

Morphology and modulated force – thermomechanical master curves of polypropylene-bentonite nanocomposites

Antonietta Genovese, Daniel Kaminski, M. Asfaquar Rahaman and Robert A. Shanks

*School of Applied Sciences, RMIT University
GPO Box 2476V, Melbourne, VIC 3001, Australia*

Polypropylene (PP) nanocomposites have been prepared by solution blending with bentonite, a montmorillonite (MMT) clay, at levels of 1-3 %vol. Polypropylene-graft-maleic anhydride (PP-g-MA) was used to provide compatibility. The clay dispersion morphology was analysed by small angle X-ray scattering and it was found that an increase in concentration of MMT lead to the increase in the radius of gyration. This indicated that the particles aggregated or agglomerated in the polymer matrix. The modulated force-thermomechanical (mf-TM) analysis of the nanocomposites was conducted to construct master curves based on the time-temperature superposition (TTS) principle using the Williams-Landel-Ferry (WLF) model, to extrapolate their properties over extended frequencies.

1. Introduction

Nanostructured hybrid organic-inorganic polymer composites have attracted considerable attention to enhance the properties of materials via nanoscale reinforcement. Inorganic layered structured materials such as graphite, vermiculite, mica and montmorillonite (MMT) are sought for having a large aspect ratio and nano-scale thickness [1, 2]. Nanocomposites (NC) are known to exhibit superior physical and mechanical properties compared with conventional composites, including improved moduli, optical properties, reduced gas permeability and increased heat resistance [3-5].

The commercial importance of polypropylene (PP) has promoted the development of PP composites reinforced with particles, fibres, and more recently layered inorganic fillers [3, 6, 7]. There is a requirement to provide compatibility between the different phases as with conventional micron scale fillers. PP has a non-polar molecular chain structure and in order to promote intercalation–exfoliation of clay layers, two approaches are typically used. From the polymer aspect, polarity is introduced by including polar functionality. Poly(propylene-g-maleic anhydride) (PP-g-MA) poly(propylene-g-glycidyl methacrylate) (PP-g-GMA) and poly(propylene-g-acrylic acid) (PP-g-AA) act as compatibilisers when blended with neat PP. The polarity provides coupling with polar groups on the clay surface and improves the interfacial adhesion [5, 8]. Filler particles are treated with organic surface modifiers such as surfactants. The treatments enhance the reinforcement, and in the case of cationic alkyl ammonium salts, the surfactant may intercalate clay layers to form a hydrophobic environment for PP chains to enter interlayers.

The clay used in this study is Bentone-34, a montmorillonite (MMT) clay that has a 2:1 layered structure, comprised of two silica tetrahedra fused to an edge-shared octahedral sheet (usually alumina or magnesia). The sheets are weakly held by van der Waals forces and can be partially separated or exfoliated. The aim of this investigation is to prepare NCs with emphasis on thermomechanical behaviour resulting from the presence of MMT content and PP-g-MA. TTS response of the NC will be measured and computed using the WLF model.

2. Experimental and methodology

Preparation of composites

All the materials used for the preparation of NC were dried in an oven at 80 °C for 12 h before use. A master batch was prepared by mixing 90:10 PP:PP-g-MA by a solution blending

(dissolved in xylene at 120 °C). The bentonite was dispersed in the hot master batch solution using an Ultra Turrax (IKA Werk, model T45) disperser for 15 min with a shear rate of 5000 rpm. The hot clay dispersion was poured into cooled methanol to precipitate the mixture. The mixture was filtered and dried in a vacuum oven (100 °C, 48 h) to remove solvent. Four NC were prepared with as listed in Table 1.

Table 1. Nomenclature and composition of polypropylene bentonite nanocomposites (masterbatch composed of 90 %vol PP and 10 %vol PP-g-MA).

Nanocomposites	Polypropylene (%vol)	Master Batch (%vol)	Bentonite (%vol)	R _g (nm)	D
Polypropylene	100	0	0		
PPMaBen-1	-	99.0	1.0	6.74	-2.82
PPMaBen-2	-	98.0	2.0	7.22	-2.78
PPMaBen-2.5	-	97.5	2.5	7.37	-2.69
PPMaBen-3	-	97.0	3.0	7.66	-2.58

R_g is the radius of gyration and D is the fractal dimension, from Guinier and Porod plots, respectively.

