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Bureau, Martin N.; Ton That, Minh Tan

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SELECTIVE COMPATIBILIZATION FOR STIFFER, HIGH IMPACT TPO/CLAY NANOCOMPOSITES

Martin N. Bureau and Tan Minh Ton-That*
Industrial Materials Institute, National Research Council Canada

Abstract

Different compatibilization strategies from master batch mixing using a twin-screw extruder with various coupling agents were investigated to improve the stiffness of nanocomposites based on a high impact TPO (n-Izod > 600 J/m) with 2% and 4% of organoclay content. Three coupling agents based on grafted maleic anhydride polymers (gMA) were used to tailor the compatibility of the organoclays to either or both the rubbery domains and the polyolefin matrix. A detailed microstructural of the different nanocomposites revealed the preferential presence of organoclays in the rubbery domains, the matrix or both depending on the masterbatch sequential compounding strategy, i.e. the type of coupling agent(s) mixed with the type of organoclay. As anticipated, the presence of organoclays in both the matrix for improved tensile properties (Young's modulus and stress and strain at yield) and in the rubbery domains for higher impact resistance (n-Izod at 0 and 23°C and flat sheet impact at -40°C). A control experiment on a blend of PP and an ethylene-propylene copolymer with a PPgMA coupling agent and organoclay compounded in a similar fashion led to the usually improved tensile properties but reduced impact resistance. In this case, the organoclay was found present in the matrix only, as the coupling agent used could not compatibilize the organoclay to the copolymer phase. It is concluded that organoclays act on the rubbery phase to increase its toughening effect in the TPO, presumably by increasing the cavitation stress of the TPO.

Introduction

Polymer nanocomposites based on nanoclays have been the subject of a very large number of publications since the pioneering papers of Toyota Research Institute [1]. In most if not all cases, when reasonable increases in mechanical stiffness and strength was achieved as a result of nanoclay platelets dispersion, intercalation and/or exfoliation and good nanoclay platelet-matrix interactions, it was done to the cost of reduced ductility, fracture toughness and impact resistance. In particular, works on melt compounded blends of commercial TPOs with organoclays and maleic anhydride-grafted polypropylene at various amounts reported fairly important improvements in stiffness accompanied by as important reduction in impact strength [2-4]. A fair amount of work has therefore been targeted towards improving stiffness and strength without negatively affecting these other important properties. In our laboratory, we have undertaken an important pre-industrial project to address this problem. This paper reports our effort to use selective compatibilization, i.e., different coupling agents with specific affinity for each of the nanocomposite constituents, in a nanoclay-based TPO nanocomposites to obtain improved tensile strength and modulus and impact strength.

Materials & Methods

A thermoplastic polyolefin TPO proprietary grade, provided by Basell, was used as the matrix of reference in this work. It was chosen for its high notched Izod impact strength at room temperature (> 600 J/m). DSC analysis of the TPO revealed the presence of three glass transitions: one at -33°C, another at -5°C and a third at 36°C. TEM and AFM analysis of the TPO showed presence of 40%vol fine and uniformly dispersed domains, most likely corresponding to an elastomeric phase, within which leaflets were noted, presumably of talc. The nanoclay reinforcement chosen, LDH Perkallite F100 supplied by Akzo Nobel, was a synthetic clay based on layered aluminum/magnesium double hydroxide organically-modified with hydrogenated fatty acid, with an aspect ratio of 200 according to the supplier. Three coupling agents based on grafted maleic anhydride polymers (gMA) were used to tailor the compatibility of the organoclays to either or both the rubbery domains and the polyolefin matrix. The first (Fusabond P MZ203D, supplied by DuPont Packaging & Industrial Polymers) is a PP impact copolymer with a propylene-ethylene backbone (P-EgMA). The second (Polybond 3200, supplied by Chemtura) is a homopolymer PP grafted with maleic anhydride (PPgMA). The third (Royaltuff 498, supplied by Chemtura) is an ethylene-propylene ethylidene norbornene rubber grafted with maleic anhydride (E-P-ENGMA).

