PII: S0032-3861(97)00099-2

Polymer Vol. 38 No. 22, pp. 5557–5564, 1997

0032-3861/97/$17.00 + 0.00

Preparation and properties of self-reinforced polypropylene/liquid crystalline polymer blends

A. R. Postema* and P. J. Fennis
Koninklijke/Shell-Laboratorium Amsterdam, Badhuisweg 3, 1031CM Amsterdam, The Netherlands
(Received 1 April 1996; revised 6 December 1996)

The mechanical properties of self-reinforced liquid crystalline polymer/polypropylene (LCP/PP) blends strongly depend on the viscosity ratio of the blend components in the melt. This ratio was determined for PP blends with different commercial LCPs (Vectra A950 and Vectra B950), by means of capillary rheometry, under conditions representative for the blending process during extrusion. It was found that optimal mechanical properties were achieved when the LCP/PP viscosity ratio at 285°C ranges between 2 and 4 at a shear rate of 800–1000 s^{-1}. The LCP/PP viscosity ratio appears to be shear stress dependent. This creates the option of fine tuning the LCP droplet deformation process by means of the extrusion rate. This shear stress dependence is more pronounced for PP blends with Vectra B950 than for blends with Vectra A950. © 1997 Elsevier Science Ltd.

(Keywords: self-reinforced; polypropylene; liquid crystalline polymer; blends)

INTRODUCTION

The feasibility of reinforcing polypropylene (PP) with liquid crystalline polymers (LCPs) in conventional thermoplastic processing equipment was demonstrated by a number of different authors[1–3]. The option we envisage for these blends is to produce pellets in which the LCP phase is present as a highly oriented fibre phase. The pellets can subsequently be used as a base material for further processing into final shaped articles, e.g. by means of injection or compression moulding. This subsequent processing has to take place at temperatures above the melting temperature of PP and below the distortion temperature of the LCP fibres.

In order to obtain excellent mechanical properties, high uniaxial orientation of the LCP molecules in their fibres is essential (additional to the necessity of having fibres with high aspect ratios). These high molecular orientations can be achieved by using a melt-drawing step immediately after the hot extrudate leaves the extruder die[2,3], followed by rapid cooling. Relatively thick extrudates, suitable to be cut into pellets, were obtained by using a 'multi-filament' extrusion process. Hence, blend materials were obtained having properties comparable with glass fibre reinforced PPs. Advantages of the reinforcing blends over the glass-reinforced materials are the ease of preparation (including high production speeds), reduced weight and potential recyclability.

The present study explores further the processing variables which are important to process self-reinforcing blends successfully. For an efficient conversion of the dispersed LCP droplets into fibres during the extrusion of the blend[4], the Weber number W_e (i.e. the ratio of viscous force to interfacial force) has to be several times larger than a critical value $W_{e,crit}$, i.e.

$$W_e \gg W_{e,crit}$$

with

$$W_e = \sigma R \eta / \gamma$$

in which σ is the interfacial energy, R is the radius of the LCP droplet, η is the viscosity of the matrix (PP) and γ is the shear rate. If W_e is only slightly higher than $W_{e,crit}$ the droplets will break up into finer droplets after little elongation, whereas no deformation occurs if $W_e < W_{e,crit}$. $W_{e,crit}$ depends on the mode of deformation (shear *versus* elongational flow) and the viscosity ratio, $P = \eta_{LCP}/\eta_{PP}$, of the blend components. In general, it is found that in shear flow $W_{e,crit}$ is minimal at $P \sim 1$ and increases rapidly to infinity at $P > 1$. Although in the present process most of the droplet deformation takes place outside the extruder (i.e. in elongational flow), this shear process is relevant for the pre-droplet deformation. Small deformations inside the extruder have large effects on the total deformation and on possible coalescence phenomena of the dispersed phase in the conical extruder die.

This paper focuses on the absolute values of the viscosity ratio under those conditions in which *in situ* LCP fibre formation takes place. Knowledge of this absolute viscosity ratio will assist in optimizing the blend's mechanical properties and processing characteristics. It will be shown that, in contrast to what is

---

*To whom correspondence should be addressed. Present address: Chemical Research Centre, Shell Louvain-la-Neuve, Avenue Jean Monnet 1, B-1348 Ottignies Louvain-la-Neuve, Belgium generally stated in the literature[5-11], optimum mechanical properties are found if the viscosity of the dispersed LCP phase is two to four times higher than the viscosity of the PP matrix phase.

EXPERIMENTAL

The thermotropic LCPs used in this study were Vectra A950 and Vectra B950 (both from Hoechst Celanese). Vectra A950 (batch No. 22.924.950) is a random copolyester of *p*-hydroxybenzoic acid (73 mol%) and 6-hydroxy-2-naphthoic acid (27 mol%). Vectra B950 (batch no. 33.44.682 CEL, CM 90-524016) is a random copolyesteramide of 2-hydroxy-6-naphthoic acid (60 mol%), terephthalic acid (20 mol%) and 4-aminophenol (20 mol%). Both polymers have a solid–nematic phase transition temperature of 280°C. Prior to use the LCPs were dried to constant weight, at 140°C, under reduced nitrogen pressure. Various grades of i-PP (with melt indices ranging from 0.7 to 20 dg min^{-1}, see *Table 1*) were used in order to vary the viscosity of the matrix, without changing the LCP viscosity. All the PP samples used had approximately similar molecular weight distributions (see also Discussion).

