

Effect of Nano-Silica Filler on the Rheological and Morphological Properties of Polypropylene/Liquid-Crystalline Polymer Blends

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Received 22 March 2002; accepted 9 May 2002

ABSTRACT: A fumed hydrophilic nano-silica-filled polypropylene (PP) composite was blended with a liquid-crystalline polymer (LCP; Rodrun LC5000). The preblended polymer blend was extruded through a capillary die; this was followed by a series of rheological and morphological characterizations. The viscosity of the PP matrix increased with the addition of the hydrophilic nano-silica. At shear rates between 50 and 200 s⁻¹, the composite displays marked shear-thinning characteristics. However, the incorporation of LC5000 in the PP composite eliminated the shear-thinning characteristic, which suggests that LC5000 destroyed the agglomerated nano-silica network in the PP matrix. Although the viscosity ratio of LCP/PP was reduced after the addition of nano-silica fillers, the LCP phases existed as droplets and ellipsoids. The nano-silicas were concentrated in the LC5000 phase, which hindered the formation of LCP fibers when processed at high shear deforma-

tion. We carried out surface modification of the hydrophilic nano-silica to investigate the effect of modified nano-silica (M-silica) on the morphology of the PP/LC5000 blend system. Ethanol was successfully grafted onto the nano-silica surface with a controlled grafting ratio. The viscosity was reduced for PP filled with ethanol-M-silica when compared to the system filled with untreated hydrophilic nano-silica. The LC5000 in the (PP/M-silica)/LC5000 blend existed mainly in the form of fibrils. At high shear rates (e.g., 3000 s⁻¹), the LC5000 fibril network was formed at the skin region of the extrudates. The exclusion of nano-silica in the LC5000 phase and the increased viscosity of the matrix were responsible for the morphological changes of the LCP phase. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1484–1492, 2003

Key words: polypropylene (PP); liquid-crystalline polymer (LCP); viscosity; morphology

INTRODUCTION

Thermoplastic liquid-crystalline polymers (TLCPs) have generated intense interest from both academic and industrial researchers. The inherent low viscosity and ability to deform into long fibrils are the main attractions for blending TLCP with thermoplastics. When added to thermoplastics, TLCPs can act as both processing aids and reinforcing agents. Several researchers have attributed the viscosity minimum to interfacial slip or slip at the die wall.^{1–3} Dispersed phases that maintain large elongations would provide large surface areas over which slip can occur. Should partial migration take place, this would increase slip in the higher shear rate regions. Migration would also assist slip at the die wall, where a plug flow of high-viscosity fluid is lubricated by a low-viscosity component. The viscosity ratio between the dispersed phase

and the matrix is an important factor for the control of phase morphology in polymer blends. To achieve a better dispersion of liquid-crystalline polymer (LCP) in the matrix polymer, the LCP phase should have a lower viscosity than the matrix polymer; that is, viscosity ratio should be lower than unity (Beery et al.⁴). Generally, the fibrillation of LCP is much easier in high-viscosity matrices, such as polyethersulfone, poly(etherether ketone), and polysulfone, than in low-viscosity matrices, such as polypropylene (PP) and polyethylene.

Particulate inorganic fillers are widely used in thermoplastic industries to reinforce the polymer matrix and to improve heat-resistance characteristics of materials.^{5,6} The high anisotropy of the short-fiber-reinforced thermoplastic can also be avoided by using particulate fillers. Generally, the viscosity of the thermoplastic will dramatically increase after the addition of fillers. When particulate-filled thermoplastic is blended with TLCP, the TLCP will reduce the viscosity of the blend and enhance the processability of the blend. Furthermore, the reduced viscosity ratio of

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TABLE I
Specifications of the Nano-Silica (Aerosil 200)

Surface	BET surface area (m ² /g)	Primary particle size (nm)	Ignition loss (%)	pH in 4% aqueous solution	Purity (% of nano-silica)
Hydrophilic	200 ± 25	12	<1	3.6–4.3	99.8

TLCP to matrix will favor the fibril formation of TLCP, providing further reinforcement of the blend. Previous researchers^{7–9} have used this type of ternary system to bring about a viscosity reduction in the blend. The fillers used were either short fibers or whiskers, and the TLCP contents were kept low (< 10 wt %). He et al.⁷ introduced a new technique for the formation of reinforcement with two orders of magnitude improvement in the mechanical properties for the resultant composite.

