

TENSILE AND FRACTURE BEHAVIOUR OF DIE-DRAWN POLYPROPYLENE-CLAY NANOCOMPOSITES

A Alshehri*, J Sweeney, P Caton-Rose, P D Coates

Engineering School, Design and Technology/IRC in Polymer Science and Technology, Bradford University, UK.

* SABIC Technology Center-Riyadh, KSA

Introduction

The internal interfacial area with nanoscale dimensions between the clay particles distinguishes polymer-clay nanocomposites from other traditional filled plastics. This structure results in an essential property modification in polymer-nanocomposites at small filler contents. Therefore, polypropylene-nanocomposites (PPNCs) achieve better stiffness than the pure polypropylene (PP) by adding 2 to 5% clay. The improved performance of these materials is established by the particle sizes, interparticle interactions, and their surface structure. The nanoparticle surface may be treated to provide hydrophobic characteristics and thus enhanced in its capability to be linked to the polymer matrix. A considerable enhancement of some PP properties such as stiffness and strength can be produced by solid-state molecular orientation [1, 2]. This important area has not been investigated for PPNCs. Orientation mainly influences properties in the direction of drawing, whereas nanoparticles improve properties in all direction. For this reason, a combined study of orientation and nanoparticle reinforcement on stiffness and fracture behaviour is of particular interest.

Experimental

Materials

Montmorillonite (MMT), which relates to the family of two silica tetrahedral to one octahedral silicate layers nanoparticles, was introduced to PP. The melt flow index (MFI) of PP is 6 g/10 min, when tested at 230°C using 2.16kg. DuPont™ Fusabond® PM613-05 was chosen as a compatibilizer. PPNCs material has been produced with 3% and 5% clay at various PPMA loadings (3%, 6% and 9%).

Apparatus and Procedures

A Prism Eurolab KX 16 mm co-rotating twin-screw extruder with rod die was used. The small laboratory scale extruder has a length to diameter (L/D) barrel ratio of 40:1 with a twin-screw that has three mixing sections.

PP material was introduced to the extruder through a primary feeder, whereas a secondary feeder was used to introduce the clay material in powder form and PPMA in pellets form. Clay was dried at 80°C for 24 hours prior to processing. The PP/clay and PP/PPMA master batches were prepared based on 80% PP, 20% clay and 20% PPMA. The master batches produced were then introduced again to the

secondary feeder to obtain the desired weight percentages of PPNCs. Mixing has been explored to include a simple mixing route, i.e. mixing the PP with master batches followed by a non-shear mixing (one-step master batch mixing) to obtain the desired weight percentages of PPNCs. All PPNCs were then injected into tensile test specimens by a 100 ton FANUC injection moulding machine equipped with ASTM mould. The screw diameter is 32 mm and L/D ratio is 22:1.

Solid-state uniaxial molecular orientation has been introduced to PPNCs by the die-drawing process at draw ratio of 2, 3 and 4. A constant width small reg die with 15° half angle was used, the die thickness at the exit is 2 mm, the die width is 20 mm and the die length is 7 mm. The set die temperature (154 °C) was just 11 °C below the melting temperature (165 °C).

Tensile stress-strain measurements with video-extensometry and tensile fracture of double edge-notched tension (DENT) specimens have been used to evaluate the Young's modulus at a small-strain rate (0.0053 min⁻¹) and the total work of fracture. Different sample geometries of tensile and fracture test are given in Table 1 and 2.

All PPNCs were characterized by hot stage polarizing optical microscopy (HS-POM). The POM images were recorded at a magnification of 100x at different temperatures. Micrographs of transmission electron microscopy (TEM) were compared for different PPNCs. The feret's diameter (FD), which was suggested by Walton [3] to measure the size of irregularly, shaped particles, and average number of clay particles per unit area are used to analyze the TEM micrographs. Wide angle x-ray diffraction (WAXD) study was done using an X'Pert Pro X-Ray diffractometer. Bragg's law is used through the equation: $\sin\theta = n\lambda_e/2d$, where d is the spacing between the ordered clay layers and $\lambda\lambda$ is the wavelength =0.154 nm. The intensity of x-ray diffraction is given with scan of the diffracted angle (2 θ).

