Quantitative Characterization of Clay Dispersion in Polymer-Clay Nanocomposites

Shaobo Xie,[1] Eileen Harkin-Jones,[1] Yucai Shen,[1] Janet Hill,[1] Peter Hornsby,[1] Marion McAfee,[1] Tony McNally,[1] Raj Patel,[2] Hadj Benkreira,[2] Phil Coates[2]*

Summary: A novel methodology has been developed to describe the microstructure of polymer-clay nanocomposites quantitatively. It builds on the image analyses of transmission electron microscopy and optical microscopy micrographs, and two parameters, degree of dispersion and mean interparticle distance per unit volume of clay, are proposed to characterize the level of clay dispersion. It provides insights into the 'real' clay dispersion using a combination of both microscopical and macroscopical aspects.

Keywords: clay; image analysis; nanocomposite; optical microscopy; transmission electron microscopy (TEM)

Introduction

It is well documented that the efficiency of the clay as a reinforcing agent strongly depends on the extent of dispersion throughout the polymer matrix. While it is difficult to obtain the fully exfoliated structure in polymer-clay nanocomposites, quantitative characterization of clay dispersion is still a challenge of today's nanocomposites science. X-ray diffraction (XRD) and transmission electron microscopy (TEM) are two techniques commonly used for the evaluation of the quality of clay intercalation and exfoliation. Both methods provide useful information but with some drawbacks as well. XRD is ideal for the characterization of an intercalated structure which revealed a lower 2θ angel or a larger d-spacing compared to the original clay. But XRD alone can lead to a misinterpretation of the true nanocomposite structure. For example, The disappearance of the silicate reflection is not necessarily accompanied by complete exfoliation,[1] and a smaller interlayer distance than that of the original clay may also be found in the clay nanocomposites.[2] TEM can provide direct information on clay layers in the real space, however it can only explore very small volume of the sample and may not be representative. A complete picture of clay dispersion cannot be obtained even by combining XRD data with TEM due to the multi-scale dispersion of clay in the polymer matrix with the coexistence of single platelets, nanotactoids of different thicknesses and micro-size agglomerates. It is also important to reveal the overall dispersion/distribution of clay particles at the macroscopical level using optical microscopy (OM).

Several methods have been developed to describe the layer dispersion quantitatively.[3–6] The obtained quantitative parameters include the average particle aspect ratio, the particle density, the degree of exfoliation, and the distance between platelets. All of them are on the basis of image analysis of TEM micrographs. Perrin-Sarazin *et al.* [7] combined TEM with SEM analyses to describe the clay dispersion at all micro-, sub-micro- and nano-levels using a parameter particles surface density. Recently Vermogen *et al.* [8] have applied

[1] School of Mechanical and Aerospace Engineering, Queen's University, Belfast BT9 5AH, UK
E-mail: shaoboxie@gmail.com
[2] School of Engineering, Design & Technology, Bradford University, Bradford, West Yorkshire BD7 1DP, UK

image analysis to the different length-scales of polypropylene/clay nanocomposites structure. This involved measuring a range of particle dimensions on agglomerates, on tactoids of various sizes and on individual platelets based on the definition of different particle classes. Several parameters have been obtained to understand the distribution of particle morphologies, including mean thicknesses, mean lengths, aspect ratio of tactoids, and the extent of agglomeration. Undoubtedly, the observation based on TEM and OM presents a relevant picture of the microstructure, but the parameters obtained complicates the description of the dispersion of nanocomposites since one has to compare them using histograms of the dispersion parameters of the different classes of tactoids.[9] Very recently Basu *et al.* [10] have proposed a quantitative TEM characterization methodology based upon the stereological principles. Two parameters, exfoliation number and inter-particle distance, have been developed to quantify the layer dispersion degrees from the TEM images. Better dispersion and more exfoliation mean a higher exfoliation number and lower interparticle distance. However, macroscopical dispersions of micron size agglomerates are not included in these parameters.

