

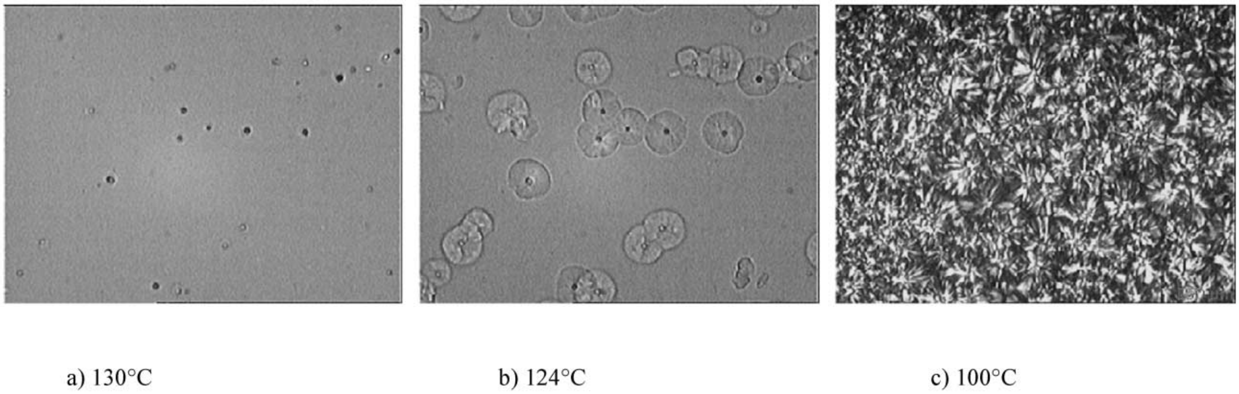
### 3.3. Gel-permeation chromatography analysis

MWDs of the materials were determined by using Waters alliance GPCV2000. Samples were dissolved by agitating 10–15 mg of the polymer in 10 ml of TCB at 160°C for 2 h prior to injection. The analysis was carried on at 140°C and the chromatograms were processed with Millennium software in order to obtain MWD curves and molecular weight averages. The chromatogram of EP1 sample (Fig. 8) showed two peaks in both refractometer and viscometer signals. The larger positive peaks at around 16 min correspond to PP component, whilst the small viscometer and negative dRI peak at around 21 min correspond to HOCP. The concentration of PP component calculated from the area under its dRI peak was equal to 50% of the total EP1 concentration, which confirmed the accuracy of the analysis. The MWD curves for the tested polymers are shown in Fig. 9 and the calculated MW averages are listed in Table 1. It was not possible to obtain accurate results for the HOCP component, because its peak corresponds to MW lower than $1 \times 10^3$.

It can be seen from the GPC results that PP component of EP1 has very similar $M_w$ and $M_z$ averages as MA3 and much higher than MM1. One can calculate that the whole series of MA3/EP1 will also have similar $M_w$ and $M_z$ values. On the other hand, MW averages of the PP component of MM1/EP1 blends will increase with increasing %EP1.

### 3.4. Dynamic shear measurements

Dynamic (oscillatory) shear tests were performed using a Rheometrics stress-controlled rheometer SR 200, equipped



a) 130°C

b) 124°C

c) 100°C

Fig. 7. (a–c) Crystallisation of PP from MM1/EP1-80/20 melt.

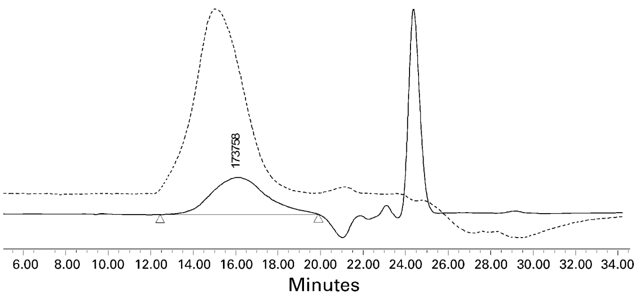


Fig. 8. GPCV chromatogram of EP1 (solid line — dRI, dashed line – – – viscometer).

with 25 mm parallel plates. The temperature and frequency range (190–250°C and 0.01–300 rad/s) were chosen to allow the most accurate calculation of rheological parameters, such as zero-shear viscosity ($\eta_0$) and flow activation energy ($E_a$), as well as to enable analysis by time–temperature superposition (TTS) and Cole–Cole plots. According to the phase diagram proposed in Ref. [4], at the maximum applied temperature (250°C) the melt should be homogeneous for all the concentrations. At other temperatures, the morphology of the melt should depend on the EP1 concentration.

