Influence of EP/PP viscosity ratio on the surface morphology and elasticity of injection moulded PP/EP

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Abstract: The influence of the viscosity ratio between (ethylene–propylene) copolymer (EP) and polypropylene (PP) on the EP surface distribution in injection moulded disks of PP/EP resins has been investigated by transmission electron microscopy (TEM) and by atomic force and force modulation microscopies (AFM and FMM). TEM images taken on transverse sections parallel to the injection direction reveal that, for high EP/PP viscosity ratios, large (>1 μm) undeformed EP nodules are observed up to the surface. The AFM and FMM observations performed on the surface reveal soft regions of the same size embedded in a more rigid matrix (undeformed EP nodules present at or just below the surface). For low viscosity ratios, EP rubber nodules, strongly elongated parallel to the surface, are observed by TEM. From FMM measurements, the elastic modulus is found to be homogeneous across the surface and is comparable to that measured above EP nodules on the high viscosity ratio resin.

Keywords: polypropylene; blends; surface; elasticity; TEM; AFM

INTRODUCTION

The surface content and distribution of (ethylene–propylene) copolymer (EP) of injection-moulded toughened polypropylene resins (PP/EP) have an important impact on many surface properties, such as gloss, paint adhesion and hardness. These surface properties are increasingly important in the multiple applications of these resins, for instance for paint adhesion in the automotive industry. It has already been shown that the introduction of EP in PP provides better paint adhesion, but its role remains speculative.[1–4] A major drawback to the understanding of the influence of EP on PP/EP surface properties is the lack of knowledge concerning the blend surface morphology (EP content, EP lateral distribution, etc). This is essentially due to the similar chemical composition of both polymers that prevents surface analysis by classical chemical surface spectroscopies.

It was previously shown that atomic force microscopy (AFM) and force modulation microscopy (FMM) can provide novel information concerning the elastic and viscoelastic properties of PP/EP resins at the microscopic level, enabling the distribution of EP rubbery nodules to be mapped and the macroscopic behavior of these resins (e.g. differences in the impact resistance) to be explained.[5] Moreover, recent work showed that AFM techniques (force curves and force modulation measurement, FMM cartography) can be used to characterize the surface elastic properties of PP/EP blends.[6,7] In particular, these studies demonstrated that FMM can map the surface and the subsurface distribution of EP nodules.

In the present work, the effect of EP versus PP viscosity ratio on the surface distribution and the surface morphology of EP in injection moulded PP/EP was studied. This comprised the analysis by transmission electron microscopy (TEM) of thin sections cut parallel and perpendicular to the injection directions, together with sections parallel to the surface. The TEM results were correlated to the analysis of the surface topography and the surface elasticity measured by AFM and FMM.

EXPERIMENTAL

Materials

The resins used in this study were provided by Solvay (Brussels, Belgium). Samples, PP/EP (1) to PP/EP (4), are 'reactor blends' produced in the gas phase by a two-stage polymerization process. They

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differ in the viscosity ratio between the EP and the PP phases which corresponds to the ratio of the solution intrinsic viscosities of the xylene-soluble fraction (mainly EP) and the xylene-insoluble fraction (mainly crystalline PP). The main characteristics of the samples are listed in Table 1. Disks of these resins were injection moulded and analysed by TEM and by AFM and FMM.

TEM analyses

For TEM analyses, the samples were stained with $RuCl_3 \cdot H_2O$ in NaClO. 90-nm-thick sections were then cut at low temperature (−40 °C). For all resins, transverse sections parallel to the injection direction were studied. For the PP/EP (4) resin, two kinds of additional sections were made: perpendicular to the injection direction and parallel to the surface.

AFM and FMM analyses

AFM and FMM analyses were carried out with an Autoprobe CP (Park Scientific Instruments, Sunnyvale, CA) in air directly on the disk surface. The experiments were conducted on the PP/EP (1) and PP/EP (4) resins. In order to obtain a good contrast in force modulation,[8,9] a cantilever with a high stiffness equal to 14.2 $N\,m^{-1}$ was used (Ultralever® 2.0 µm). The tip apex radius, measured by high resolution scanning electron microscopy (FEG-SEM), was equal to 60 nm.