Melt intercalation appears to be by far the most common method for the preparation of polymer-clay nanocomposites industrially. Processing parameters such as temperature, residence time and shear stress have significant effects on the structure of the resulting composites,[11,12] which in turn influences the properties of the processed material. So evaluation of clay dispersion, taking account of the effects of composition and processing factors, relative to the physical properties of the nanocomposites are of great importance. The present work is part of a much larger study aimed at systematically looking at processing parameters for the optimization of processing route as a means for informed scale-up for industrial preparation and application. In this work, a quantitative methodology has been developed by combination of TEM and OM observations to describe clay dispersion in polymer-clay nanocomposites. Polypropylene/clay system was selected as an example to show the effects of processing conditions on clay dispersion using the proposed quantifiers.

Experimental Part

Materials

Polypropylene homopolymer SABIC® PP produced by Saudi Basic Industries Corporation was used as matrix. It has a melt flow rate (MFR) of 10.5 g /10 min at 230 °C and 2.16 kg. PP functionalized with 1.0 wt% of maleic anhydride PPgMA (POLYBOND® 3200) from Crompton-Uniroyal Chemical was used as compatibilizer. Clay nanofiller (Cloisite 20A, abbreviated to 20A) was purchased from Southern Clay Products Inc., which was known to be ion-exchanged with dimethyl dihydrogenated tallow ammonium cations.

Processing of PP Nanocomposites

Two PP/PPgMA/20A nanocomposites PPNC1 and PPNC2 were prepared by a newly-designed mini-mixer, which can replicate effectively mixing achieved in large co-rotating twin screw extruder.[13] The processing parameters are nearly the same except different residence time and temperature. Table 1 shows the compositions and processing conditions.

Characterization

Optical microscopy observations were carried out at 200 °C to determine the proportion of clay agglomerates present

Table 1.
Compositions and processing conditions of the prepared PP nanocomposites.

	PPNC1	PPNC2
Residence time (min)	8	2
Temperature (°C)	190	230
Speed (rpm)	20	20
Clay loading (wt%)	2	2
Compatibilizer loading (wt%)	6	6
Polymer MFR(g/10 min)	10.5	10.5

in the nanocomposites. The observations were conducted using a Nikon microscope and a magnification of $\times 20$. TEM micrographs of the samples were obtained using a Philips CM100 TEM instrument recorded at 100 kV. About 50 nm thin slices were prepared using a Leica ultramicrotome. Image analysis was conducted using Photoshop (Adobe) and Fovea Pro (Reindeer Graphics) for binary conversion. The resulting binary images were analyzed by Scion Image (Scion) to automatically measure the perimeter and area of each particle.

Rheological measurements were performed on a GeminiTM 200 Advanced Rheometer (Malvern Instruments Ltd., UK) with a parallel plate geometry using plates of diameter 25 mm. Disk samples were prepared by compression molding in a press at 190 °C with a pressure of 150 bar. The sample thickness was 0.9 ± 0.05 mm and the gap width was 0.85 mm. Frequency sweeps were carried out from 0.01 Hz to 100 Hz at a strain of 0.01 and a temperature of 190 °C.

Results and Discussion

A novel methodology has been developed to describe the microstructure of polymer-