Blends of the various PP grades with the LCPs (90/10 w/w) were extruded on a Schwabenthan Polytest 30P single screw extruder, equipped with a single hole strand die (12/1 conical contraction; die diameter 1.5 mm) and the following temperature settings were applied: hopper zone, cool; zone 1, 220°C; zone 2, 250°C; zone 3, 265°C; extruder head, 275°C. The mass temperature of the blends leaving the extruder was 285°C. After leaving the extruder the hot strands were immediately drawn to the maximum draw ratio and subsequently quenched in a waterbath. The gap between extruder and waterbath was approximately 20 cm. The draw ratio of the blends was defined as the ratio of the cross-sectional areas of the extruder die and drawn strand.

The shear rate in the extruder die during the preparation of the blends was approximately 800–1000 s^{-1}, as calculated from the extruder output Q, according to

$$\gamma = 4Q/\pi R^3$$

in which R is the radius of the extruder capillary, and Q is the volume output (calculated from the mass output and the blend density).

The ratio of the viscosities of the blend components ($P = \eta_{\mathrm{LCP}}/\eta_{\mathrm{PP}}$) was determined (indirectly) by means of rheometry on an Instron capillary rheometer under conditions identical to the blend extrusion process, i.e. $T = 285°\mathrm{C}$ and shear rates of 100–2000 s^{-1}. A capillary was used with the following dimensions: l/d ratio = 81, $d = 1.26$ mm and an entrance angle of 90°. A Rabinowitch correction was applied for non-Newtonian flow.

Table 1

Polymer grade	Melt index (dg min^{-1})
PP1	0.7
PP2	2.8
PP3	5.5
PP4	11.0
PP5	15.0
PP6	20.0

Tensile testing of the extruded blends was carried out on an Instron 1122 testing machine using a cross-head speed of 1.0 mm min^{-1} for the modulus and 2.0 mm min^{-1} for the tensile measurements. The initial gauge length was 50 mm. To prevent the samples from slippage, the specimens were held by using sand-paper between sample and grips. The mechanical properties were determined as the average of at least eight measurements. Standard deviations were less than 10%.

Morphology studies were performed using confocal scanning laser microscopy (CSLM) on longitudinal cross-sections of the PP/LCP blend strands.

RESULTS AND DISCUSSION

In order to obtain insight into the shear rates required for LCP droplet deformation, PP3/Vectra A950 (95/5 w/w) blends were extruded by means of an Instron capillary rheometer, at various shear rates. After leaving the rheometer the hot blend was immediately quenched to room temperature. *Figure 1* displays the morphologies of the blends processed at different shear rates. At shear rates of 133 s^{-1} and higher the dispersed droplet phase is successfully transferred into a fibre phase.

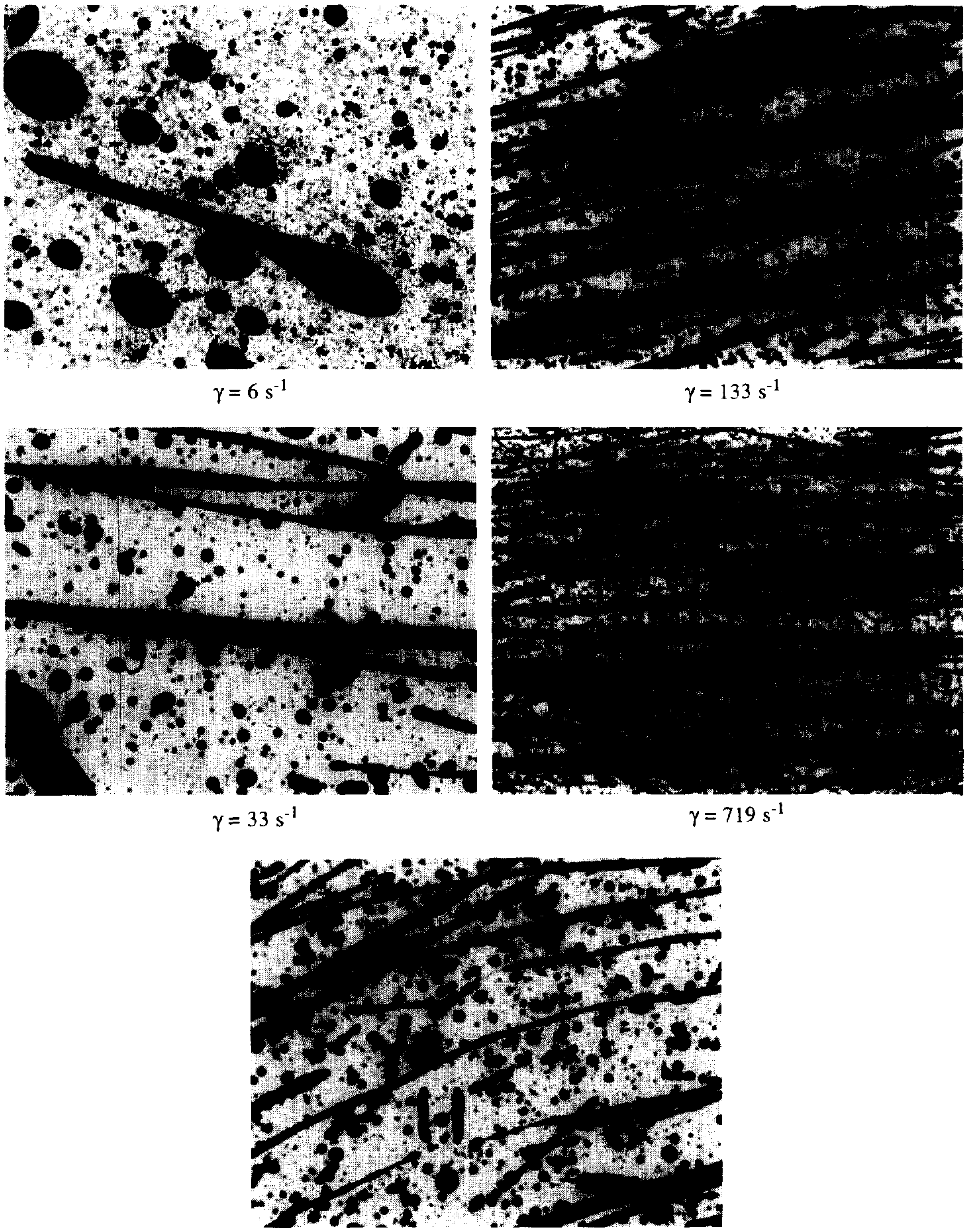
The PP/LCP blend had a remarkably low viscosity (lower than the viscosity of the individual blend components). This reduction in viscosity was also found for other blend compositions, but appeared to be dependent on the applied shear rate. The variations in viscosity–composition curves of the blends has been attributed to a number of reasons[12,13]:

(a) incompatibility between the two phases leading to more deformable droplets;
(b) formation of an oriented LCP phase which tends to lubricate the PP melt;
(c) formation of thin surface layers of the dispersed phase polymer (the LCP) on the polymer matrix, leading to plug flow behaviour;
(d) lack of adhesion between the two phases (i.e. interfacial slip viscosity);
(e) suppression of the high elasticity of the matrix by the LCP component.

All the above reasons seem to originate from the lack of adhesion between the apolar PP and the more polar LCP phase. Consequently, it is expected that the use of compatibilizers in the blending process will reduce this beneficial viscosity effect.

The PP/LCP blends processed for further study were extruded at shear rates of approximately 1000 s^{-1}. The results of the mechanical tests are presented in *Figures 2* and *3*, for PP blends with Vectra A950 and B950, respectively. The PP3 and PP4 grades give the highest tensile properties with both LCPs. Using Vectra A950, no significant differences in mechanical properties were observed between the use of PP3 or PP4. For blends with Vectra B950 the PP4 grade gave the highest stiffness values, whereas the PP3 grade gave slightly better strength values.

The viscosity ratios of the PP/LCP blends were determined as follows. Owing to the high processing temperature, degradation of the PP matrix (during extrusion of the blend) has to be expected. This degradation, of course, could in principle be prevented by using special stabilizing agents. However, because the addition of low molecular weight species to the blend may eventually



$\gamma = 6\ s^{-1}$

$\gamma = 133\ s^{-1}$

$\gamma = 33\ s^{-1}$

$\gamma = 719\ s^{-1}$

$\gamma = 65\ s^{-1}$

Figure 1 Morphology of PP4/Vectra A950 (95/5) blends at various shear rates

have negative effects on the blend's mechanical properties—by the formation of weak interfacial boundary layers—no extra stabilization was employed. As a result, at the spot of the largest LCP droplet deformation (in and just outside the extruder exit), the matrix viscosity will be significantly reduced. To determine the correct viscosity values at this stage and temperature, the various PP-grades were first extruded under the same conditions as applied in the LCP/PP blending process. The processed and consequently 'pre-degraded' PPs (further indicated with an asterisk, PPs*) were used in the rheological experiments. A direct viscosity determination of PP* at 285°C would again result in incorrect values, due to additional degradation during the capillary rheometer test itself. For this reason, rheological measurements on one of the PP grades, the PP4*, were performed at several temperatures ranging from 190 to 295°C. The flow curves of these experiments are shown in *Figure 4*. It can be seen that at high temperatures the extrapolated zero-shear viscosity is somewhat lower than would be expected. To evaluate this degradation, the results were plotted on an Arrhenius graph (see *Figure 5*) of log (apparent viscosity) *versus* reciprocal temperature[14]. The slope of the lines—for various shear stresses—represents the flow activation energy (E_{act}) of the PP, which should be constant if the material is stable. However, the viscosity clearly deviates from the extrapolated lines at higher temperatures (lower $1/K$ values), the deviation increasing with lower shear stresses (rates). This result is to be expected, since the degradation of PP