Table 1 Different Sample Geometries of Tensile Video Extensometer Test

Geometry	Isotropic Samples ($\lambda=1$)	Drawn Samples ($\lambda=2$)	Drawn Samples ($\lambda=3$)	Drawn Samples ($\lambda=4$)
Width, mm	10.0	10.0	8.6	7.4
Thickness, mm	4.0	2.0	1.6	1.36
Gage L, mm	87	34	34	34
Speed, mm/min	0.458	0.179	0.179	0.179

Table 2 Different Sample Geometries of Fracture Test

Geometry	Isotropic Samples ($\lambda=1$)	Drawn Samples ($\lambda=2$)	Drawn Samples ($\lambda=3$)	Drawn Samples ($\lambda=4$)
Width, mm	10.0	10.0	8.6	7.4
Thickness, mm	4.0	2.0	1.6	1.36
Notch L, mm	1.5	1.5	1.29	1.11
Gage L, mm	40	40	40	40

Results and Discussion

POM

The results show that the morphology of the PPNCs differs not only by the effect of clay loading, but also it is a function of the PPMA contents and its interference with clay. Fig. 1 shows that PP with 3% clay and 3% PPMA is more grainy than the compatibilized 5% clay system, with many very small spherulites as a result of higher nucleation rate (many sites). Crystallization start temperatures for all samples are very similar and within 5 °C difference in range. However, the PP with 3% clay and 3% PPMA did crystallize at earlier stages (130 °C), completing a full spherulite image at 120 °C over 115 °C for other composites. This material, compared with others, has the smallest spherulite size. A delay of 10 °C of PP and PPMA to have full spherulite images is a clear sign that clay layers acted as a nucleating agent, which promote the crystallization of PP. In the absent of the compatibilizer (Fig. 2), the POM analyses show that spherulites size was reduced for the 3% clay loading and then kept in the same region for 5 % clay loading. In PPNCs, obtaining these smaller spherulites by the use of nucleating agent of clay particles with good bonding to the non-polar PP matrix may give a more uniform structure that can improve the modulus due to the high stiffness of inorganic particles.