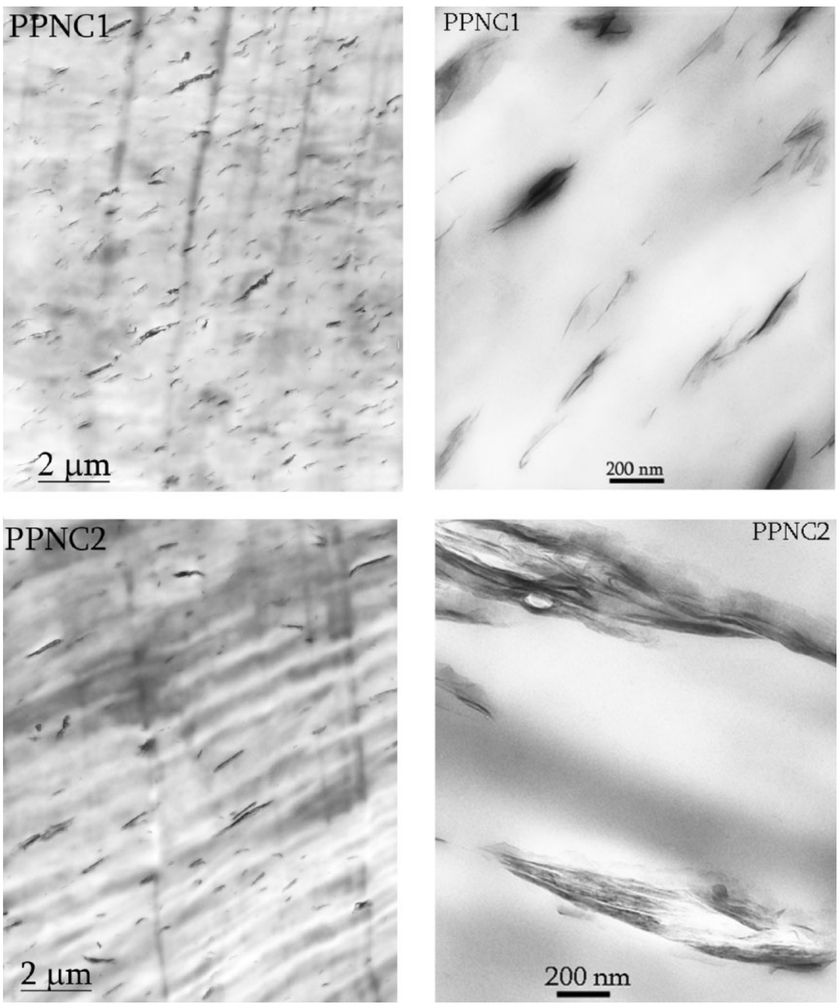

Figure 1.
TEM micrographs of the cross-sections of the extruded pellets of PPNC1 and PPNC2 at different magnifications.

clay nanocomposites quantitatively. Two parameters, degree of dispersion (χ) and mean interparticle distance per unit volume of clay (λ_V), are proposed to characterize the level of clay dispersion. χ is defined as the percentage of exfoliated platelets in the total clay content. It is a dimensionless parameter ranging from 0 to 100, with 0 indicating no exfoliation and 100 indicating complete exfoliation. It can be calculated from the proportion of micron size agglomerates (Agg%)[8] and exfoliation number (ξ)[10] according to the Eq. (1):

$$\chi = \xi \times (1 - \mathrm{Agg}\%) \qquad (1)$$

The mean interparticle distance (λ) can be obtained from TEM image analysis.[10] Because either an increase in clay loading or the increase in exfoliation can result in a reduction in λ, a new parameter, mean interparticle distance per unit volume of clay (λ_V) is defined for convenient comparison of the level of clay dispersion in nanocomposites with different clay loading. λ_V can be calculated using the Eq. (2):

$$\lambda_V = \lambda / (100 \times \Phi_C) \qquad (2)$$

where Φ_c is the volume fraction of clay in the composites, given by the Eq. (3):

$$\Phi_C = 1 + \rho_C(1 - \mu_C) \Big/ \rho_p \mu_C \qquad (3)$$

where ρ is density and μ is mass fraction. The subscripts c and p refer to clay and

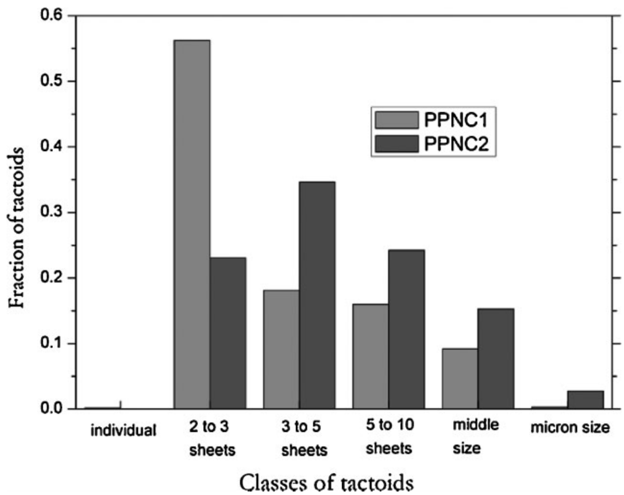

Figure 2.
Histograms of the frequency of the different classes of tactoids of PPNC1 and PPNC2.