Topographic AFM images and elastic FMM images were taken at different positions on the disk surface. Force-curve and force-modulation measurements were also carried out at different spots on the surface for an estimation of the local surface modulus using the Hertz elastic model.[6,7,10,11] In order to evaluate the effect of the indentation depth, FMM images of the same regions were obtained with different static contact forces.

RESULTS AND DISCUSSION

TEM results

TEM images obtained on sections parallel to the injection direction are presented in Fig 1. A progressive increased deformation of the EP nodules in the injection direction with the decrease of the viscosity ratio is observed. For the PP/EP (1) resin, the EP nodules are almost spherical, even close to the surface, while for the PP/EP (4) resin, the EP nodules are elongated in the injection direction. The deformation is more important close to the surface

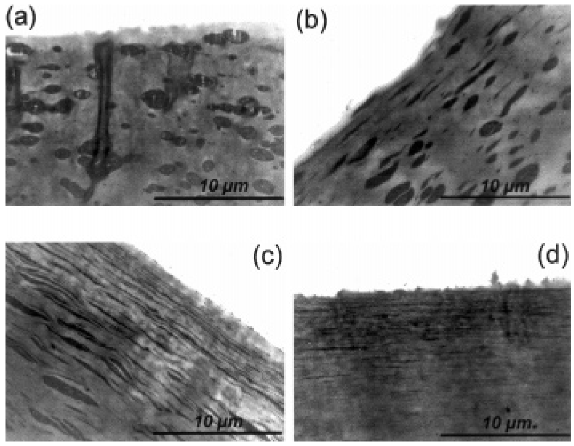

Figure 1. TEM images obtained on sections parallel to the injection direction: (a) PP/EP (1) resin; (b) PP/EP (2) resin; (c) PP/EP (3) resin and (d) PP/EP (4) resin. On these micrographs, the amorphous phase, i.e. essentially EP nodules, appears darker than the crystalline PP matrix because it is more quickly oxidized by the staining agent.

where the shear rate during injection is more pronounced. A higher concentration of EP nodules near the surface also seems to appear when the viscosity ratio decreases.

TEM images of sections perpendicular to the injection direction and of sections parallel to the disk surface are shown in Fig 2 for the low viscosity ratio resin. These images reveal that the EP nodules below the surface are in fact rather plate-like in shape, with their long axis oriented in the injection direction. Very few rod-shaped EP nodules can be observed. These results are in good agreement with those of Levitt *et al*[12] showing that the widening of the drops is inversely proportional to the ratio of drop/matrix elasticities.

These observations confirm that the EP/PP viscosity ratio strongly influences EP nodules morphology close to the surface. At high viscosity ratio, i.e. high EP viscosity, the nodules are almost undeformed. At low viscosity ratio, i.e. low EP viscosity, the high shear rate close to the mould surface strongly deforms and orients the nodules in the injection direction. The TEM observations also reveal that the outermost surface is composed of a more or less thin pure PP skin in all cases.

These modifications of EP morphology and distribution with the EP/PP viscosity ratio will strongly affect the surface elasticity of the resins, as will be revealed by AFM and FMM analyses.

Table 1. Characteristics of the resins used in the present study

Resin	C_2 *in EP* (%)	*EP* (%)	*MFI* $(g(10\,min)^{-1})$	$\eta_{xylene\ sol}$ $(l\,g^{-1})$	$\eta_{xylene\ ins}$ $(l\,g^{-1})$	η_{sol}/η_{ins}
PP/EP (1)	53	13.8	6.4	0.290	0.178	1.63
PP/EP (2)	56	14.9	5.7	0.204	0.169	1.21
PP/EP (3)	56	13.9	4.7	0.169	0.175	0.97
PP/EP (4)	57	12.1	5.2	0.130	0.172	0.76