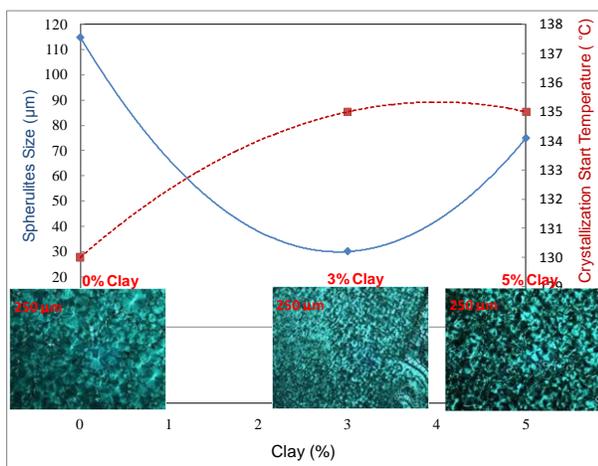


Fig. 1 Spherulitic size and crystallization start temperature of PPNCs with PPMA

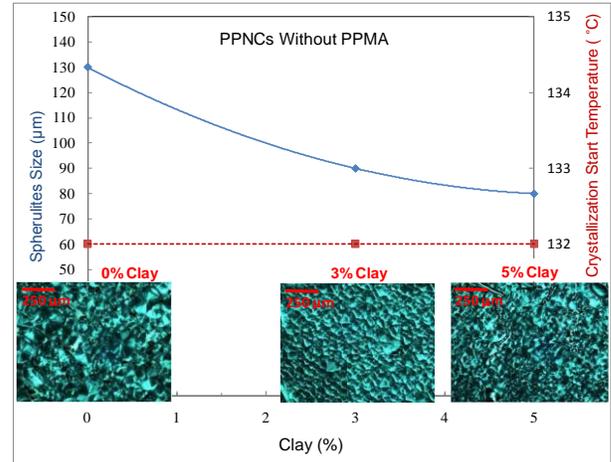


Fig. 2 Spherulitic size and crystallization start temperature of PPNCs without PPMA

WAXD and TEM

Meanwhile all WAXD results are summarized in Table 3. Figures 3 and 4 show the TEM micrographs and analyses of PPNCs that contain 3% and 5% clay loading with different PPMA contents. All WAXD results are compared to the peak of the pure clay, where the 001 plane peak was observed at $2\theta = 2.88^\circ$, and to the non-existing peak of pure PP material. A very little change in the basal spacing when 3% of clay loading is involved and no change for the 5% clay loading, which is due to the incompatibility of the polar hydroxyl groups on the surface of the clay layers and the nonpolar PP. From TEM micrograph, it can be clearly seen that clay particles without compatibilizer are poorly dispersed as aggregates in the continuous polymer phase. The number of particles is increased tremendously with a reduction in feret diameter with increase of the PPMA levels. Therefore, a distinct shift to lower angle is observed as the PPMA is added at the 3 % level. This enhancement in the degree of exfoliation reaches the maximum at 6% PPMA and shows no further improvement at 9% PPMA contents (Fig. 3). Similar results at a lower level were observed for 5% clay loading as 3% PPMA is added (Fig. 4). As compared to all 5% clay loading composite, 6% PPMA content achieved the highest d-spacing. The higher d-spacing PPNC samples correspond to the better distribution image. This might be explained by reduction of the number of stacked clay platelets in the non-crowded packed matrix by the effect of shear and/or introduction of functional groups of the treated polar MMT to the PP matrix. From the diameter results of the well compatibilized clay systems, it can be assumed that the diameter of the tactoids is not only influenced by the clay content but rather by the PPMA content and shear introduced to the PPNCs system.

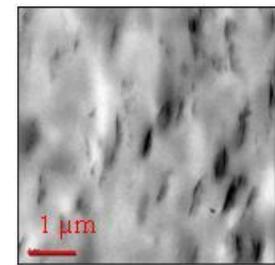
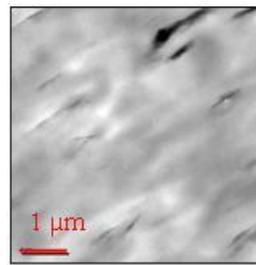
The sample produced from one-step master batch mixing has 3.54 nm of interspacing layers as compared to 3.14 nm for the pure clay. Thus the interspacing of silicate layers was swollen significantly by the intercalated polymer.

However, this increment is not accompanied with a good distribution of the tactoids intercalated clay particles in the

Table 3 Wide Angle X-Ray Diffraction Analysis of PPNCs

Sample Identification	d001 Angle (Degree)	Basal Spacing(nm)
PP+3% Clay	2.71	3.26
PP+5% Clay	2.87	3.15
PP+3%Clay+3%PPMA	2.24	3.61
PP+5%Clay+3%PPMA	2.63	3.32
PP+3%Clay+6%PPMA	2.16	3.67
PP+5%Clay+6%PPMA	2.48	3.43
PP+3%Clay+9%PPMA	2.24	3.61
PP+5%Clay+9%PPMA	2.55	3.38
PP+3%Clay+3%PPMA (One-Step MB Mixing)	2.35	3.54

the one-step master batch mixing. This kind of structure might influence the consistency of a property measurement from area to another for the same composite material.