The surface property of the particulate filler plays an important role in the properties of the composite. A good example was given by Ashton and Briggs.¹⁰ Using silica-filled poly(methyl methacrylate) containing 50 vol % silica, with and without 3-(trimethoxysilyl)propyl methacrylate (MPS) as the coupling agent, they measured the mechanical performance of the composite and demonstrated the importance of the bonding between the filler and the matrix. The composite containing the MPS had a flexural failure stress of 115 MPa, whereas the composite without a coupling agent had a flexural failure stress of 65 MPa. Various methods can be used to modify the surface characteristics of the filler. The most widely used method is the use of a coupling agent, which has two functional groups at either end of the molecule.¹¹ However, the reaction of the coupling agent with filler is difficult to control, and often multiple layers of coupling agent are formed on the filler surface. To control surface modification, chemicals or polymers with functional groups that can react with the hydroxyl groups on the silica surface may be used.^{12,13}

The aim of this study was to blend nano-silica-filled PP composite with LC5000 to improve the processability and reinforcement of LC5000. The influence of nano-silica with different surface properties on the behavior of the PP/nano-silica composite and its blend with LC5000 was investigated.

EXPERIMENTAL

Materials

PP was provided by Mitsui Noblen (Tokyo, Japan). The melt flow index of the PP used was 4.0 g/10 min. The LCP (Rodrun LC5000) provided by Unitika (Tokyo, Japan) was a copolymer of *p*-hydroxybenzoic acid (HBA) and poly(ethylene terephthalate) (PET) (80/20). Fumed nano-silica (Aerosil 200) was kindly

supplied by Degussa Ag (Dusseldorf, Germany). The hydrophilic nature of the nano-silica powder was caused by the presence of silanol groups on its surface. The particle has a spherical surface and is also free of pores. The specifications of the nano-silica Aerosil 200 are shown in Table I. Ethanol used in the surface modification of nano-silica was from Aldrich (St. Louis, MO) and was used without further purification. Anhydrous toluene solvent was also supplied by Aldrich and was used without further purification.

Sample preparation

PP and LCP were dried at 110°C under vacuum for at least 12 h before use. For nano-silica, the powder was dried at 110°C under vacuum for at least 48 h and kept in vacuum oven until blending. Melt blending of PP and nano-silica powder with or without surface modification was carried out in a Haake Rheocord 90 twin-screw extruder. The temperatures of the heating zones from hopper to orifice were set at 160, 190, 200, 200, and 200°C, respectively. The screw speed was 40 revolutions per minute. We quenched, pelletized, and reextruded the extrudate to ensure uniformity in the dispersion of the nano-silica powder. PP/nano-silica (without surface modification) composites containing 5 wt % of nano-silica were extruded. The melt blending of nano-silica and PP/nano-silica with LC5000 was also carried out in the same extruder, except that the temperatures of the heating zones were 200, 260, 270, 280, and 280°C, respectively. The pelletized blends were dried under vacuum at a temperature of 110°C for at least 12 h before further use.

Surface modification of nano-silica was performed with ethanol. For low grafting ratios (τ_s), the dried nano-silica powder was dispersed in a mixed solution of ethanol and acetone. Specifically, ethanol/acetone (20/80 vol %) was used, and 6 g of nano-silica was added to the mixed solvent. The mixture was raised to 200°C for 2 h in a sealed container under nitrogen gas. The grafting reaction of ethanol took place by a direct esterification of the surface silanol groups of the Aerosil nano-silica and the hydroxyl end group of the ethanol. For high τ_s , an excess of ethanol was mixed with nano-silica to favor ether formation where the nano-silica was dispersed in ethanol. The mixture was then heated, maintained at the reflux temperature for 8 h, and subsequently cooled. The excess ethanol was

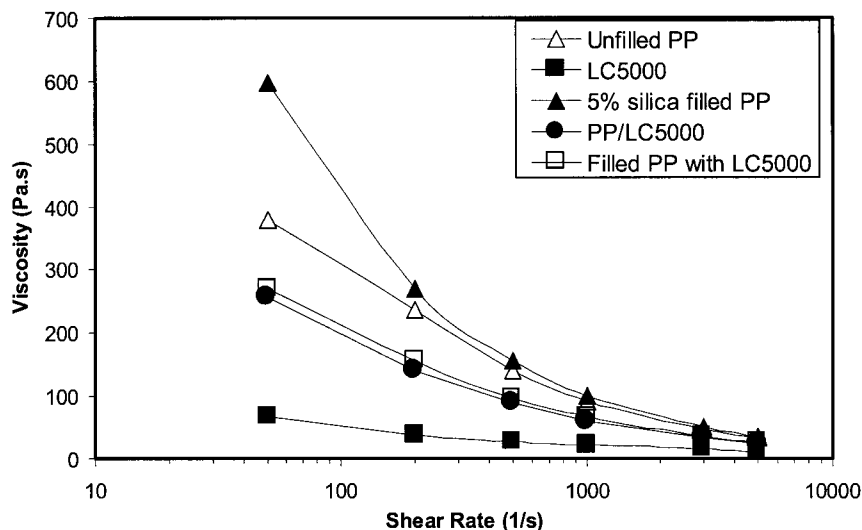


Figure 1 Viscosity versus shear rate of LC5000, PP, PP/nano-silica composite, and their blends at 280°C.