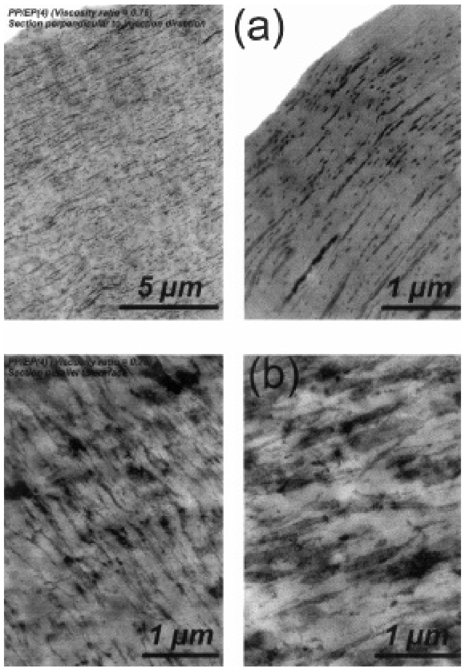

Figure 2. TEM images obtained on sections of the PP/EP (4) resin: (a) sections perpendicular to the injection direction and (b) sections parallel to the surface. EP nodules appear darker.

AFM and FMM results

On the resin with a high viscosity ratio (PP/EP (1)), the surface morphology appears slightly oriented in the injection direction (Fig 3). The EP nodules that appear in the FMM images (darker regions) are almost undeformed. The effect of the contact force, and hence of the indentation depth, can be observed: at low indentation depth, several EP nodules are visible, while at higher indentation depth, most of the nodules are no longer visible or their contrast weakens (nodules 1 and 2). This could be interpreted as follows: at low contact force, nodules at or just below the surface are imaged, while at higher contact force the tip indents through these nodules and the measured rigidity corresponds to that of the PP matrix. This is consistent with previous works which showed that the surface elastic properties measured by force modulation are influenced by the subsurface properties.

On the PP/EP (4) sample (low viscosity ratio resin), the surface morphology is clearly oriented in the injection direction (Fig 4). However, few EP nodules or even none could be observed at or below the surface at any contact force, as revealed by the weak contrast on the FMM images.

It seems that the surface of this resin exhibits homogeneous elastic properties. However, the measured elastic response (ratio between the tip modulation and the sample modulation amplitudes)[6,7,9] does not correspond to that of pure PP. For the high viscosity ratio resin, a large contrast of elastic response is observed between the PP matrix and the EP nodules. The measured values are summarized in