Using a twin-screw compounder, two different masterbatches were produced with 10%wt nanoclay and 10%wt coupling agent (s). A 34-mm Leistritz twin-screw extruder was used for compounding at a mixing temperature of 200°C, a screw speed of 200 rpm and a feed rate of 5 kg/h. The screw elements and feeding location are shown in Figure 1.

The first masterbatch (MB-A) consisted of LDH Perkallite F100 and Royaltuff 498 in TPO. It was designed as such to promote miscibility of the organoclay to the elastomeric phase present in TPO. The second masterbatch (MB-B) consisted of LDH Perkallite F100 and equivalent amounts of Polybond 3200 and Fusabond P MZ203D in TPO. In both cases, organoclay was fed through a side feeder. MB-A and MB-B were then diluted with TPO to a nominal 2 and 4%wt nanoclay. Contrary to the first, this second masterbatch was designed to promote miscibility of the organoclay to the matrix of the TPO. The compositions of the TPO nanocomposites, designated as n-TPO-X-# where n stands for nanocomposite, X for MB type (A or B, or both) and # for nominal clay content (2 or 4%), are shown in Table 1.

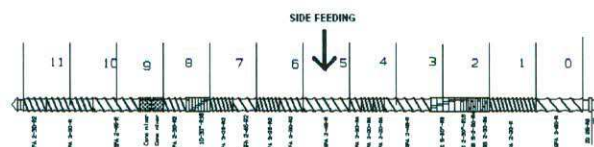


Figure 1. Screw elements and feeding location used on the 34-mm Leistritz twin-screw extruder.

Table 1. Composition (%wt) of the TPO nanocomposites.

| Materials | MB-A | MB-B | Global TPO Content | Global Clay Content |
|----------------------|----------|----------|--------------------|---------------------|
| TPO | | | 100 | 0 |
| nTPO-A2 nTPO-A4 | 20 40 | | 96 92 | 2 4 |
| nTPO-B2 nTPO-B4 | | 20 40 | 96 92 | 2 4 |
| nTPO-AB2 nTPO-AB4 | 10 20 | 10 20 | 96 92 | 2 4 |

For characterization purposes, the TPO control and TPO nanocomposites were molded by injection at 200°C using a 50-ton Boy press. All molded specimens had a nominal thickness of 3.2 mm. X-ray diffraction (XRD) analyses were done using a Bruker Discover 8 diffractometer operating at 40 kV and 40 mA with CuK α radiation in the Bragg–Brentano configuration. The analyses were done at relatively small angles ($0.5^\circ \leq 2\theta \leq 8^\circ$) to determine the degree of intercalation and exfoliation of clay using the clay interlayer spacing, d_{001} , by means of Bragg's law ($\lambda = 2d_{001} \sin\theta_{001}$). TEM observations were made on cryogenically ultra-microtomed thin sections using a high resolution TEM Hitachi H 9000 at 200 kV.

Tensile testing was done at room temperature according to ASTM D638 using a mechanical tester with a non-contact video extensometer. The tests were done at a crosshead speed of 5 mm/min. Young's modulus, yield stress and strain at break were obtained from the tensile stress-strain curves. A minimum of five tests was performed for each reported value.

Notched Izod impact testing was also done at room temperature according to ASTM D256. The notch was produced by careful machining following ASTM guidelines. Values reported are averages of at least 10 tests.

Finally, multi-axial impact fracture testing by means of flat sheet impact tests were performed at -40°C according to ASTM D5628 for more representative impact testing. 50-mm diameter disks were used. Values reported in terms of absorbed energy at maximum load and total energy absorbed during impact testing are averages of at least 10 tests.