then removed by rotary evaporation. In addition, the unreacted ethanol was further removed by prolonged extraction (24 h) with acetone in a Soxhlet extractor. The grafted nano-silica was first dried in air to remove the bulk of the solvent and was then dried in a vacuum oven for 24 h (at a temperature of 60°C to avoid thermal degradation).

Rheological characterization

The rheological test of the blend was carried out on a Rheograph 6000 capillary rheometer (Goettfert). A round-hole die with a diameter of 1 mm and a length of 10 mm was used. The entry angle of the die was 180°. Six shear rates (50, 200, 500, 1000, 3000, and 5000 S^{-1} , respectively) were used to study the effect of shear rate on the rheological properties of the blend. The barrel temperature was 280°C. The viscosity obtained was the apparent viscosity, and the entrance correction was not applied. The extrudates were quenched immediately in cold water and collected for morphology observation and other testing.

Morphological observations

The tensile fracture surfaces of the capillary-extruded specimens and the selectively extracted sample were examined with scanning electron microscopy (SEM; Jeol, JSM-5410LV). A very thin layer of gold was sputter-coated onto the specimen surface to make it electrically conductive. Energy diffraction X-ray (EDX) was used to determine the distribution of nano-silica in the composite. For the solvent-extracted sample, the extrudates were placed in a centrifuge test tube and refluxed with toluene to dissolve the PP matrix. The LCP phase was separated by centrifugation. The separated LCP was immersed in fresh solvent and separated twice. A drop of the residue was deposited onto the disk for observation in the SEM.

Thermal analysis

A thermogravimetric analyzer (TA Corp.) was used to determine the nano-silica content in the blend and LCP phase. A heating rate of 10°C/min was used, and

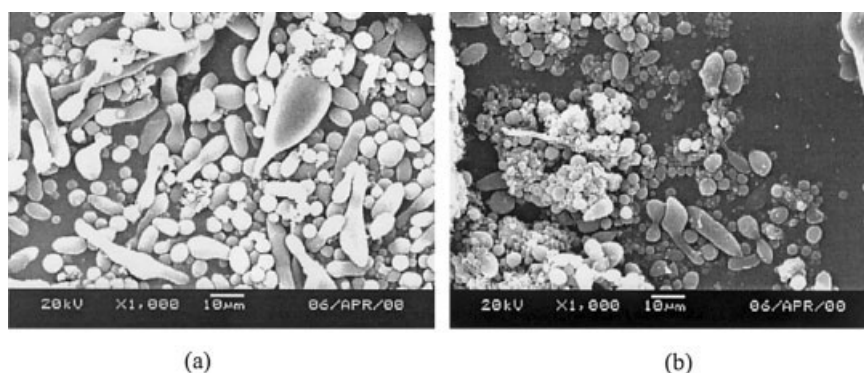


Figure 2 SEM pictures of the LCP domains of (a) PP/LC5000 80/20 and (b) (PP/nano-silica)/LC5000 (80/5)/20.

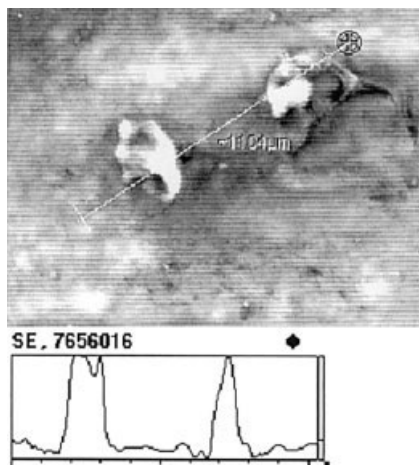


Figure 3 EDX linear silicon scanning of the PP/LC5000/nano-silica ternary blend.

the sample was kept at isothermal conditions at 850°C for 3 h.