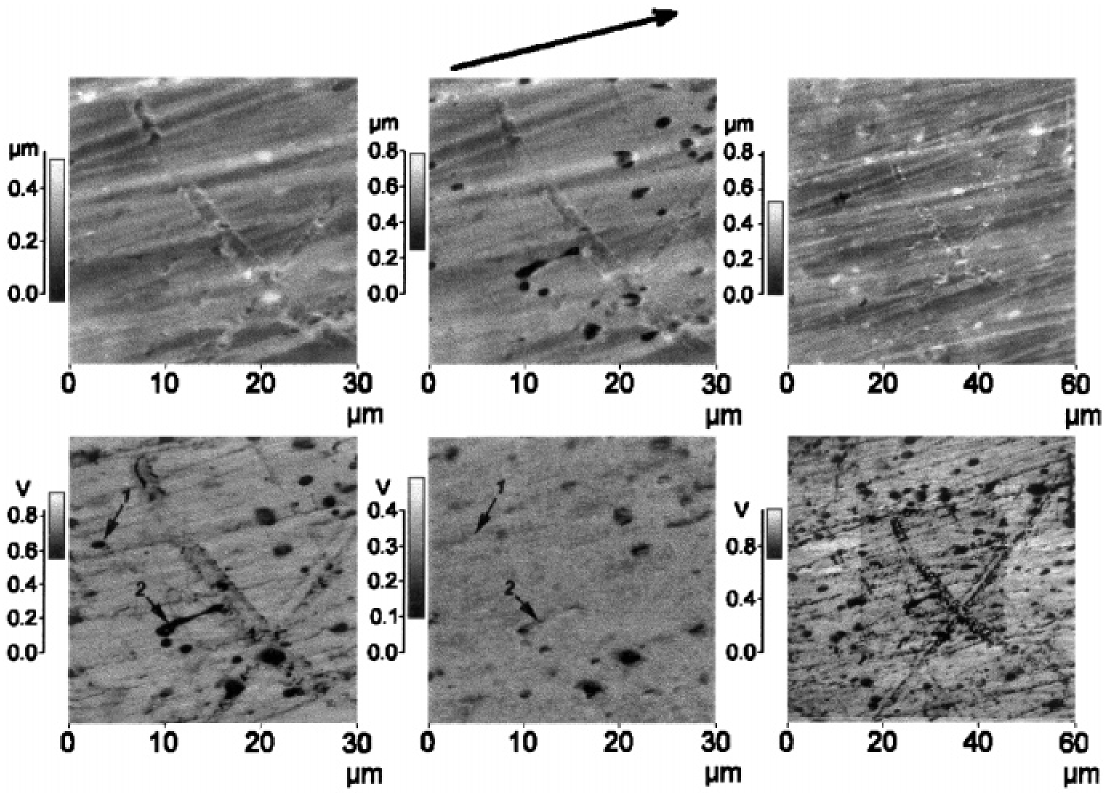

Figure 3. Typical topographic AFM images (three upper images) and elastic response FMM images (three lower images) taken on the surface of the PP/EP (1) resin. The injection direction is indicated by the arrow. The two left images were recorded with a contact force F_0 equal to 50 nN; for the two central images, $F_0 = 200$ nN; and for the two right images, $F_0 = 25$ nN. On the topographic micrographs, higher regions appear brighter and lower ones are darker. On the FMM images, the stiffer zones are brighter (PP matrix) and the softer ones darker (EP nodules).

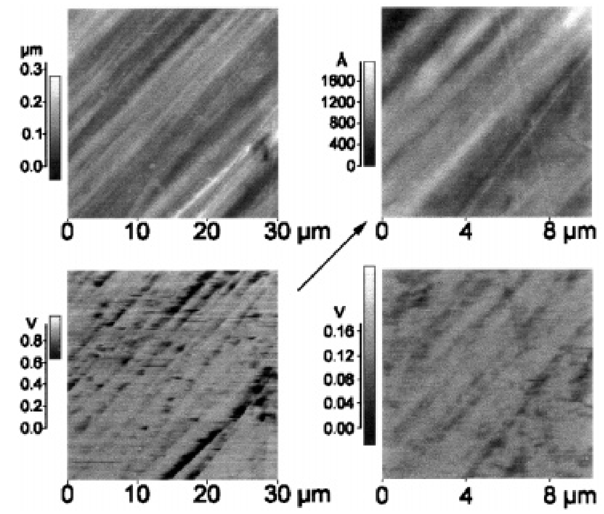

Figure 4. Typical topographic AFM images (two upper images) and elastic response FMM images (two lower images) taken on the surface of the PP/EP (4) resin. The injection direction is indicated by the arrow. The images were recorded with a contact force F_0 equal to 50 nN. The same remark as for Fig. 4 applies for the grey scales in the topographic and the FMM images. The darker zones observed on the force modulation micrographs are very probably artifacts due to the surface topography (tip sliding on the side of surface ridges rather than indenting the surface).