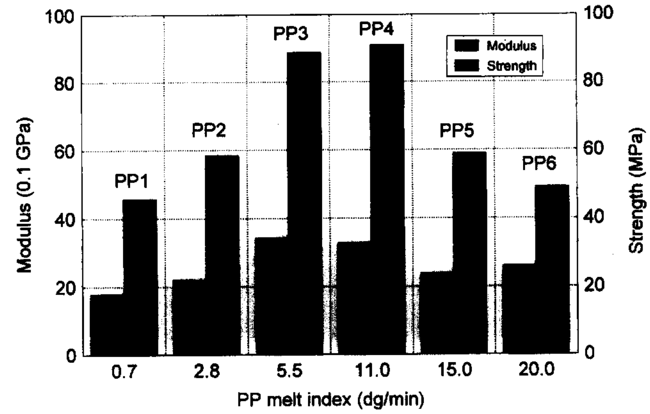


Figure 2 Mechanical properties of PP/Vectra A950 (90/10) blends for various PP grades

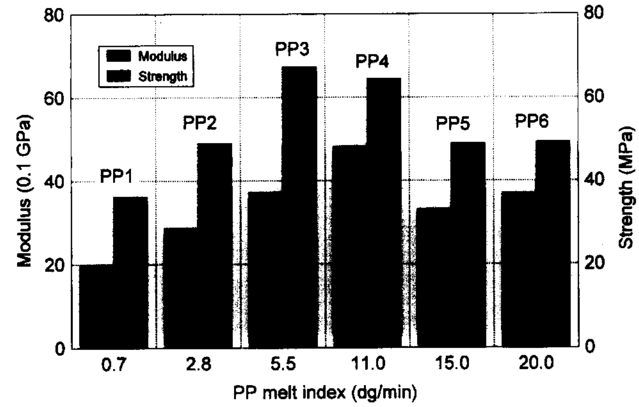


Figure 3 Mechanical properties of PP/Vectra B950 (90/10) blends for various PP grades

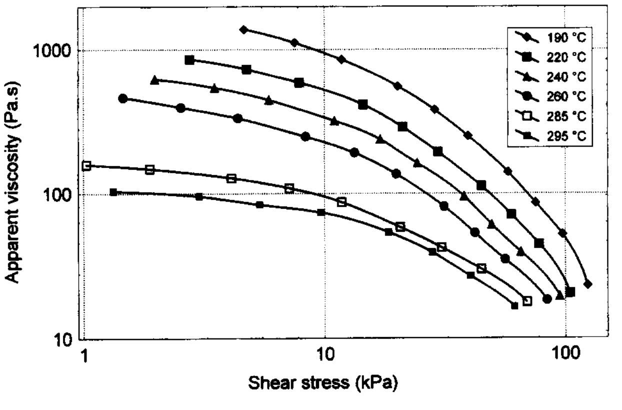


Figure 4 Viscosity *versus* shear stress of PP4 at various temperatures

is time dependent and the test is carried out by starting at the highest shear rates. Hence, the higher shear stresses shown are measured after about 5 min residence time, whereas the lower shear stresses are measured after more than 10 min residence time. Quantitatively, the drop in viscosity of the PP at 285°C at periods of 5 and 10 min are approximately 15 and 45%, respectively. At temperatures below 260°C a linear relationship was found indicating the stability of the PP at these temperatures and residence times (nominally 25 min). The activation energy of flow ($E_{act} = 40.8\,kJ\,mol^{-1}$) as determined from the Arrhenius plots was used to 'calculate' the viscosities of the PP for various shear stresses, at the exact moment of LCP droplet deformation in the blending process.

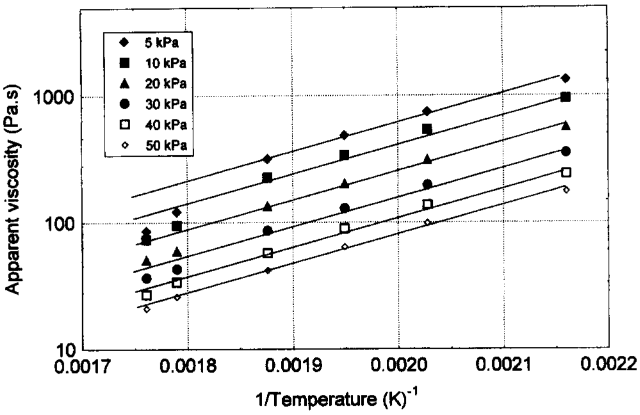


Figure 5 Temperature dependence of viscosity of PP4* at various shear stresses

The viscosity curves for the other PP* grades at 285°C were computed using the viscosity curve measurements at 240°C in combination with the above determined E_{act}. The results are shown in *Figure 6*.

The viscosities of the Vectras turn out to be also time dependent, as exemplified in *Figure 7* for Vectra A950, where during a 5 min extrusion period at the lowest shear rate ($3\,s^{-1}$), the measured force increases by 25%. This observation is in line with results reported in the literature on the rheology of LCPs in the nematic phase, at temperatures just above the solid–nematic phase transition[15]. It is believed that, under the influence of shear, ordered structures are formed with a significant higher melting point. However, at shear rates of about