NC sheets were prepared using a hot press at 180 °C with a load of 1 tonne. The sheets were annealed in an oven at 100 °C for 12 h followed by 50 °C for 6 h.

Thermomechanical properties

Modulated force thermomechanometry (mf-TM) of PP and NCs were conducted using a Perkin-Elmer Pyris Diamond DMA in tensile mode. Test specimens were subjected to a sinusoidal applied stress at frequencies of 0.1, 0.2, 0.5, 1, 2, 5, 10, 50, and 100 Hz at over the range of -35 to 130 °C, heating rate of 2 °C.min⁻¹. The sample geometry was 4 x 1.5 x 10 mm.

TTS [9] operates on the principle that low temperature is equivalent to high frequency response and high temperature associated with low frequency response. The TTS method involves testing a material over a range of frequencies at constant temperature increments. These isothermal curves are frequency versus modulus (storage and loss). From these curves a reference temperature is chosen and all other curves are shifted horizontally and/or vertically to superimpose on the reference curve. A single curve is created with a frequency or time domain (x-values) extending beyond that of the isothermal frequencies curves. The newly formed curve is referred to as a master curve. The magnitude of the horizontal shift or vertical shift is the shift factor (denoted by a_t for horizontal shift factor and a_v for vertical shift factor). Vertical shifts are sometimes required to account for change in density at different temperatures. This vertical shift factor is described in Equation 1 as

$$a_v = \frac{T_g \rho_g}{T \rho} \quad (1)$$

Where ρ_g is the density of material at the glass transition temperature, T is temperature and ρ is the density at T.

Models have been created to describe the relationship between shift factors and temperatures to form master curves based upon TTS. A common shift factor model used is the Williams-Landel-Ferry (WLF) model. It relates shift factors to temperature in terms of

$$\log(a_t) = \frac{-C_1(T - T_r)}{C_2 + (T - T_r)} \quad (2)$$

Where $\log(a_t)$ is the temperature of the reference curve, and C₁ and C₂ are numerical constants for the particular material relating to free volume expansion.

3. Results and discussion

The X-ray scattering pattern of pure polypropylene and each of the NC showed a primary diffraction peak at $2\theta = 0.13$ indicating a long period $d_{001} = 67.87$ nm. The intensity of the peaks

was observed to increase with the increase of the nanoparticle content in the NC. These results imply that in all NCs, the clay particles were dispersed in a similar fashion despite their concentration as all the NCs shows scattering peak at the same 2θ angle. The long period between the clay layers indicate that the clay particles were exfoliated and dispersed widely rather than the polypropylene molecules intercalating in the clay layers. This may be due to the lack of miscibility between hydrophilic clay particles and hydrophobic polypropylene molecules [10]. The PP-g-MA and clay ratio in each NC was altered with increasing concentration of clay. PPMaBen-1 had the highest PP-g-MA–clay ratio that was gradually decreasing with increasing clay content and PPMaBen-3 had the lowest. But interestingly, all the NC film showed scattering peaks at the same 2θ angle and therefore, it can be concluded that MA content in the range used, had little effect on the intercalation of polypropylene and unmodified clay. The increase of intensity of the scattering peak of the NC with increase of the clay content implies uniform dispersion of clay particles in the polymer matrix. Figures 1 and 2 display the corresponding Guinier and Porod plots of the NC showing their regions. The radius of gyration (R_g) and fractal dimension (D) calculated from the linear region are presented in Table 1. Results from the Porod plot shows that the D values of all the NC are between -2 and -3 . This indicates that clay particles in the polypropylene matrix are mass fractal with a three dimensional structure. R_g value increases from 6.74 nm to 7.66 nm as the clay load increases in the NC. The increase of radius of gyration indicated that at higher concentration MMT particles interacted forming agglomerates [11]. This is supported by the increase of Porod slope from -2.82 to -2.58 as the particles in the system became more mass fractal with clay loading.