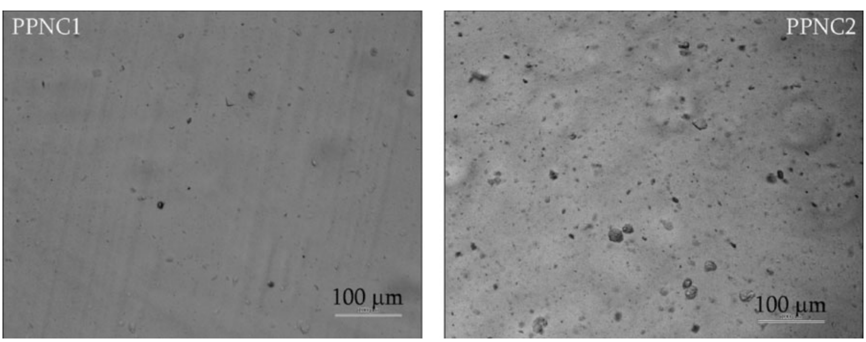

Figure 3.
OM micrographs of the extruded pellets of PPNC1 and PPNC2.

polymer. ρ_c is 1.8×10^3 kg/m^3 for 20A (the clay used in this study), and ρ_P is 900 kg/m^3 for polypropylene. A reduction in λ_V indicates the improved exfoliation of clay particles.

Figure 1 shows the TEM micrographs of PPNC1, PPNC2 at different magnifications. Visually PPNC1 exhibits better clay dispersion than PPNC2. The former contains more and thinner particles with smaller interparticle distance. Figure 2 is the graphical representation of the thickness distribution of clay platelets in PPNC1 and PPNC2 based on quantitative analysis of their TEM images using Vermogen's method.[8] Fifty-six percentage of tactoids in the extruded PPNC1 contain 2–3 platelets compared to 23% in the PPNC2 pellets. At the same time, PPNC1 has higher concentration of single platelets than PPNC2, while the latter has higher concentration of micron size agglomerates. Obviously PPNC1 indeed has better clay dispersion than PPNC2 from a microscopic aspect.Figure 3 shows the optical micrographs for PPNC1 and PPNC2. It is clear from the OM photographs that PPNC1 presents fewer agglomerates than PPNC2. The quantitative analysis results using our proposed method shown in Table 2 make this comparison easier. PPNC1 has a higher exfoliation number (30 vs. 11), lower Agg% (17 vs. 55) and lower λ_V (333 vs. 642) than PPNC2. The degree of dispersion (χ) describes the clay dispersion comprehensively. Based on ξ and Agg%, the χ values of these two samples capture the 'real' levels of clay dispersion. As shown in Table 2, PPNC1 has a much higher χ value (25 vs. 5) than PPNC2. This may be due to its lower processing temperature and higher residence time. The former will bring about a higher melt viscosity, thus a higher shear field, and the latter can promote diffusion process, both of which facilitate exfoliation. It must be noted that this methodology provides insights into the 'real' clay dispersion considering both microscopical and macroscopical aspects. And the mean interparticle distance per unit volume of clay (λ_V) describes the relative distribution of clay particles.

Table 2.
Image analysis results.

