EFFECT OF MATRIX PLASTICISATION ON THE CHARACTERISATION OF POLYPROPYLENE /CLAY NANOCOMPOSITES

Yu Dong[a] and Debes Bhattacharyya[b]

[a] Department of Mechanical Engineering, Curtin University of Technology
GPO Box U1987, Perth, WA 6845, Australia.
[b] Centre for Advanced Composite Materials, Private Bag 92019, The University of Auckland, Auckland, New Zealand.

Introduction

The matrix plasticisation, rarely addressed for polypropylene (PP)/clay nanocomposites, might bring some uncertainty in their material characterisation for good mechanical performance. This paper describes such possible negative plasticisation effect from maleated PP (MAPP) by using X-ray diffraction (XRD) analysis, transmission electron microscopy (TEM), differential scanning calorimetry (DSC) and mechanical testing. An amount of MAPP in excess of a certain saturation level is found to adversely affect the mechanical properties of nanocomposites, thus losing its compatibiliser role.

Experimental Details

Materials and Sample Preparation

PP homopolymer H380F (melt flow index MFI=25 g/10 min) was supplied by Clariant (New Zealand) Ltd and MAPP Exxelor™ PO1020 (MA content: 0.5-1 wt%, MFI=~430 g/10 min) was selected as the compatibiliser from ExxonMobil Chemical (Germany). NANOLIN™ DK4 organoclay (d_{001}=3.56 nm), modified with octadecylammonium salt, was obtained from Zhejiang Fenghong Clay Chemicals, Co. Ltd, China. PP/clay nanocomposites were prepared by twin screw extrusion of PP and MAPP pellets with downstream clay feeding and then recompounded to extend the residence time. Finally dried nanocomposites were injection moulded to prepare testing samples. The material preparation was described in details elsewhere [1]. The nanocomposite formulations were based on various MAPP contents from 0, 3, 6, 10 to 20 wt% (fixed clay content: 5 wt%).

Experimental Characterisation

The wide angle X-ray diffraction (WAXRD) patterns were captured by Bruker D8 ADVANCE with Cu-k_α (λ=1.54Å) in the 2θ range of 2-30^o at a scan rate of 0.4°/min. The TEM analysis was performed for cryosectioned thin films of 70 nm thickness with a Philips CM12 at accelerating voltage of 120 kV. A DSC-Q1000 TA instrument was used to measure the crystallisation behaviour of nanocomposites from -60 to 220^{o}C at the heating and cooling rates of 10 ^{o}C/min. Tensile, flexural and impact tests were conducted according to ASTM D638, D790 and D6110, respectively, with average data from five samples.

Results and Discussion

The sizes of clay tactoids are greatly reduced with the mix of partially intercalated/exfoliated clay platelets (lateral dimension of 200-500 nm) when increasing the MAPP content, Fig.1. Beyond the MAPP content of 6 wt%, the clay dispersion is not considerably enhanced, implying the threshold of compatibility for the optimal amount of MAPP.

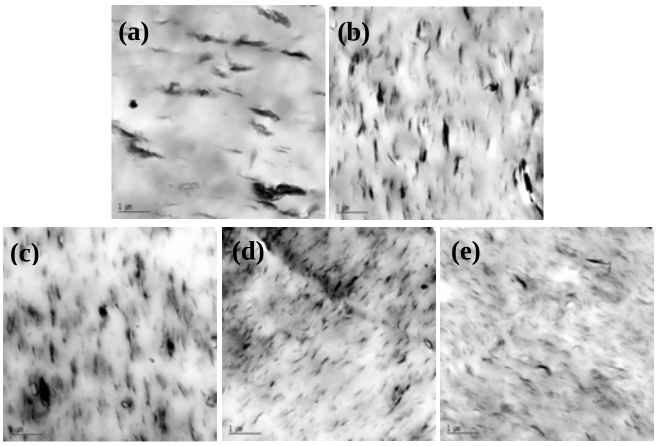

Fig.1 TEM micrographs of 5 wt% filled PP/clay nanocomposites at 15000× magnification with various MAPP contents: (a) 0 wt%, (b) 3 wt%, (c) 6 wt%, (d) 10 wt% and (e) 20 wt%.

Tensile moduli and strengths are initially enhanced but then almost level off at a higher MAPP content (10-20 wt%) whilst the impact strengths decline dramatically with increasing the MAPP content due to the brittle nature of MAPP, Fig.2. At the lower MAPP content (0-3 wt%), a higher level of impact strength can be maintained with over 61% increase compared to that of neat PP.