RESULTS AND DISCUSSION

PP/LC5000/untreated nano-silica blend

Figure 1 shows the rheological results of the LC 5000, PP, PP/nano-silica composite, and their blends at the temperature of 280°C. At a shear rate range of 5×10^1 to $1 \times 10^4 \text{ s}^{-1}$, all the melts showed rheological behavior of non-Newtonian fluids, as indicated by the decrease in their apparent viscosities with increasing shear rates. The viscosity of LC5000 was the lowest over the whole shear rate regime. The viscosity of unfilled PP was higher than that of LC5000 at all shear rates, indicating that the viscosity ratio of the dispersed/matrix phases (λ) was less than 1. With increasing shear rates, the viscosity difference between LC5000 and PP decreased, and at a shear rate of 5000 s^{-1} , λ was very close to 1. The addition of 20 wt % LC5000 into the PP matrix resulted in a slight decrease in the viscosity of the blend. The addition of 5 wt % nano-silica to PP dramatically increased the viscosity

of the matrix from about 380 Pa s to about 600 Pa s at a shear rate of 50 s^{-1} . Special attention must be paid to the large shear-thinning effect of the filled PP. The hydrophilic surface of the fumed nano-silica might have interacted with each other through the interparticle bridging formed by hydrogen bonding, which resulted in a network structure containing nano-silica particles. At lower shear rates, the network structure was not disrupted; however, at increasing shear rates, the hydrogen bonds were broken, and the viscosity decreased dramatically. The addition of 20 wt % LC5000 to the composite eliminated the large shear-thinning effect, and the blend showed a weaker dependence of viscosity on shear rates. The fine dispersion of the low-viscosity LC5000 phase and the more polar surface of the LC5000, which resulted in the migration of the hydrophilic silica to the LCP phase, are believed to be the reasons for the elimination of the large shear-thinning effects. The disappearance of significant shear thinning for the PP/nano-silica/LCP blend was mainly due to the destruction of the network structure formed by nano-silica particles and LCP. Additionally, the incorporation of LCP greatly decreased the viscosity of the blend; hence, the processability of the composite was enhanced.

Figure 2 shows the SEM pictures of the LCP domains after the PP phase was selectively removed in the PP/LC5000 and (PP/nano-silica)/LC5000 blends. The shear rate used for the sample preparation was 1000 s^{-1} . The LCP phase in the PP/LCP blend appeared as both spherical droplets and ellipsoids. The LCP domain size was not uniform; that is, the larger ones were about 10–20 μm , whereas the smaller ones were about 1 μm or smaller. This was attributed to the incompatibility of the polymer blends, which resulted in a heterogeneous coalescence kinetic process. The poor interfacial adhesion would result in a poor dispersion of the minor phase in the matrix. When the PP matrix was preblended with 5 wt % nano-silica, the viscosity of the matrix was significantly increased, but the morphology remained unchanged. The LCP phases were again in the form of droplets or ellip-

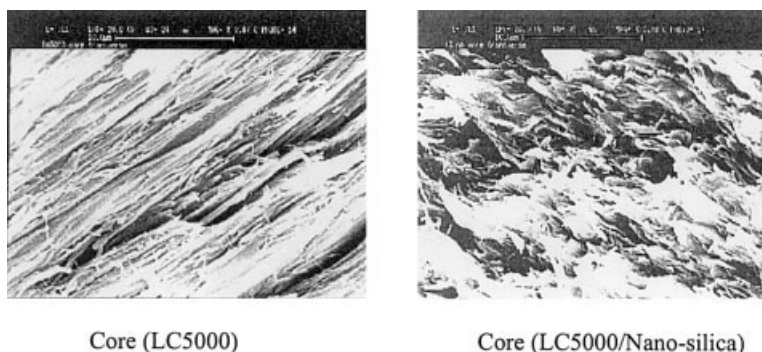


Figure 4 SEM pictures of the fracture surface of LC5000 without and with nano-silica filler.