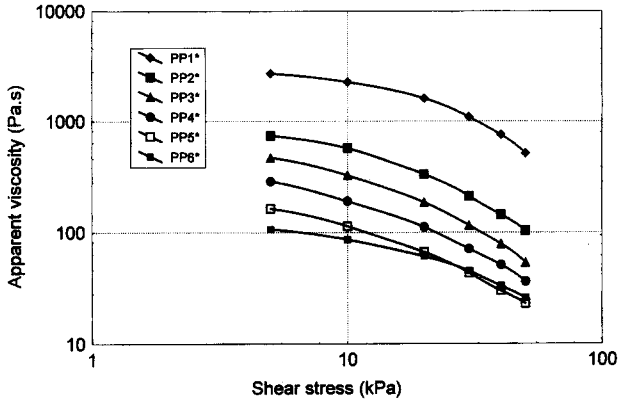


Figure 6 Computed viscosity curves of pre-degraded PPs at 285°C

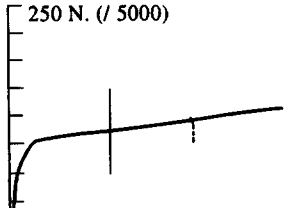


Figure 7 Experimental force–time plot for the extrusion of Vectra A950 at 285°C at a shear rate of $3\,s^{-1}$

$50\,s^{-1}$ and higher, time dependent effects were no longer apparent.

From the determined viscosity data of the Vectras and the various PP* grades at 285°C, the LCP/PP*(P) viscosity ratios were calculated as a function of shear stress. The results are plotted in *Figures 8* and *9* for PP blends with Vectra A950 and Vectra B950, respectively. Because of the different shear thinning behaviour of the PPs* and the Vectras, P strongly depends on the applied shear rate. Consequently, in a continuously changing shear field (increasing shear stress in the extruder die), the blend material will experience a continuously changing viscosity ratio. This is more pronounced for the blends with Vectra B950 blends than for the blends with Vectra A950. The practical advantage of this shear-dependent viscosity ratio is that the droplet deformation process can be optimized by fine tuning the shear stress by means of the extrusion rate and extruder screw/die design.

Figure 6 shows that typical shear stresses utilized during extrusion of the PP3 and PP4 grades are of the order of 40–50 kPa. For these two shear stresses, the maximum attained mechanical properties of the blends are plotted against P (from *Figures 8* and *9*) in *Figures 10–13*. Apparently, at $P \sim 2$–4 optimum mechanical properties were obtained.

It should be noted that P is determined just after the blend leaves the extruder exit and prior to drawing. During the melt-drawing step the strain rates are much higher (e.g. drawn-down ratio $\times\gamma$). As shown by Grace[4], the droplet deformation during drawing (elongational flow) is much easier, because $W_{e,\mathrm{crit}}$ is relatively low and almost constant. This is confirmed by CSLM photographs of the morphology of the PP/Vectra B950 blends (see *Figures 14a–f*). Although the blends all had a different P, after drawing they all contained a fibrous LCP phase. The presence of numerous fine fibrils in all the different blends clearly demonstrates that elongational flow—as occurring during drawing—is considerably more effective in deforming the LCP droplets than shear flow (a weak flow, due to its non-zero rotational component), which takes place during extrusion.

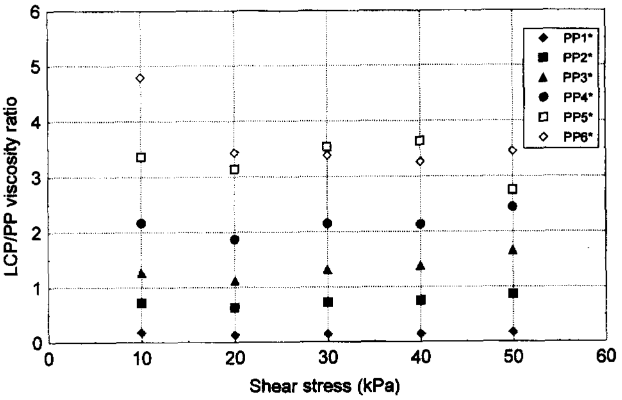


Figure 8 Vectra B950/PP* viscosity ratios as a function of shear stress for various PP grades

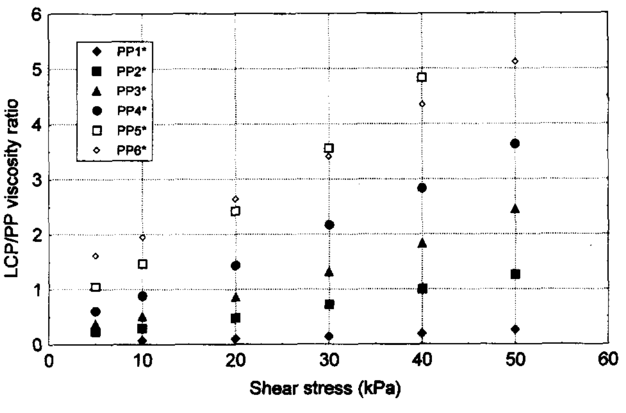


Figure 9 Vectra B950/PP* viscosity ratios as a function of shear stress for various PP grades