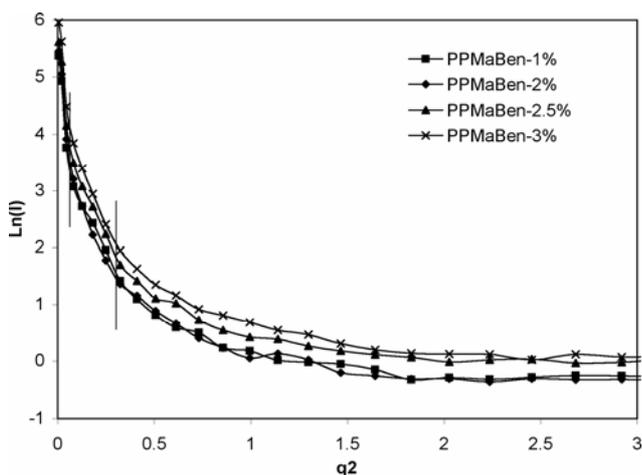


Fig. 1. Guinier plot for PP and NC

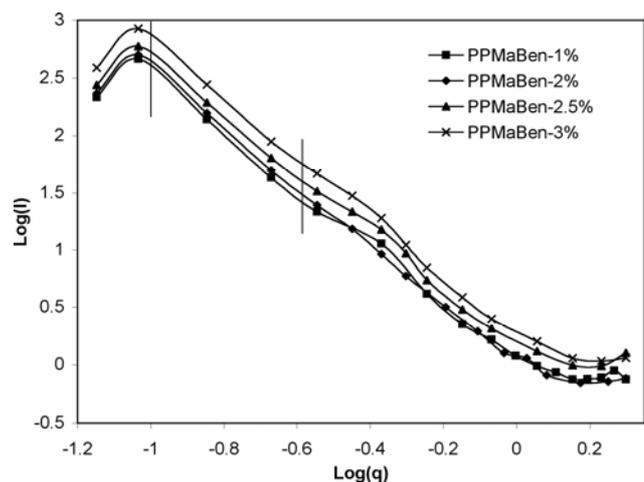


Fig. 2. Porod plot for PP and NC

PP undergoes several relaxation transitions dependent on temperature. Figure 3 shows the storage, loss and $\tan(\delta)$ curves at frequencies as described in the method. PP exhibited a glass transition that was evident from the $\tan(\delta)$ curve peak from -20 to 20°C . Following the PP exhibited a crystalline slip transition that spanned from about 30 to 100°C . The major change in PP behaviour is through the glass transition where the storage modulus decreased significantly due to temperature activated structural relaxations. An increase in the stiffness was observed with addition of MMT. The 1% vol MMT increased the E' -modulus by an order of magnitude compared with neat PP. The 2% vol MMT provided a further increase, but the change with 2.5 and 3% vol was less pronounced. This was attributed to the clay particles having been dispersed throughout the PP matrix and imparting rigidity in the composite in addition to existing interactions between clay particles and polymer. PP-g-MA bonds to MMT while its PP sequences co-crystallise within PP. In this manner, physical crosslinks are formed between PP-g-MA and clay and by the PP crystals.

Taking the elastic response exhibited by the PP at the various frequencies, the curves were shifted with reference to the response at 30°C . The resultant master curve generated from the PP is shown in Figure 4. Two regions in the log-frequency domain can be observed, signified by a change in the slope of the master curve. At low log-frequency, the master curves are distinguished with

subsequent addition of clay. As frequency increased, the curves approach a common modulus, the plateau modulus. This plateau region signifies that at high frequency the time for polymer molecular motions to occur is limited by the time-frame of the experiment. In the lower frequency range the increase in time permits slower polymer segmental relaxations. The presence of MMT particles appears to restrict motion comparable with clay content and state of dispersion.