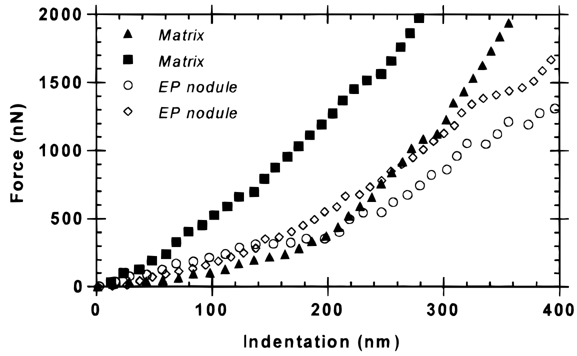

Figure 5. Typical force curves measured on the surface of the PP/EP (1) surface on the PP matrix (solid symbols) and above EP nodules (open symbols).

Table 2. For the low viscosity ratio resin, the dynamic response is almost the same everywhere on the surface, and its value varies around that measured above the EP nodules of the PP/EP (1) resin.

The FMM images thus suggest that the surface of the high viscosity ratio resin displays heterogeneous elastic properties with EP nodules dispersed at or below the surfaces in the PP matrix. On the contrary, the surface of the low viscosity ratio resin has elastic properties that are almost homogeneous and close to those measured above EP nodules on high viscosity ratio resins. The force curve measurements carried out at different spots on the surfaces of both samples confirm these hypotheses.

Typical force–indentation curves measured on the matrix and above the EP nodules of the PP/EP (1) resin are given in Fig. 5. The curves measured on the matrix present a steeper and more regular slope than those measured on EP nodules. The value of the surface elastic modulus of the matrix, calculated from these curve using the Hertz model,[7,10,11] is of the order of 100 MPa. Surprisingly, this value is one order of magnitude lower than that expected for pure PP (approximately 1000 MPa). The very rapid crystallization conditions near the surface 'freezing' both PP and EP amorphous phases in disorganized microdomains could perhaps explain this observation. The force curves measured above EP nodules are more irregular: they exhibit regions with a weak slope separated by a zone with a steeper slope. The calculated modulus for EP from the weak slope region is around 25 MPa, i.e. almost one order of magnitude lower than that measured on the matrix. The irregular shape could be explained by successive crossings of EP nodules and matrix by the tip during indentation.

The force–indentation curves measured on the PP/EP (4) (Fig 6) show relatively regular shapes and have almost the same slope whatever the measurement position on the surface. The surface elastic modulus of the low viscosity ratio resin is estimated to vary between 20 and 35 MPa, i.e. around the value measured above EP nodules on the high viscosity ratio resin.

When the force–indentation curves of both resins are compared (Fig 7), the curve measured on the matrix of the high viscosity ratio resin exhibits the steepest slope in accordance with the expectation of a

Table 2. Comparison between the dynamic responses[a] and the elastic moduli measured on the PP matrix and the EP nodules of the PP/EP (1) resin and on the surface of the PP/EP (4) resin

	Dynamic responses (d_1/z_1)	*Elastic modulus* (*MPa*)
PP/EP (1) on PP matrix	0.71	100
PP/EP (1) on EP nodules	0.32	25
PP/EP (4)	0.21–0.42	20–35

[a] The dynamic response is defined as the ratio between the tip response amplitude, d_1, and the sample modulation amplitude, z_1.[7]

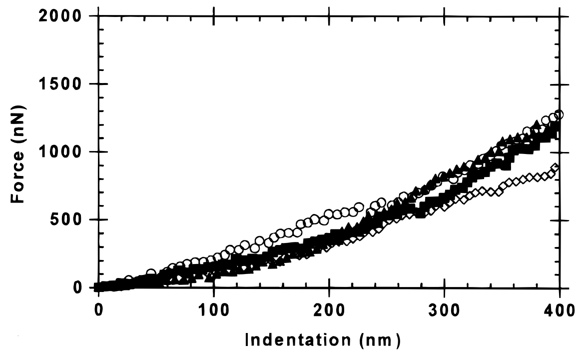

Figure 6. Typical force curves measured on the surface of the PP/EP (4) surface.