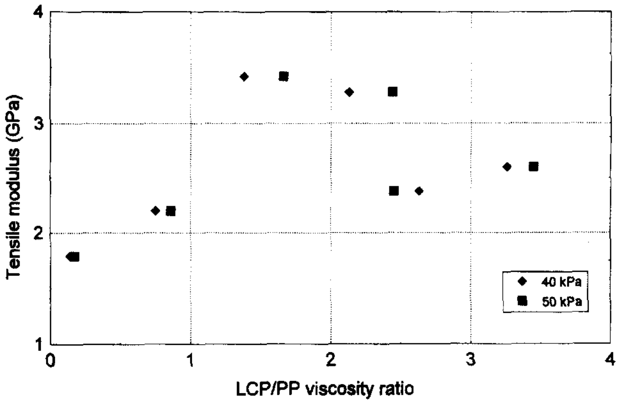


Figure 10 Maximum blend modulus *versus* Vectra A950/PP viscosity ratio at 285°C

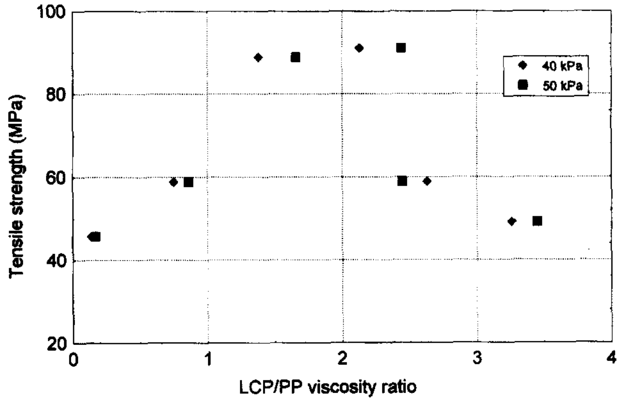


Figure 11 Maximum blend strength *versus* Vectra A950/PP viscosity ratio at 285°C

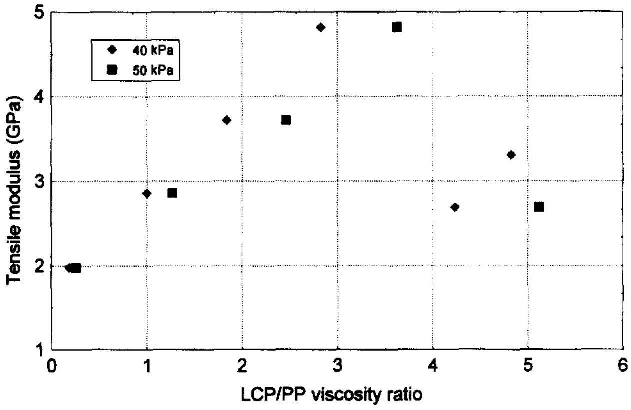


Figure 12 Maximum blend modulus *versus* Vectra B950/PP viscosity ratio at 285°C

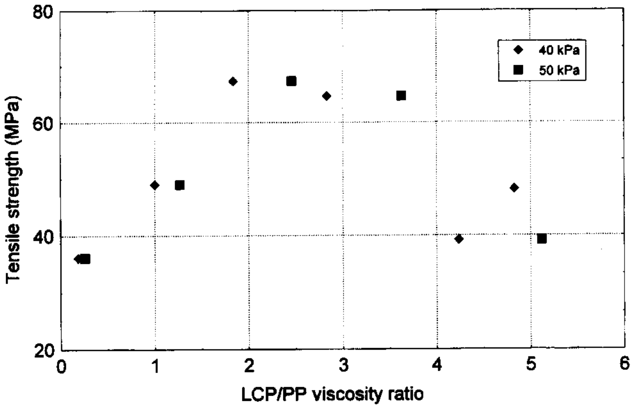


Figure 13 Maximum blend strength *versus* Vectra B950/PP viscosity ratio at 285°C

Apparently, the intrinsic droplet 'pre'-deformation in the extruder die determines the ultimate blend properties.

Figure 14a displays a CSLM photograph of a PP1/Vectra B950 blend, showing a relatively small fraction of very irregular LCP fibres inside the PP matrix. The majority of the LCP phase is still present as partially elongated small LCP droplets. It is likely that during extrusion the larger LCP droplets were stretched out by the hydrodynamic forces, but after exceeding a critical stretch they broke up under the influence of the interfacial interaction (via Rayleigh distortions[16]) into smaller droplets ($W_e > W_{e,crit}$). During the following drawing process the droplets were already too small to be deformed into well oriented fibres.

Figure 14b shows the PP2/Vectra B950 blend. This blend contains a much higher proportion of LCP in fibre form and on average the fibres are much thicker in diameter, indicating that the parent droplets have been much larger in size than in the PP1-blends. According to *Figure 9*, a P of ~ 2–4 is not even reached at the higher stress values. During the extrusion process the droplets were already deformed effectively enough to suppress the Rayleigh distortions. Additional drawing of the extrudate strands stabilizes the liquid LCP jets even more.

Figures 14c and *14d* show a very high fraction of the Vectra B950 in fibre form in the PP3 and PP4 blends, all having similar thickness. The fibres are much thinner compared with the ones obtained in the PP2/Vectra B950 blends, probably due to a very effective droplet deformation in the extruder die. For the PP3 blend $P \sim 3$ at 50 kPa, whereas for the PP4 blend $P \sim 3$ at 40 kPa.