Samples	PPNC1	PPNC2
Agg% (%)	17	55
exfoliation number (ξ)	30	11
degree of dispersion (χ)	25	5
λ_V (nm per vol%)	333	642

The present analysis also shows correlation with rheological results. Figure 4 shows the storage modulus and complex viscosity of PP, PPNC1 and PPNC2. PPNC1 indeed exhibits higher storage modulus and complex viscosity than PPNC2. This is due to more physical network formation in PPNC1 by the better dispersed clay particles compared to PPNC2.[14]

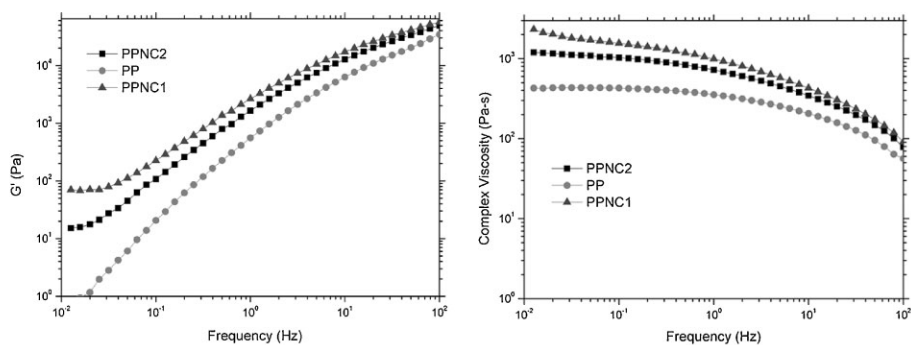

Figure 4.
Storage modulus and complex viscosity curves of unfilled PP, PPNC1 and PPNC2.

Conclusion

A new method to quantitatively characterize the level of clay dispersion in polypropylene-clay nanocomposites has been developed by a combination of TEM and Optical Microscopy. Two parameters, degree of dispersion (χ) and mean interparticle distance per unit volume of clay (λ_V) have been proposed. This method can be used to describe and compare the extents of clay dispersion in polymer matrices under various processing conditions.

Acknowledgements: This research was supported by the UK Engineering and Physical Sciences Research Council.

[1] A. B. Morgan, J. W. Gilman, *J. Appl. Polym. Sci.* **2003**, *87*, 1329.
[2] M. Zanetti, G. Camino, D. Canavese, A. B. Morgan, F. J. Lamelas, C. A. Wilkie, *Chem. Mater.* **2002**, *14*, 189.
[3] T. D. Fornes, D. R. Paul, *Polymer* **2003**, *44*, 4993.
[4] K. R. Ratinac, R. G. Gilbert, L. Ye, A. S. Jones, S. P. Ringer, *Polymer* **2006**, *47*, 6337.
[5] M. Bertmer, M. Wang, M. Krüger, B. Blümich, V. M. Litvinov, M. van Es, *Chem. Mater.* **2007**, *19*, 1089.
[6] Z. P. Luo, J. H. Koo, *Polymer* **2008**, *49*, 1841.
[7] F. Perrin-Sarazin, M. T. Ton-That, M. N. Bureau, J. Denault, *Polymer* **2005**, *46*, 11624.
[8] A. Vermogen, K. Masenelli-Varlot, R. Séguéla, J. Duchet-Rumeau, S. Boucard, P. Prele, *Macromolecules* **2005**, *38*, 9661.
[9] R. S. Rajeev, E. Harkin-Jones, K. Soon, T. McNally, G. Menary, C. G. Armstrong, P. J. Martin, *Eur. Poly. J.* **2009**, *45*, 332.
[10] S. K. Basu, A. Tewari, P. D. Fasulo, W. R. Rodgers, *Appl. Phys. Lett.* **2007**, *91*, 053105.
[11] H. R. Dennis, D. L. Hunter, D. Chang, S. Kim, J. L. White, J. W. Cho, D. R. Paul, *Polymer* **2001**, *42*, 9513.
[12] S. Bourbigot, G. Fontaine, S. Bellayer, R. Delobel, *Polymer Testing* **2008**, *27*, 2.
[13] H. Benkreira, R. Butterfield, M. Gale, R. Patel, *Plastics, Rubber and Composites* **2008**, *37*, 74.
[14] M. J. Solomon, A. S. Almusallam, K. F. Seefeldt, A. Somwangthanaroj, P. Varadan, *Macromolecules* **2001**, *34*, 1864.