a: One-step MB mixing
Avg. diameter: 0.43 μm, SD:0.31
Avg. no. of particles: 7.5, SD:6.25
b: Two-step MB mixing
Avg. diameter: 0.31 μm, SD:0.16
Avg. no. of particles: 17.6, SD:3.45

Fig. 5 Micrographs of PPNCs with 3% clay and 3% PPMA

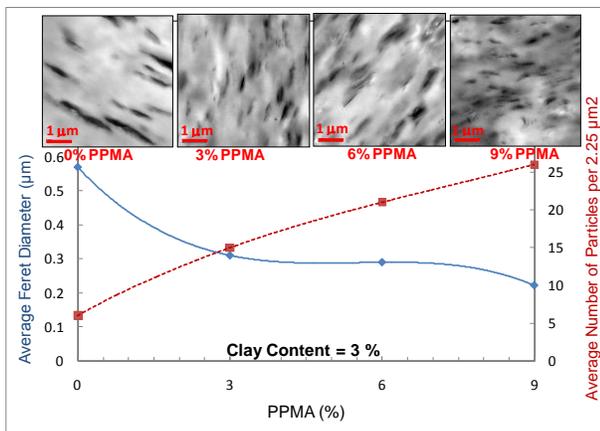


Fig. 3 TEM micrographs and analyses of PPNCs for 3% clay systems

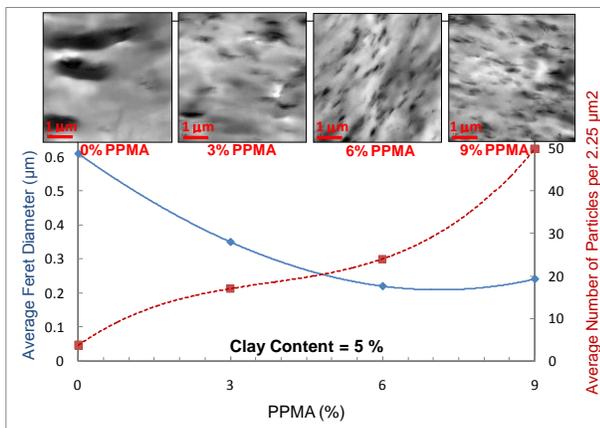


Fig. 4 TEM micrographs and analyses of PPNCs for 5% clay systems

PP matrix and it shows the critical use of one-step mixing even for a dispersed clay particles. Therefore, the two-stage mixing is an essential to achieve a successful interaction and distribution of the PPNCs. This result is confirmed by TEM micrograph (Fig. 5), which shows very large fluctuations in diameter and average number of particles for

Tensile Modulus

For inorganic clay particle reinforced non-polar PP, the PPNC-matrix interaction is an important factor in determining the mechanical properties of composites because a weak interface would impart lower modulus. The PP with 3% clay and 3% PPMA shows the greatest improvement among all 3% composites systems (40% more than PP, which is indicated by a dot in Fig. 6). In contrast, the greatest improvement in 5% systems is found to be for the PPNC with 6% PPMA loading (50 % more than PP). Similar results of improvement were reported in previous works by Liu et al [4] and Deshmane et al. [5]. The particle bonding to the polymer molecules, in presence of the compatibilizer, may restrict the mobility that contributes to the improvement of the tensile modulus in a polymer/clay composite. Increasing the clay content will greatly constrain the polymer chains' mobility so that the modulus is improved. This restriction in mobility is minimized when the PPMA is not involved so that a lower increment in tensile modulus was obtained for the non-compatible 3% and 5% clay systems. A discontinuation in this improvement is then observed as the PPMA increases over a certain level in both systems. The degree of loading of PPMA must be based on the clay content to achieve maximum improvement of composite properties.