The complex viscosity curves of MA3/EP1 melts at 190°C are shown in Fig. 10. Fig. 11 shows storage modulus ($G'$) curves at the same temperature. The dynamic shear tests were also performed for 90/10 and 85/15 MA3/EP1 blends, but the corresponding $\eta^*$ and $G'$ curves were omitted for clarity. The first observation is that adding small amounts of EP1 did not change the rheological behaviour by any significant amount. With further increase of EP1 concentration (more than 30%), the values of $\eta^*$ and $G'$ dropped more rapidly. The greatest gap was between 30/70 blend and pure EP1, at all temperatures. However, at 250°C the $\eta^*$ curves were more equally spaced than those at lower temperatures, leading to conclusion that morphological factor (phase separation) plays important role at 190°C. Similar to $\eta^*$ curves, $G'$ curves of MA3/EP1 blends were parallel but shifted down with increasing EP1 concentrations.

The rheological behaviour of MM1/EP1 blends was different, as shown in Fig. 12 (complex viscosity) and Fig. 13 (storage modulus). While MA3 and EP1 had similar shear thinning behaviour, MM1 was less shear thinning and its $\eta^*$ and $G'$ curves showed different shapes. This is the reason for crossover in Fig. 12. The reason for the different behaviour of MA3 and MM1 blends can be due to the fact that the former PP grades were blended with polypropylene already present in EP1, which may increase the polydispersity of the MM1 blends, compared to pure MM1, causing more shear thinning.

Further analysis of dynamic shear data was performed by plotting Cole–Cole plots (i.e. elastic component of complex viscosity, $\eta''$, as a function of its viscous component, $\eta'$). Utracki et al. [8] found that the shape of the plots was semi-circular for miscible PP/polyethylene blends, but not for the immiscible ones. Those authors stated that this behaviour should be expected for other systems, as well. The Cole–Cole plots for MA3/EP1 blends are shown in Fig. 14 and for MM1/EP1 blends in Fig. 15. Only the plots for 190°C are presented. As seen in Figs. 14 and 15, for both series of blends, the shape of the curves remained semi-circular for all concentrations. Since the Cole–Cole plots represent a relationship between elastic and viscous response of the melt to applied stress, as a consequence of relaxation properties of polymer chains, one can conclude that the influence of phase separation on the above processes was not predominant. It appears that only the characteristics and concentration of PP in the studied systems were responsible for the observed quantitative changes in rheological properties (viscosity, elasticity), rather than morphological factors.

Further analysis of the rheological data, including TTS (master-curve approach), modelling the zero-shear viscosity, ($\eta_0$) and calculating the flow activation energy ($E_a$), was carried out. As suggested by Domoulin et al. [8], the melts of miscible blends are 'thermo-rheologically simple' and the corresponding master-curves of $\eta^*$, $G'$ or $G''$ should be obtained by horizontal shifting of the experimental data. Such behaviour was noticed for the concentrations of EP1 of up to 50% in both series of blends, while horizontal

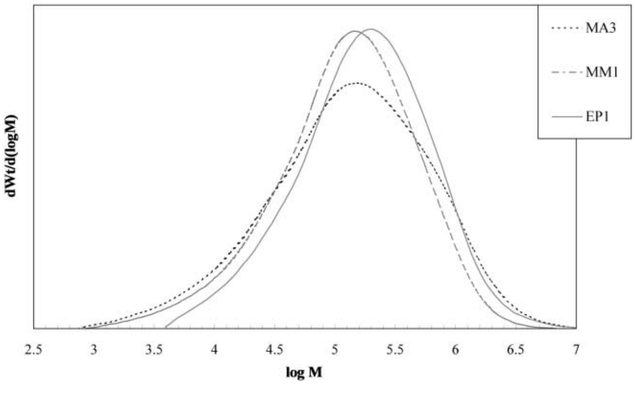


Fig. 9. MWD curves of PP samples.