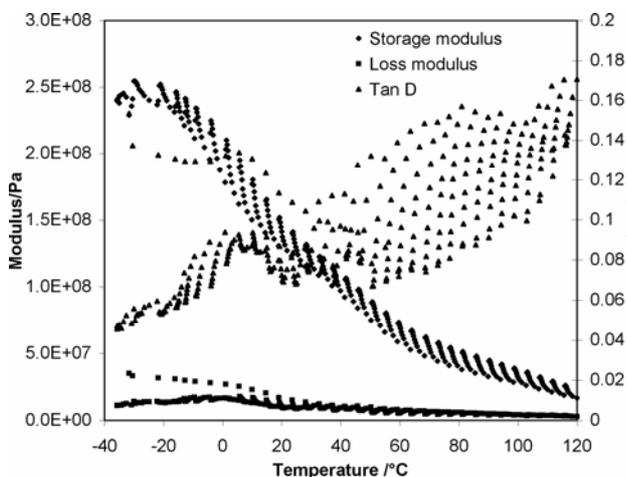


Fig. 3. df-TM of PP.

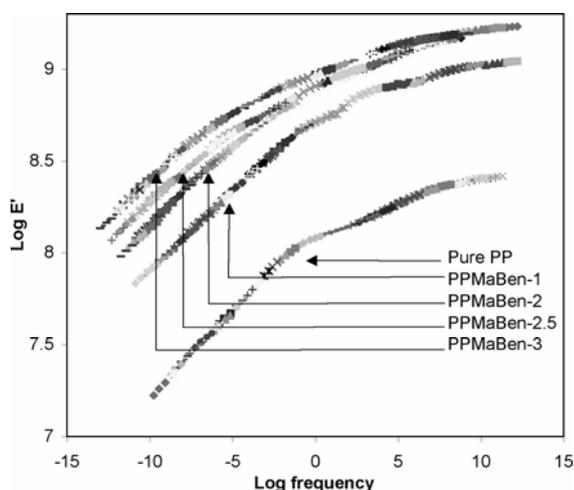


Fig. 4. E'-modulus master curves of PP and NC.

Conclusion

The morphology of PP – bentonite nanocomposites indicated the clay particles in the matrix were mass fractal with three-dimensional structure. This was supported by the radius of gyration increase with clay loading and at higher content, tended to exhibit interactions that indicated the formation of agglomerates. Master curves of the thermally activated glass transition and crystal slip mechanism were constructed, extending the normal time-temperature relationship. At low log frequency, there is dependence on clay content but at higher log frequency, the response was less determined by clay content as the plateau region was being reached and relaxation response of polymer limited.

References

- [1] Y.-S. Ding and Zhang Z.-C., *Gaodeng Xuexiao Huaxue Xuebao*, **25**, 1351 (2004).
- [2] A. Rande, K. Nayak, D. Fairbrother and N.A. D'Souza, *Polymer*, **46**, 7323 (2005).
- [3] S. Parija, S.K. Nayak, S.K. and Verma, S.S., Tripathy, *Polymer Composites*, **25**, 646 (2004).
- [4] C.I.L. Park, C. Won Mook, K. Mun Ho and O. Park, *Journal of Polymer Science, Part B: Polymer Physics*, **42**, 1685 (2004).
- [5] D.N. Bikiaris, A. Vassillou, E. Pavlidou and G.P. Karayannidis, *European Polymer Journal*, **41**, 1965 (2005).
- [6] P. Kodgire, R. Kalgaonkar, S. Hambir, N. Bulakh and J.P. Jog, *Journal of Applied Polymer Science*, **81**, 1786 (2001).
- [7] S. Hambir, N. Bulakh, P. Kodgire, R. Kalgaonkar and J.P. Jog, *Journal of Polymer Science, Part B: Polymer Physics*, **39**, 446 (2001).
- [8] M.L. Lopez-Quintanilla, S. Sanchez-Valdes, L.F. Ramos de Valle and F.J. Medellin Rodriguez, *Journal of Applied Polymer Science* **100**, 4748 (2006).
- [9] M.L. Williams, R.F. Landel, and J.D. Ferry, *Journal of the American Chemical Society*, **77**, 3701 (1955).
- [10] G. Mani, F. Qinguo, S.C. Ugbolue and Y. Yiqi, *Journal of Applied Polymer Science*, **97**, 218 (2005).
- [11] Y. Chen, S. Zhou, G. Gu and L. Wu, *Polymer*, **47**, 1640 (2006)