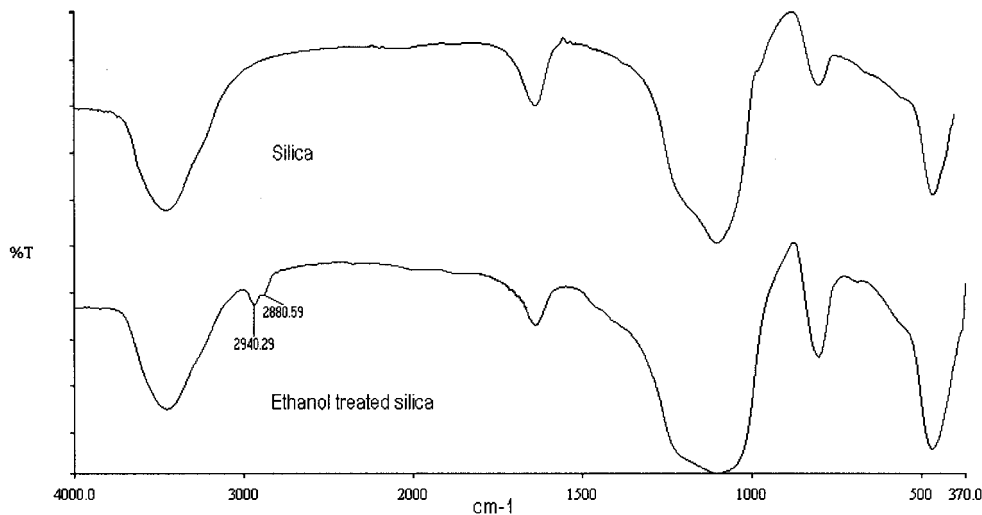


Figure 5 FTIR (KBr) spectra of nano-silica and ethanol-M-silica.

soids, but the size of the LCP was smaller than the blend without nano-silica. The distribution of the LCP was also more uniform. When LC5000 was blended with the PP/nano-silica composite, the silanol groups on the nano-silica surface may have interacted with the LCP phase. The low-viscosity LCP could easily spread over the finely dispersed nano-silica particles, which made the dispersion of the LCP phase more uniform. We thus envisaged that on blending the PP/nano-silica composite with LC5000, the hydrophilic nano-silica could have migrated to the LCP phase, or the LCP droplets may have been coated by the nano-silica particles. This is consistent with the viscosity data, where the incorporation of LCP in the PP/nano-silica composite eliminated the large shear-thinning effects at low shear rates. Another probable mechanism is that after the incorporation of the hydrophilic nano-silica, the PP/nano-silica matrix became more polar, which would have improved the interaction between

LCP and the matrix. This type of interaction would result in a finer dispersion of the LCP minor phase.

To provide additional evidence to support the notion that hydrophilic nano-silica had a higher affinity for the LCP than the PP phase, PP/LCP/nano-silica with a weight ratio of 80/20/5 was blended simultaneously by the mixture of all three components at once in the extruder. All of the other experimental parameters were similar to the preblending method. A linear EDX scanning on the silicon was carried out on the PP/LC5000/hydrophilic nano-silica ternary blend to determine the distribution of nano-silica in the blend. The result is shown in Figure 3, where the droplets in the SEM picture are the LCP domains. As indicated in the curve, the nano-silicas were concentrated in the LC5000 phase, and only small quantities were distributed in the PP matrix.

LC5000/nano-silica with a weight ratio of 100/5 was prepared for further testing. Figure 4 shows the

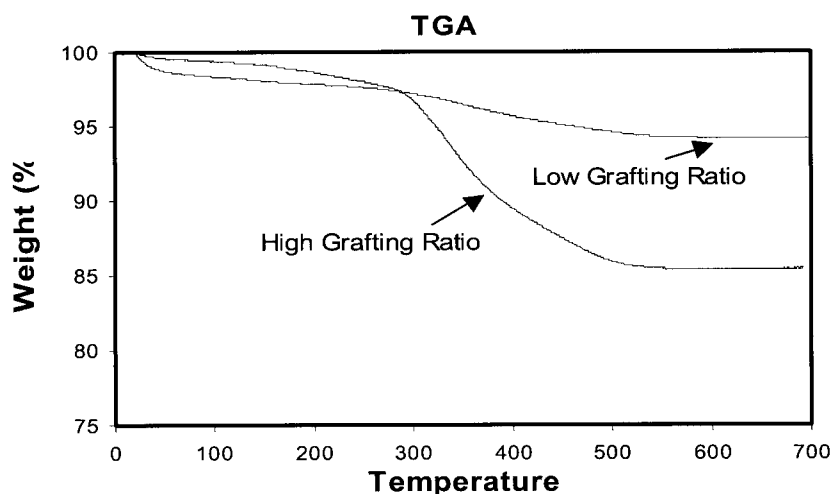


Figure 6 TGA curves of two ethanol-grafted nano-silicas.

TABLE II
Surface Coverage of Ethanol at Various τ s

	τ (%)	τ_M (chain/nm ²)	τ_{CH_2} (number/nm ²)	Surface coverage (%)
Low τ	6.2	4.0	8.1	48.4
High τ	17.1	11.1	22.2	133.4

SEM pictures of the fracture surface of LC5000 (at a direction transverse to the flow direction) with and without nano-silica filler. The addition of nano-silica fillers altered the morphology of the LCP, as shown in the micrographs. Pure LC5000 has a highly orientated structure. Continuous microfibrils with a diameter around 1 μm can be easily seen. Such a structure will result in a high anisotropy in the microstructure, resulting in better mechanical properties in the orientation direction of the fibers. The introduction of fine nano-silica filler in the LC5000 made the LCP less orientated. Also, there were many fibrils formed, but the fibrils were less orientated and also shorter than the fibrils formed in the pure LC5000. A reduction of anisotropy in mechanical properties may be expected for the nano-silica-filled LC5000. With the addition of the nano-silica filler, the LCP became more brittle and more difficult to deform under shear. When such filled LCP was present in the PP matrix, it was difficult to deform the LCP into fibrils, even though the viscosity ratio was reduced significantly.