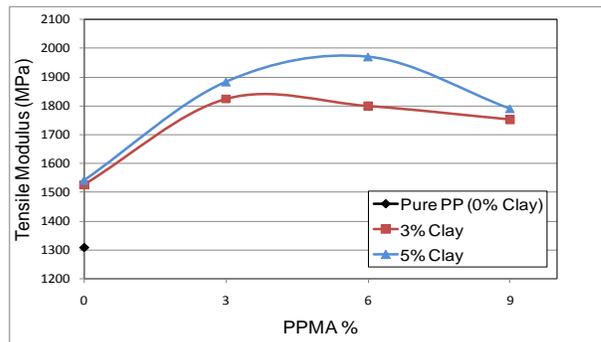


Fig. 6 Tensile Modulus vs. PPMA

Compared to all mixing procedures used, the two-step master batch procedure shows a clear indication of promoting exfoliation or intercalation of the PP molecules into the silicate layers galleries, which is reflected in the tensile modulus result, as shown in Fig. 7. This might be attributed to a high level of shear and mixing during the compounding stage. These improvements in dispersion and distribution are confirmed above in TEM and WAXD results. Conversely, although the one-step mixing achieves good compatibility with PP molecules, as reported in WAXD results, it fails to show good distribution in the TEM micrograph. Thus lower modulus as compared to two-step master batch sample is obtained, but still 12% higher than the pure PP sample.

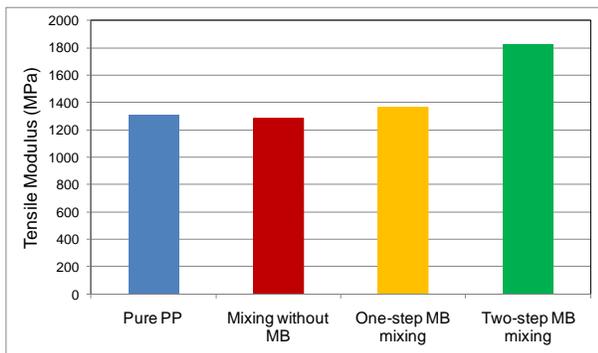


Fig. 7 Tensile modulus of 3% clay system with 3% PPMA for different mixing procedures

PP produces very high modulus polymer drawn fibres as a result of molecular orientation. Conversely, modulus decreases and toughness increases in the direction perpendicular to the axis of orientation, because stress along the axis of orientation of polymer molecules is applied against the strong covalent bonds within the polymer molecules. The modulus results of different draw ratios of PP and PPNCs are shown in Fig. 8. The 2, 3 and 4 draw ratios at 154 °C draw temperature achieve improvement in modulus of about 18%, 23% and 47% respectively. The results show similar tendency between different drawn PPNCs to that presented in the undrawn PPNCs. The drawn PP with 3% clay and 3% PPMA shows the greatest improvement among all 3% drawn composites systems (12-15% over the drawn pure PP system for all draw ratios, $\lambda = 2, 3, \text{ and } 4$). In contrast, the greatest improvement in 5% systems is found to be for the one with 6% PPMA loading (22-25% over the drawn pure PP system for all draw ratios, $\lambda = 2, 3, \text{ and } 4$).

The tendency of improvement in the drawn PPNCs is significantly minimized as compared to that obtained in undrawn samples. Addition of the polar structure MMT to the non-polar PP produces weak interface boundaries, which still exist even with using of the compatibilizer. When drawing is involved, microvoids might be more dominant in the drawn PPNCs structure. Thus the improvement of PPNCs tensile modulus tendency of undrawn compatibilized 3% clay and 5% systems is

reduced from 40% and 50% to 12-15% and 22-25% respectively over the pure PP system.

In spite of that the compatibilized systems achieve the highest modulus as shown in Fig. 8. A 4 % reduction in modulus at draw ratio 2 as compared to undrawn samples is observed for both compatibilized 3% and 5% clay systems. This might be attributed to the restriction of the molecules mobility by the PP molecules bonded to the clay galleries of the compatibilized systems at such very low drawing speed (5 mm/min). As the speed increases to 120 mm/min ($\lambda=3$), this restriction is minimized and a slight increase in modulus is observed. This behaviour is then followed by a tremendous increase in the modulus (33% over the undrawn sample) at very high speed of 950 mm/min ($\lambda=4$).