Figures 14e and *14f* show the morphologies obtained with the PP5 and PP6 blends, respectively. In the barrel of the extruder the viscosity ratio of the PP5/Vectra B950 blends is lower than for the PP6 blends. Consequently, $W_{e,crit}$ of the PP5 blends will be slightly higher and the blend is more prone to reduction of the LCP droplet size. However, both blends have $P \sim 3$ at a shear stress of approximately 25 kPa. This suggests that somewhere in the extruder exit the blend surpasses the optimum viscosity ratio for deformation of the LCP phase. At the much higher shear rates outside the extruder the PP5/Vectra B950 blend has viscosity ratios higher than those of the PP6/Vectra B950 blend at comparable shear stresses, and consequently a higher $W_{e,crit}$. The origin for this change in order is probably the fact that the PP5 grade has a molecular weight distribution slightly smaller than that of the PP6 grade, resulting in a different rheological behaviour at higher shear stresses. The consequence is a superior deformation of the LCP droplets in the PP6/Vectra B950 blends (larger difference between W_e and $W_{e,crit}$). This indeed seems to be confirmed by the CSLM photographs showing thinner LCP fibres inside the PP6/B950 blends. Wide angle X-ray diffraction experiments will be performed in the near future to see whether this superior droplet deformation is also reflected in a better molecular orientation in the LCP fibres.

It should be noted that the results of this study specifically count for combined extrusion/drawing experiments performed at 285°C. At other processing temperatures the exact values of the viscosity ratios may change, due to alteration of the blend component viscosities (different activation energies for PP and LCP, respectively) by changing the temperature. In addition, the present study only deals with PP blends containing 10 wt% of LCP. It is evident from this study that the favoured viscosity ratio $P \sim 2$–4 can be obtained in other blend compositions by fine-tuning the extruder output Q (i.e. shear stress).

The results of this study are in contrast to what is generally stated in the scientific literature[1,5–11,17,18] i.e. that the matrix should have equal or higher viscosity than that of the LCP (corresponding with $P \leq 1$). Of course, the extension of the Weber number, established for the deformation of a Newtonian droplet in a Newtonian matrix, to a non-Newtonian droplet in a non-Newtonian matrix is rather crude, since the elastic effects are not explicitly treated. These elastic effects may be the origin of the much higher viscosity ratios that can be successfully applied in the preparation of PP/LCP blends. Additional research has to be performed to reveal the effect of the elastic components in the *in situ* fibre formation process.

Finally, one should note that in addition to the viscosity ratio LCP/PP, the absolute viscosity values for both components are important. Firstly, the Weber number is linearly related to the matrix viscosity η, i.e. $W_e = \sigma R\eta/\gamma$. Secondly, due to the action of the interfacial tension, the cylindrical liquid LCP thread may break up (Rayleigh disturbances[6,9]) into a line of small droplets. The conversion rate of fibrils into droplets will increase with increasing interfacial tension and decreasing fibril diameter[20]. As the retarding forces are viscoelastic in nature, high viscosities of both the PP matrix and the fibrillar LCP phase will slow down this undesirable process.

CONCLUSIONS

The present study concludes:

1. The mechanical properties of self-reinforced PP/LCP blends strongly depend on the viscosity ratio of the blend components in the melt.
2. Optimum mechanical properties are achieved when the LCP/PP viscosity ratio at 285°C ranges between 2 and 4 at shear rates of 800–1000 s^{-1} for a combined extrusion/drawing process.
3. The LCP/PP viscosity ratio depends on the applied shear stress. This creates the option of fine-tuning the viscosity ratio by means of the extrusion speed and