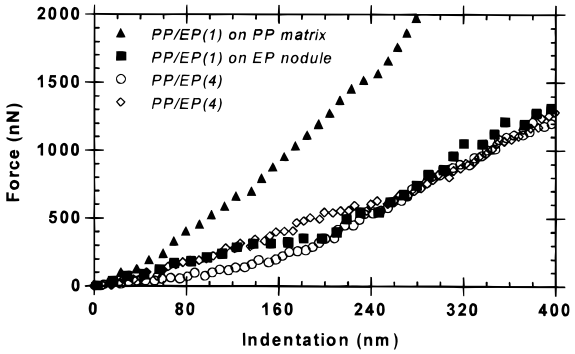

Figure 7. Comparison between force curves measured on the high viscosity ratio resin (solid symbols) and force curves obtained on the low viscosity ratio resin (open symbols).

higher rigidity of the PP matrix. The curves measured above the EP nodules of PP/EP (1) and on the surface of PP/EP (4) have comparable slopes, suggesting that the surface of the low viscosity ratio resin has a surface rigidity very similar to that above the EP nodules of the first resin.

These results, combined with those obtained by TEM, show that the resin with the highest EP/PP viscosity ratio presents heterogeneous surface elastic properties corresponding to a rough dispersion of almost spherical EP nodules below the surface. By modifying the imaging contact force, it is possible to visualize nodules at different depths. In contrast the low viscosity ratio resin presents homogeneous surface elastic properties at the resolution of our measurements (>100 nm). The measured surface rigidity is comparable to that measured above EP nodules on the high viscosity ratio resin. No effect of the contact force is observed. This could be explained by the easier deformation of the EP nodules into platelets and by their fine dispersion below the thin PP surface layer.

CONCLUSIONS

The TEM images reveal that the decrease of the viscosity ratio between the dispersed EP phase and the PP matrix in *in-situ* PP/EP resins increases the deformation and the concentration of EP nodules close to the surface. EP nodules appear to be almost spherical for a high viscosity ratio resin, while they are sheet-shaped for the lowest viscosity ratio resin as a consequence of the higher matrix elasticity.

AFM and FMM analyses confirm and complete these observations. For the high viscosity ratio resin, the surface exhibits heterogeneous elastic properties. EP nodules, mostly underformed, are observed at or below the surface. Increasing the static contact force enables EP nodules to be visualised at various depths. For the low viscosity ratio resin, the nodules are oriented in the injection direction. At the resolution scale of FMM, the surface elastic properties appear to be homogeneous and are close to those of EP nodules at the surface of high viscosity ratio resins. This confirms the fine dispersion of sheets of EP just beneath the surface.

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REFERENCES

1 Bonnerup C and Gatenholm P, *J Adhesion Sci Technol* 7:247 (1993).
2 Clemens RJ, Batts GN, Lawniczak JE, Middleton KP and Sass C, *Prog Org Coatings* **24**:43 (1994).
3 Prater TJ, Kaberline SL, Holubka JW and Ryntz RA, *J Coatings Technol* **68**:83 (1996).
4 Ryntz RA, Xie Q and Ramamurthy AC, *J Coatings Technol* **67**:45 (1995).
5 Nysten B, Legras R and Costa J-L, *J Appl Phys* **78**:5953 (1995).
6 Tomasetti E, Nysten B, Legras R and Henri-Mazeaud B, *STM'97, 9th International Conference on Scanning Tunnelling Microscopy*/Spectroscopy and Related Techniques, Hamburg, Germany, July 1997 abstract Tu9.2PO1, p 159.
7 Tomasetti E, Nysten B and Legras R, *Nanotechnology* **9**:305 (1998).
8 Radmacher M, Tillmann RW and Gaub HE, *Biophys J* **64**:735 (1993).
9 Burnham N, Gremaud G, Kulik AJ, Gallo P-J and Ouveley F, *J Vac Sci Technol B* **14**:1308 (1996).
10 Hertz H, *J Reine Angew Math* **92**:156 (1882).
11 Sneddon IN, *Int J Eng Sci* **3**:47 (1965).
12 Levitt L, Macosko CW and Pearson SD, *Polym Eng Sci* **36**:1647 (1996).