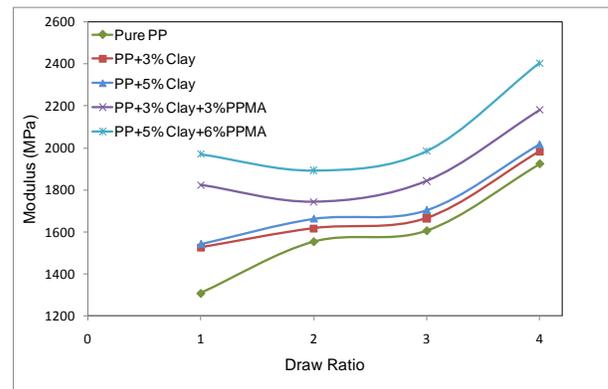


Fig. 8 Effect of draw ratio on tensile modulus of different drawn PPNC samples

Shifts in the curves to higher modulus of the drawn uncompatibilized systems over the PP curve are due to the high modulus of inorganic clay particles and possible interaction with the PP functional groups. Plateaus are presented for these systems between 2 and 3 draw ratios, followed by increase in modulus at high drawing speed for all three systems as microvoids might be more dominant in the matrix. Ability of orientation, presence of high modulus clay and the possible developed microvoids are the main factors that control the tensile modulus in such uncompatibilized systems.

Fracture Toughness

Figures 9 and 10 show the total work of fracture of PPNCs as compared to the pure PP and the thermal images that were taken for ligament yielding just before the failure stage for both undrawn and drawn specimens. The undrawn PP shows 12% and 15% higher toughness than the undrawn uncompatibilized and compatibilized 3 % clay systems respectively, but 14% lower than the 3% clay system that produced from one-step master batch compounding. The toughness tends to improve as enough uniform microvoids might be introduced to the system. The TEM micrographs of the one-step master batch sample do not show good distribution of clay particles, but 30% lower in feret diameter than the 3% uncompatibilized clay system. This higher surface contact between polymer and clay of the

one-step master batch system might be enough to have the microvoids structure that improves the toughness. Conversely, the large agglomeration areas reduce the surface contact of 3% clay system and do not allow the system to resist the failure. At the same time, the well distributed 3% clay system with compatibilizer makes very high surface contact but such interaction structure of the polymer into clay gallery may reduce the generated microvoids and cause a reduction in the toughness measurement. As the draw ratio increases to 2, the possible existence of microvoids in such well distributed compatibilized systems are grown and reached to a favourable degree that allows higher fracture toughness as compared to PP. More sample stretching, at draw ratio 3, may increase the microvoids of all 3% clay systems to a level where materials can not stand and crack propagates at earlier stages compared to PP. More stretching to draw ratio 4 does not pursue a better property, as the PP free volume does not permit any further mobility of other segments of the polymer chains.

5% clay systems of PPNCs are shown in Figure 10 and compared to the pure PP. The 5% compatibilized systems have higher total work of fracture than pure PP both undrawn and with draw ratio 2. At draw ratio 3, PP records about 34% and 11% higher toughness than the compatibilized and uncompatibilized 5% clay systems, respectively.

This behaviour is similar to the 3% clay systems with taking in consideration that the packed 5% clay system can lead to higher toughness for undrawn and low draw ratio systems, but as the draw ratio increases the microvoids coalesce with neighbouring voids that bridged the crack in process zone and eventually may lead to an earlier failure. This behaviour may explain the difference between the uncompatibilized 3% and 5% clay systems, as the 5% clay system achieves a huge improvement over the 3% clay system for undrawn samples (170%). This increment is minimized to be exactly the same as the 3% clay system at draw ratio 2 and a reduction of 5% at draw ratio 3 as the coalescence phenomena of the microvoids might be dominant.