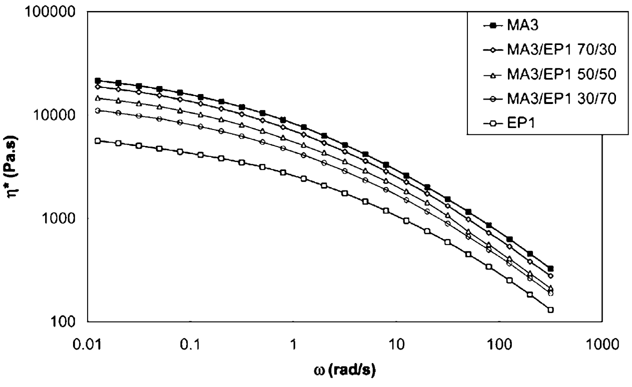


Fig. 10. Complex viscosity curves for MA3/EP1 blends at 190°C.

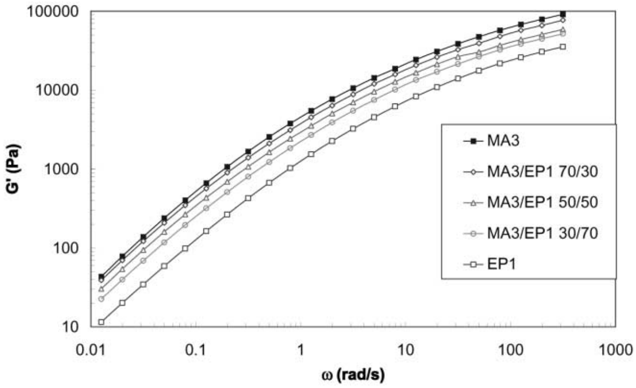


Fig. 11. Storage modulus curves for MA3/EP1 blends at 190°C.

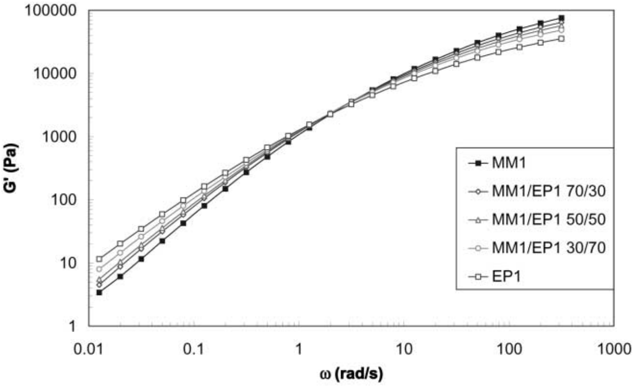


Fig. 13. Storage modulus curves for MM1/EP1 blends at 190°C.

shifting did not give perfect master-curves for MA3/EP1 30/70, MM1/EP1 30/70 and EP1. This was in agreement with the proposed morphology of the melts, i.e. for the above blends, immiscibility was expected. However, the 'perfection' of master-curves (or 'the ease' of matching the curves by shifting) was a matter of subjective opinion of the authors.

Values of zero-shear viscosity of the blends were obtained by fitting the Ellis model and presented against their compositions (Figs. 16 and 17). If we assume only the influence of HOCP on $\eta_0$ of MA3/EP1 blends (Fig. 16), several conclusions could be made. The shape of the $\eta_0$ vs %EP1 curves remained the same in the whole temperature range, although the phase behaviour of the melt was different at different temperatures. At 190°C, MA3/EP1 50/50, 30/70 and 0/100 were immiscible, while at 250°C all the melts were homogeneous. The same $\eta_0$-composition dependence is a sign of the influence of HOCP on flow, regardless of the phase behaviour. This effect could be explained as due to the decreasing the number of entanglements between PP chains. However, the effect of phase separation must be considered, as observed by sudden drop of $\eta_0$ at concentrations of EP1 above 50%, i.e. for immiscible melts.

The situation is more complicated with MM1/EP1 blends (Fig. 17), again due to the influence of blending of MM1 with PP from EP1 with higher MW averages, contributing to an increase of $\eta_0$ — an effect opposite to the influence of HOCP, so the overall $\eta_0$-composition dependence was different from that of the MA3/EP1 system. However, the viscosities of MM1/EP1 blends at higher frequencies dropped with increasing %EP1 (Fig. 12), showing that the similar effects mentioned above for MA3/EP1 blends were also apparent for MM1/EP1 blends. It seems that small HOCP molecules lubricated the flow of PP macromolecules and the effect was more obvious at higher strain rates/frequencies.