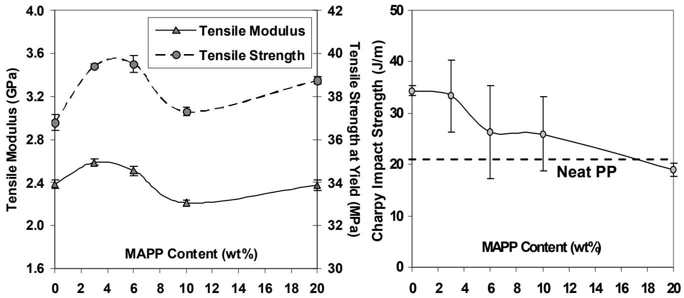

Fig.2 Mechanical properties of 5 wt% filled PP/clay nanocomposites.

The WAXRD patterns for crystalline structures of PP/clay nanocomposites at various MAPP contents are compared to those of neat PP and MAPP, Fig. 3. Five characteristic peaks of the α-PP crystalline structure are observed in all the materials at 2θ angles of about 14.0°, 16.8°, 18.6°, 21.2° and 21.9° corresponding to the lattice planes of (110), (040), (130), (111) and (131). For nanocomposites without MAPP, the other peak of β-PP structure is also identified on the lattice plane of (300) at 2θ angles of about 16.1°. β-PP structure can induce better impact resistance and greater elongation in comparison to α-PP [2,3], in good accordance with previously obtained higher impact strength of nanocomposites (MAPP: 0 wt%). In the presence of MAPP, β-PP structure completely disappears and the peak intensities of α(040) are significantly diminished when MAPP content is increased from 3 to 20 wt%. Since α-PP structure mainly contributes to the improvement of tensile modulus and better yield stress [2,3], it is believed that at a fixed clay content of 5 wt%, increasing the amount of MAPP enables to prevent the further growth of α-PP, thus leading to the lower tensile properties of nanocomposites at a higher MAPP content.

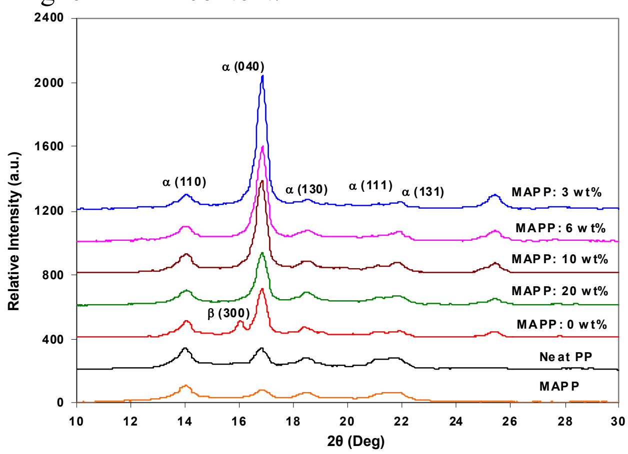

Fig.3 WAXRD patterns of neat PP, MAPP and 5 wt% filled PP/clay nanocomposites.

The effect of MAPP content on crystallisation behaviour of PP/clay nanocomposites is presented in Fig.4. When no compatibiliser (MAPP) is used in the formulation, the inclusion of clay, to the greatest extent, enhances the crystallisation temperature of nanocomposites up to 121°C owing to the conventional heterogeneous nucleation effect despite the less favourable interfacial interactions. With increasing the MAPP content, the crystallisation temperature appears to gradually decline, reaching the lowest value of 117 °C at 20 wt%. However, the crystallisation temperature of nanocomposites still remains well above that of neat PP (113°C). Such compromising results might arise from the counteracting roles of clay and MAPP as positive and negative contributors to the nucleating effect, which becomes detrimental due to the excessive amount of MAPP with low crystallinity.

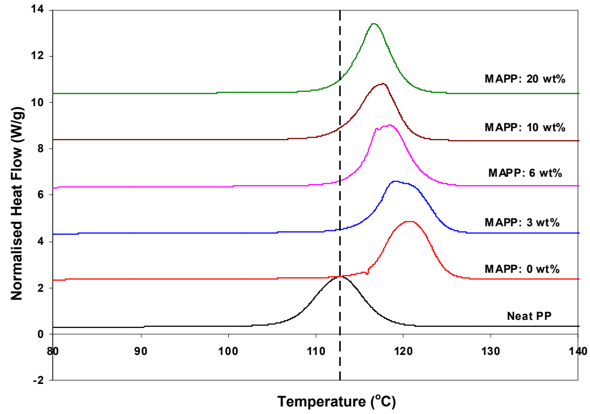

Fig.4 DSC curves of neat PP and 5 wt% filled PP/clay nanocomposites at a cooling scan.

Conclusion

The matrix plasticisation of MAPP makes a great impact on the mechanical properties, clay dispersion, crystalline structures and crystallisation behaviour of PP/clay nanocomposites. A well-balanced material formulation between clay and MAPP should be carefully selected to eliminate any adverse effect from an excessive amount of MAPP to hinder clay's positive nucleating role and growth of α-PP crystalline structures for the enhancement of mechanical properties.

Acknowledgements

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References

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