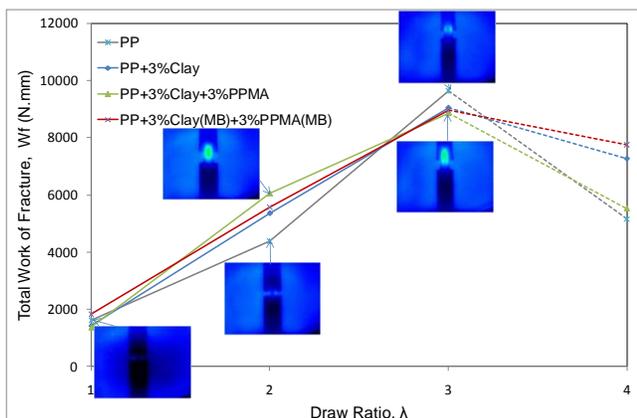


Fig. 9 Effect of draw ratio on the total work of fracture of PP and 3% clay systems PPNCs

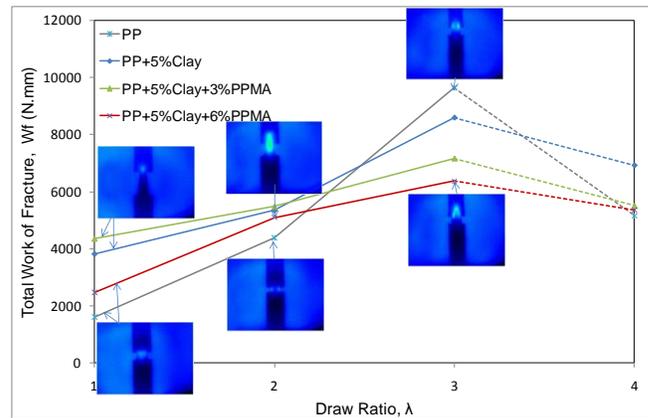


Fig. 10 Effect of draw ratio on the total work of fracture of PP and 5% clay systems PPNCs

Conclusion

The use of PPMA and an intensive mixing regime with a two-step master batch process overcame the compatibility issue and achieved around 40% and 50% increase in modulus for 3% and 5% clay systems respectively. This improvement of the two systems was reduced after drawing to be 15% and 25% over the drawn PP. The work of fracture is increased either by adding nanoclay or by drawing to low draw ratio, or both. At moderate and high draw ratios, PPNCs may undergo either an increase in the size of microvoids at low clay loading or coalescence of microvoids at high clay loading, eventually leading to an earlier failure than with neat PP.

The adoption of PPMA loading using an appropriate mixing route and clay loading can create a balance between the PPMA stiffness effect and the degree of bonding between clay particles and isotropic or oriented polymer molecules. Spherulites size, d-spacing of silicate layers, and nanoparticles distribution of intercalated microtactoids with possible semi-exfoliated particles have major roles to optimize the final PPNCs property.

References

- Coates, P. D. and Ward I. M., Drawing of polymers through a conical die. *Polymer*, 1979. 20(12): p. 1553-1560.
- Coates P. D. and Ward I. M., Die drawing: solid phase drawing of polymers through a converging die. *Polymer Engineering and Science*, 1981. 21(10): p. 612-618.
- Walton, W. H., Feret's Statistical Diameter as a Measure of Particle Size. *Nature*, 1948. 162: p. 329.
- Liu, X. and Q. Wu, PP/clay nanocomposites prepared by grafting-melt intercalation. *Polymer*, 2001. 42(25): p. 10013-10019.
- Deshmane, C., et al., On striking variation in impact toughness of polyethylene-clay and polypropylene-clay nanocomposite systems: The effect of clay-polymer interaction. *Materials Science and Engineering: A*, 2007. 458(1-2): p. 150-157.