A good correlation was found between flow activation energy ($E_a$) and morphology of the blends (Fig. 18). $E_a$ was determined from the Arrhenius plots of $\ln(\eta_0)$ vs. $1/T$. The slope of the line is equal to $E_a/R$, so $E_a = \text{slope} \times R$, where $R = 8.314$ J/kmol. The other method utilised to calculate $E_a$ was the plot of $\ln(1/a_T)$ vs. $1/T$, also known as Arrhenius plot, where $a_T$ is the shift factor for TTS. The agreement between the estimated $E_a$ values was good for concentrations of up to 50%EP1. For higher concentration, the values did not agree well because of poor superposition. The values used in Fig. 18 were calculated from $\eta_0$. One can notice a small change in $E_a$ for low concentrations of EP1 and a sharper increase for blends above 50% of EP1. The significance of $E_a$ is how 'easier' the melt can flow at a higher temperature than at a lower temperature. For blends

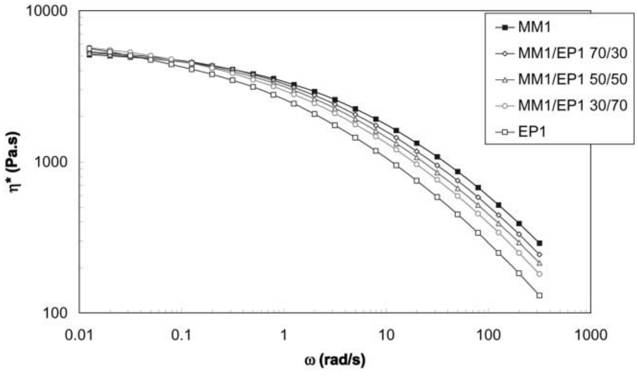


Fig. 12. Complex viscosity curves for MM1/EP1 blends at 190°C.

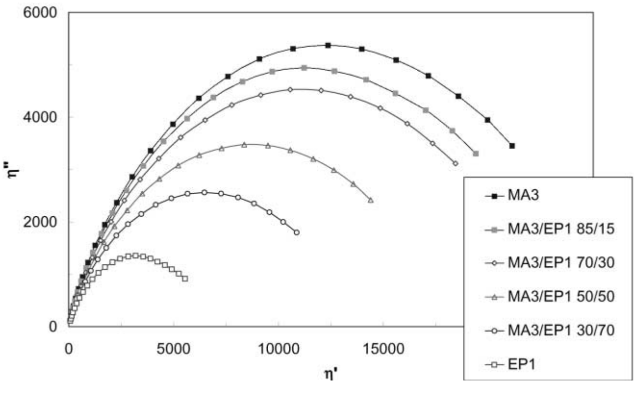


Fig. 14. Cole–Cole plot for MA3/EP1 blends at 190°C.

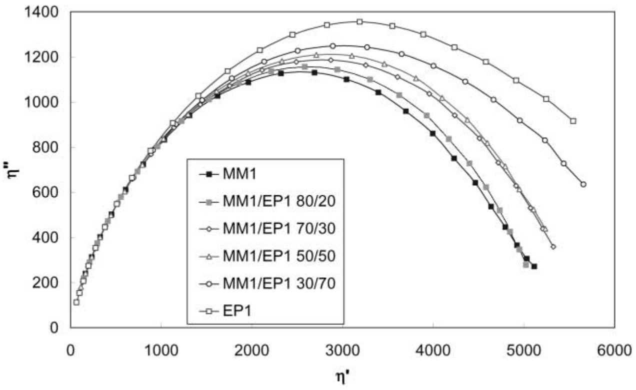


Fig. 15. Cole–Cole plot for MM1/EP1 blends at 190°C.

with less than 30%EP1, the increase of temperature from 190 to 250°C did not change the morphology of the melt, i.e. it was homogenous at all tested temperatures. The $E_a$ values of these blends were all very close to $E_a$ of pure PP (≈35–40 kJ/mol). The change of temperature from 190 to 250°C for blends with 70 and 100%EP1 changed the melt from multi-phase to the homogeneous state. Apparently, the homogenous melt flowed easier than the immiscible one, where the applied stress should not only 'move' the molecules, but also overcome interfacial forces.