Surface modification of nano-silica

The Fourier transform infrared (FTIR) spectra of nano-silica and modified nano-silica (M-silica) powder are shown in Figure 5. Compared with the spectra of nano-silica, the spectra of M-silica showed two additional absorptions at 2940 and 2880 cm^{-1} , which are characteristic of CH_3 — and CH_2 — groups. This indi-

cates that ethanol was successfully introduced onto the nano-silica surface. It is believed that after the prolonged time of extraction, the ethanol remaining on the nano-silica surface was irreversibly grafted onto the nano-silica.

The thermogravimetric analysis (TGA) curves of two ethanol-M-silicas are shown in Figure 6. A calculation of the surface coverage by the ethanol was carried out. τ , expressed in weight percentage, is defined as the weight of ethanol bonded onto 100 g of pure nano-silica. τ_M and τ_{CH_2} are defined as the number of ethanol chains and CH_2 groups, respectively, grafted onto the nano-silica surface. Knowing that the BET surface area of the nano-silica was $200 \pm 50 \text{ m}^2/\text{g}$ and that the projected area of a CH_2 group is 0.06 nm^2 , τ , τ_M , τ_{CH_2} , and surface coverage of the nano-silica could be determined.¹² The results are listed in Table II, and it shows that by varying the reaction conditions, controlled grafting could be achieved.

(PP/M-silica)/LC5000 blend

Ethanol-M-silica with low τ was added to the PP matrix, and the viscosity of the system was measured. The viscosity results for the PP/nano-silica (100/5 wt %) and PP are shown in Figure 7, where the sample after the surface modification exhibited a lower viscosity. The difference was more evident in the low-shear-rate region. The large shear-thinning effect for the hydrophilic nano-silica-filled composite was much reduced with the surface modification due to the reduced hydrogen bonds as discussed earlier. Under high shear rates, the difference in the viscosity between hydrophilic nano-silica-filled PP and M-silica-filled PP became smaller because the hydrophilic nano-silica network had been destroyed and the PP matrix played the dominant role in controlling the viscosity of the composite. It was suggested, however, that there exists another factor that contributes to the

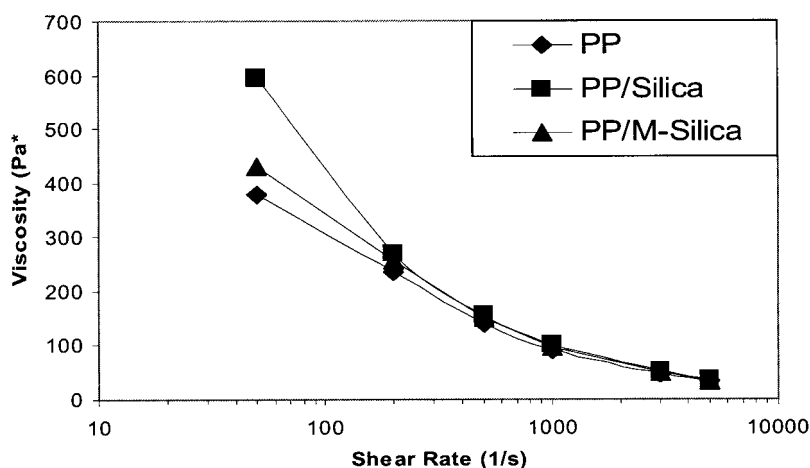


Figure 7 Viscosities of PP blended with ethanol-treated nano-silica at 280°C.