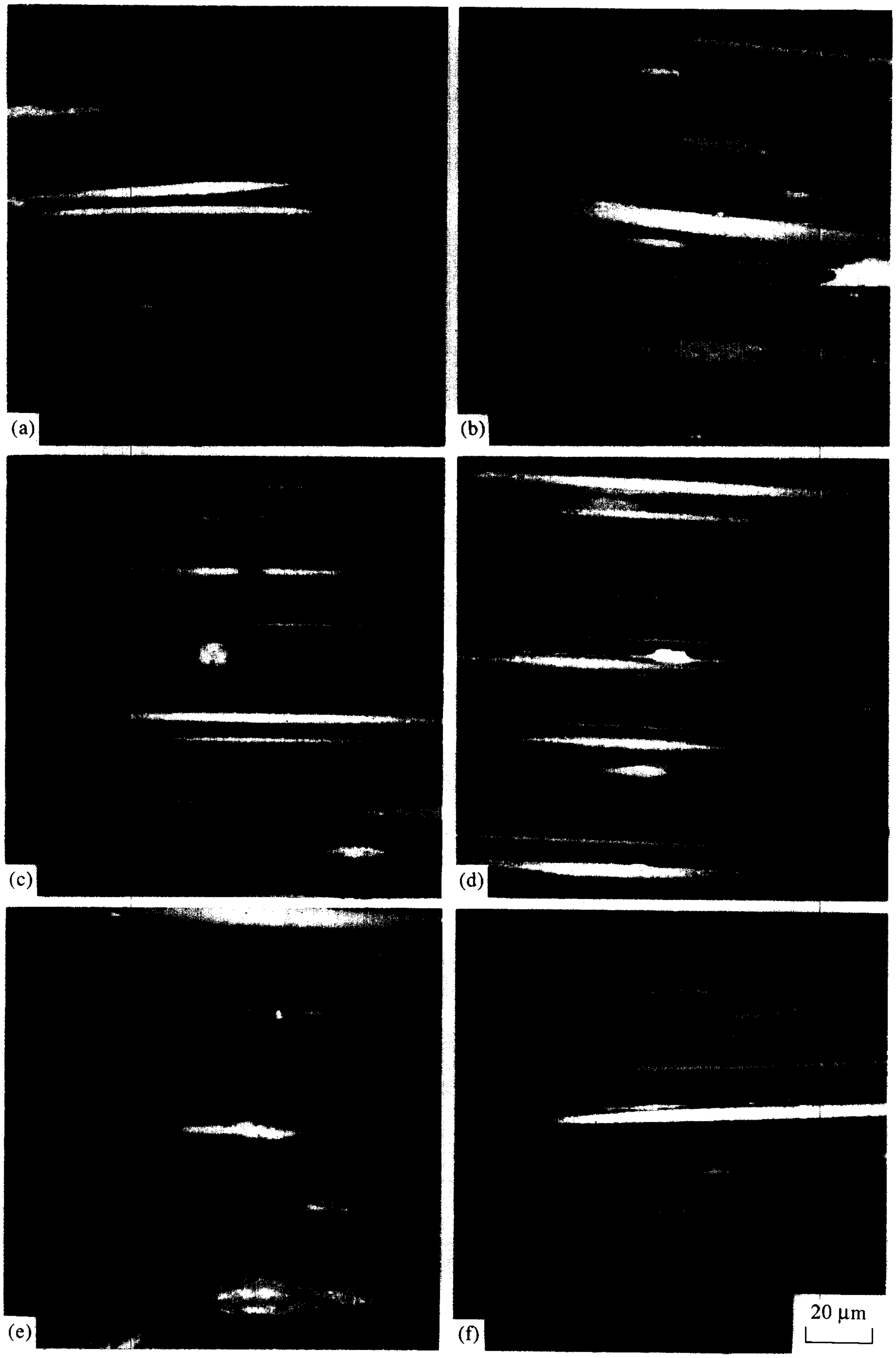


Figure 14 Confocal scanning laser micrographs of PP/Vectra B950 (90/10) blends prepared from different PP grades: (a) PP1; (b) PP2; (c) PP3; (d) PP4; (e) PP5; (f) PP6

screw/die design. This shear dependence is more pronounced for blends with Vectra B950 than for blends with Vectra A950.

4. PP blends with Vectra A950 have higher tensile strengths than blends with Vectra B950, whereas concerning stiffness values Vectra B950 appears to be superior to Vectra A950.

ACKNOWLEDGEMENTS

The authors with to acknowledge R. van der Berg and R. Bradley for their invaluable help in analysing the various samples.

REFERENCES

1. Heino, M. T. and Seppala, J. V., *J. Appl. Polym. Sci.*, 1993, **48**, 1677.
2. Postema, A. R. and Fennis, P. J., *Russian Polym. Sci.*, 1996, **38**, 36.
3. Postema, A. R. and Fennis, P. J., *Macromol. Symp.*, 1996, **102**, 399.
4. Grace, H. P., *Chem. Eng. Commun.*, 1983, **14**, 225.
5. Min, K., White, J. L. and Fellers, J. F., *Polym. Eng. Sci.*, 1984, **24**, 1327.
6. Tsebreniko, M. V., Danilova, G. P. and Malkin, A. Y. A., *J. Non-Newt. Fluid Mech.*, 1989, **31**, 1.
7. Blizard, K. G., Federici, C., Frederico, O. and Chapoy, L. L., *Polym. Eng. Sci.*, 1990, **30**, 1442.
8. Beery, D., Siegmann, A. and Kenig, S., *J. Mater. Sci. Lett.*, 1988, **7**, 1071.
9. He, J., Bu, W. and Zhang, H., *Polym. Eng. Sci.*, 1995, **35**, 1695.
10. Verhoogt, H., Ph.D. thesis, Delft University, The Netherlands, 1992.
11. Roetting, O. and Hinrichsen, G., *Adv. Polym. Technol.*, 1994, **13**, 57.
12. La Mantia, F. P., Valenza, A., Paci, M. and Magagnini, P. L., *Rheol. Acta*, 1989, **28**, 417.
13. Kulichikhin, V. G., Vasil'eva, O. V., Litvinov, I. A., Antipov, E. M., Parsanyan, I. L. and Plate, N. A., *J. Appl. Polym. Sci.*, 1991, **42**, 363.
14. Han, C. D., *Rheology in Polymer Processing*. Academic Press, New York, 1976, pp. 97–98.
15. Guskey, S. M. and Winter, H. H., *J. Rheol.*, 1991, **35**, 1191.
16. Lord Rayleigh, *Phil. Mag.*, 1892, **34**, 145.
17. Min, K., White, J. L. and Fellers, J. F., *J. Appl. Polym. Sci.*, 1984, **29**, 2117.
18. Brinkmann, T., Hoeckk, P. and Michaeli, W., *ANTEC Proc.*, 1991, 988.
19. Tomotika, S., *Proc. Roy. Soc. (London)*, 1935, **A150**, 332.
20. Elmendorp, J. J., Ph.D. thesis, Delft University, The Netherlands, 1986.