## 4. Conclusions

Blending of iPP with a commercial modifier based on HOCP can change its morphology, as well as rheological behaviour. As revealed from MDSC and HSOM results, systems containing 30% of EP1 or lower were miscible at all temperatures. Blends with 50%EP1 and more showed phase separation, depending on temperature. Percentage crystallinity, $T_m$ and $T_c$ decreased with increasing %EP1, while $T_g$ increased. Slowly crystallised samples with more than 30%EP1 showed multiple endotherms, due to inhomogenities in the melts. This behaviour was detected by using the Modulated DSC that allowed high accuracy at low scan speed (4°C/min). It also enabled detection of $T_g$ and smectic to α-form transformations.

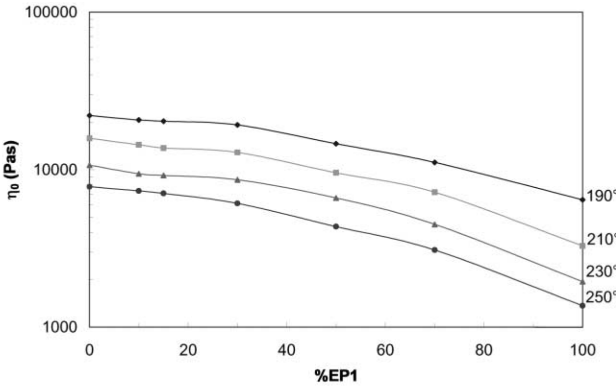


Fig. 16. Zero-shear viscosities of MA3/EP1 blends (lines are just eye-guides).

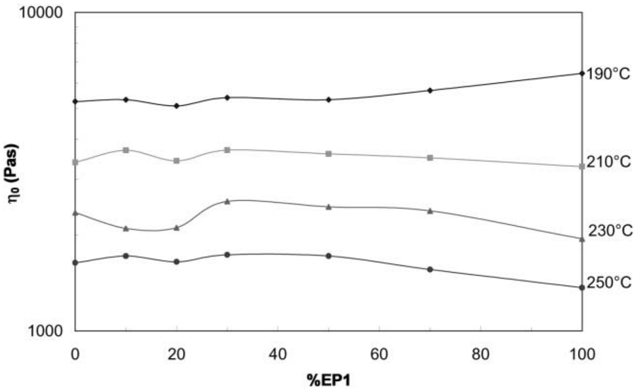


Fig. 17. Zero-shear viscosities of MM1/EP1 blends (lines are just eye-guides).

HSOM study proved the MDSC results on miscibility and showed that increasing EP1 concentration led to lower crystallisation rates and decreased the size of spherulites.

Shear flow was affected by blending. As shown by oscillatory shear measurements, small amounts of modifier (less than 30% w/w) lowered complex viscosity and storage modulus by a small amount. Higher concentrations of EP1 had more significant influence, which was also dependant on the PP grade in the blend. It was shown that the presence of PP in the modifier had a great influence on the rheological response of the blends. Although its presence did not affect morphology, it could change the MWD of the used PP grades, as was observed for MM1/EP1 systems. Detailed analysis of dynamic shear data revealed that morphology also had influence on the melts flow. Occurrence of phase separation increased the flow activation energy and effected TTS. The use of Cole–Cole plots to detect phase separation did not work for the systems investigated here.

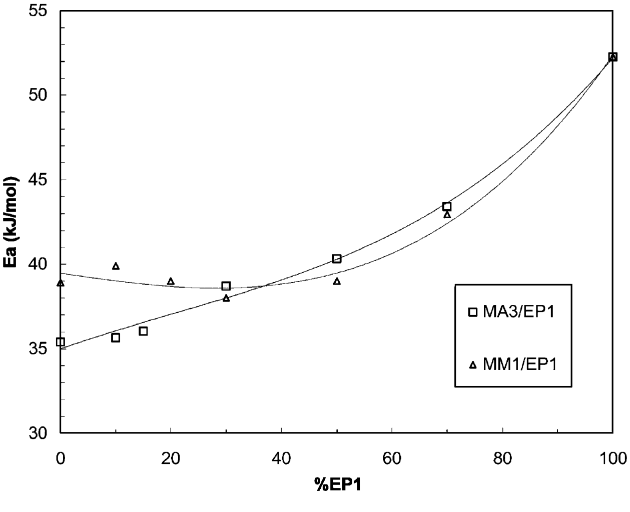


Fig. 18. Flow activation energy ($E_a$) of MA3/EP1 and MM1/EP1 blends.

## Acknowledgements

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