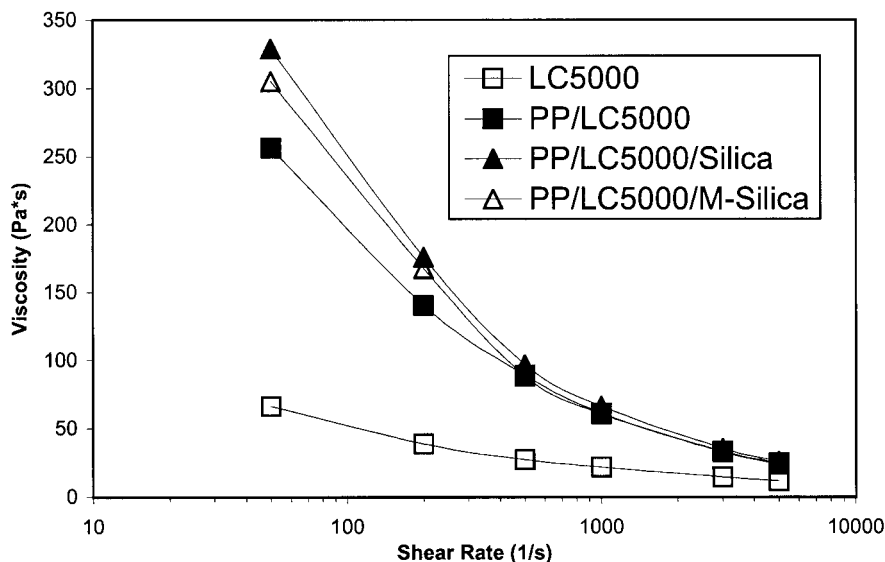


Figure 8 Viscosity of the PP/LC5000/nano-silica ternary blend as a function of shear rate.

reduction of viscosity. Kim et al.¹⁴ found the same viscosity reduction by treating fumed nano-silica with γ -methacryloxypropyl-trimethoxy silane (γ -MPS). The authors attributed the effect to the lubrication and wetting effect of γ -MPS. With the incorporation of γ -MPS, the lubrication and wetting between the filler and matrix was increased, and the viscosity of the blend was reduced. This explanation, however, cannot explain the large reduction in the shear-thinning effect at lower shear rates with the surface-modified nano-silica.

Figure 8 shows the viscosity of the ternary blend at 280°C. The incorporation of nano-silica into the blend increased the viscosity of the blend. There was little difference for samples with treated and untreated nano-silica. This may be due to the low viscosity of the pure LC5000 at 280°C. With a relatively large amount of LC5000 (20 wt %), the viscosity of the blend was largely influenced by the low-viscosity LC5000, whereas the influence of the surface property of the nano-silica was reduced. No conclusion could be

made at this point. None of the ternary blends showed the large shear-thinning phenomenon at a low shear rate, between 50 and 200 s^{-1} , indicating that the LCP component had a large influence on the rheological behavior of the PP/nano-silica composite.

Figure 9 shows the SEM micrographs of the tensile fracture surface of the ternary blend extrudates processed at a shear rate of 1000 s^{-1} . As shown in the graph, the LC5000 domains in the untreated nano-silica-filled PP matrix were mainly in the forms of droplets and ellipsoids, whereas they were mainly in the forms of fibrils in the M-silica-filled PP. The large difference in the morphology of the LCP phase indicates that the surface modification of the nano-silica had a great influence on the behavior of the blend. To further investigate the morphology of the LCP domain, we took SEM micrographs of the LCP phase by selectively dissolving the PP phase with toluene. The results (at shear rate of 1000 s^{-1}) are presented in Figure 10. At a higher shear rate of greater than 3000 s^{-1} , the LCP in the M-silica-filled

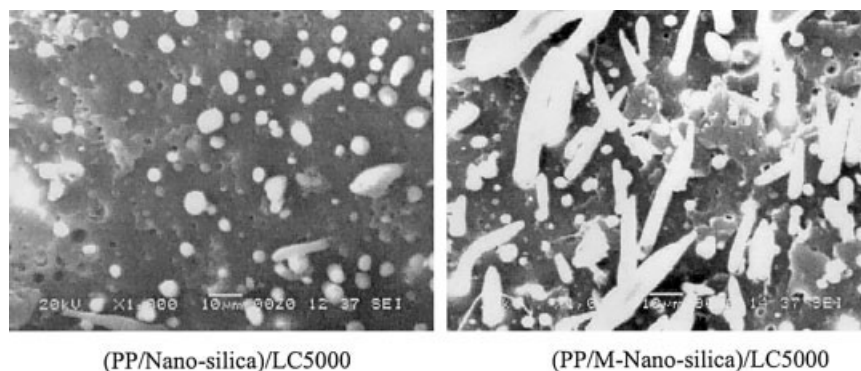


Figure 9 SEM pictures of the tensile fracture surface of the ternary blends.

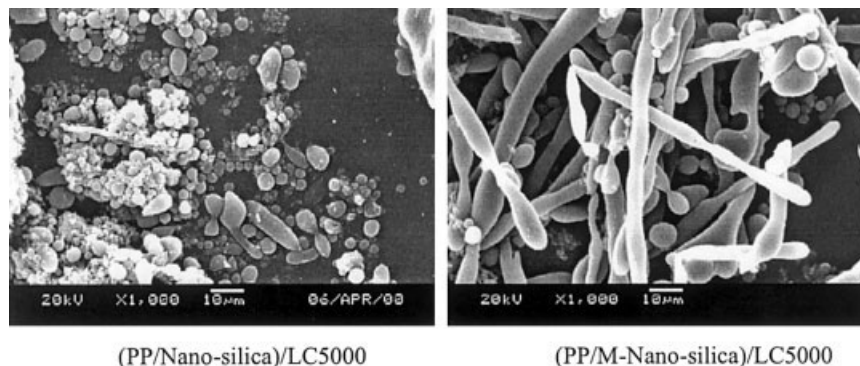


Figure 10 SEM pictures of the LCP phase after selective extraction for the three ternary blends.

blend formed a continuous fibril or even a fibril network (Fig. 11) at the surface region of the extrudate, making the dissolution of the PP phase very difficult.

We carried out EDX mapping on the (PP/nano-silica)/LC5000 and (PP/M-silica)/LC5000 systems to determine the nano-silica dispersion in the blend as shown in Figure 12. The white dots are the silicon element. For the hydrophilic nano-silica-filled blend, the nano-silica particles were distributed evenly, although the nano-silica was preblended with the PP matrix. The strong interaction between hydrophilic nano-silica and the LCP and the low viscosity of the LCP may have been the driving force for the migration of the nano-silica particle or for the coverage of the nano-silica particle by LCP. However, for the ethanol-grafted nano-silica, almost no nano-silica particles were found in the LCP domain, indicating that the nano-silica particle did not migrate to the LCP phase. The absence of nano-silica particles in the LCP phase resulted in a better fibrillar morphology of LCP.

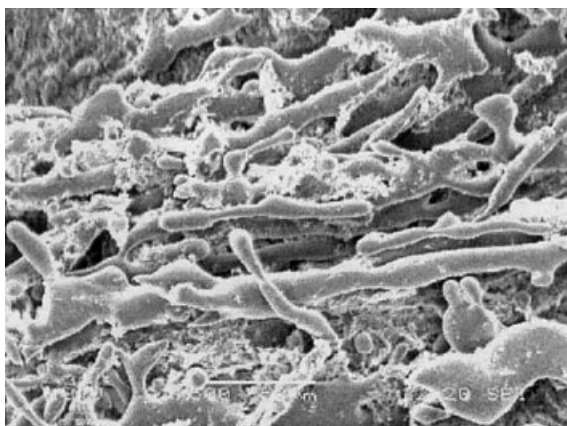


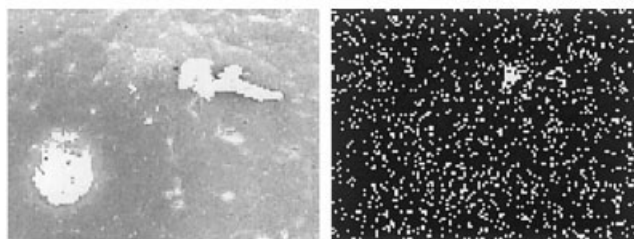
Figure 11 LCP network formed at the surface of the (PP/M-silica)/LC5000 extrudate after extraction under high shear rates.

CONCLUSIONS

Large shear-thinning effects of the PP/nano-silica composite at low shear rates were observed after the addition of 5 wt % hydrophilic nano-silica into the PP matrix. The nano-silica network formed in the PP accounted for the change. The effect was eliminated after the surface modification of the nano-silica by ethanol or the incorporation of the LCP into the blend.

Hydrophilic nano-silica and LCP have a strong polar-polar interaction. This caused the nano-silica to migrate to the LCP phase of the (PP/nano-silica)/LCP blend, which hindered the orientation of the LCP domain into fibrils. The surface modification of nano-silica by ethanol successfully prevented this trend. Better fibrillar LCP morphology was obtained after the surface modification of the hydrophilic nano-silica. An effective grafting method was developed.

Hydrophilic nano-silica filled blend



Ethanol-grafted nano-silica filled blend

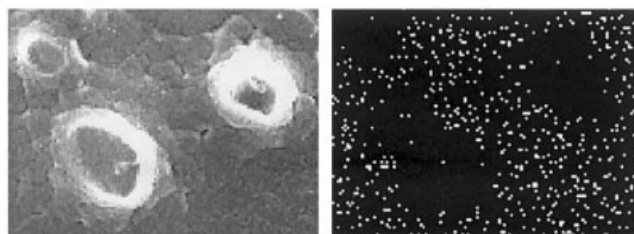


Figure 12 EDX mapping for nano-silica location in the (PP/nano-silica)/LC5000 blend.

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