Results

The small angle XRD spectra of the TPO control and TPO nanocomposites are shown in Figure 2. Calculated d-spacing of clay platelets is also included in Figure 2. The spectra of TPO nanocomposite reveal very important levels of intercalation with d-spacing ranging from 4.92 nm to 5.08 nm, when compared to initial d-spacing of organoclay of 2.5 nm according to supplier. Reported d-spacing also did not appear to be largely affected by the compatibilization strategy (maximum variation of 3%), i.e., whether a P-EgMA/PPgMA compatibilizer was used or a E-P-ENGMA was used for the nanocomposites. This observation suggests that intercalation of organoclay was quite effective either with a coupling agent blend based on homopolymer PP and ethylene-propylene copolymer or one based on ethylene-propylene ethylidene norbornene rubber. A second peak was observed for nTPO-B2 and nTPO-AB2 around 7 nm, indicating a higher degree of intercalation.

TEM micrographs of the TPO nanocomposites are shown in Figure 3 for nTPO with MB-A, MB-B and both MB at 2%wt organoclay. The TEM micrographs indicate that organoclays are well dispersed in the form of fine aggregates in the nanocomposites. Results also showed organoclay stacking of typically 20-30 nm in thickness (not shown here). With the average interlayer spacing of 5 nm obtained from XRD, one would estimated the number of clay platelets per stacking to be around 4-6. These micrographs also show the preferred presence of organoclay in the (presumably) elastomeric domains of TPO for nTPO-A, in the matrix of TPO for nTPO-B and for both for nTPO-AB. Very similar findings for the nTPO were made at 4%wt organoclay (not shown here).

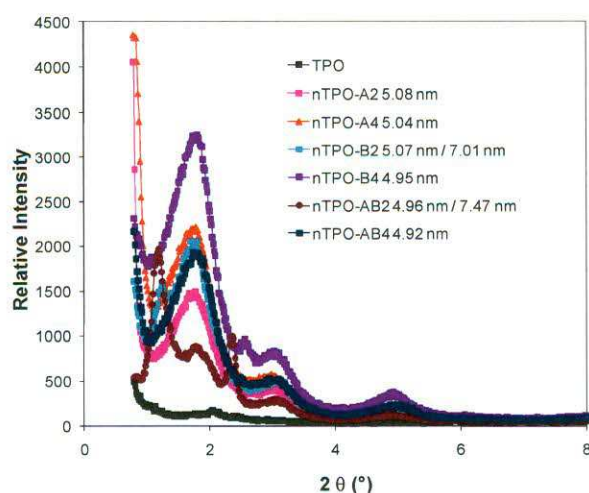


Figure 2. Small angle XRD spectrum of the TPO control and TPO nanocomposites. d-spacings are indicated.

This observation of organoclay preference for either matrix or elastomeric phases or even both phases of TPO depending on the coupling agent(s) used indicates that coupling agent(s) can be used to select the phase(s) where organoclay will be present in the TPO nanocomposite. As no evidence of phase separation related to the coupling agent was observed, it is assumed that for the TPO used in this study, a coupling agent blend based on P-EgMA/PPgMA is miscible with the TPO matrix while E-P-ENGMA is miscible with the elastomeric TPO phase.

The tensile results of the TPO tested are shown in Table 2. In general, nTPO-A showed slightly lower Young's modulus values than those of TPO, while nTPO-B and nTPO-AB showed modulus values above those of TPO control (+10% approximately). In terms of yield stress, nTPO-A also showed values below those of TPO, and nTPO-B and nTPO-AB showed values similar or above those of TPO (except for nTPO-B2, which showed -5% values). An opposite trend was observed for strain at yield, which compared to TPO values, did not change significantly for nTPO-A, but slightly decreased for nTPO-B and nTPO-AB. Elongation at break showed the same trend, although much more marked, with values of 500-600% for TPO and nTPO, while values of 100-200% were obtained for nTPO-B and nTPO-AB.

These effects on tensile behavior of the compatibilization strategy are in complete agreement with expected effects of organoclay presence in either or both elastomeric and matrix of TPO. When they are preferably located in the TPO matrix, organoclays lead to an increased rigidity, a maintained or slightly decreased yield

stress and strain, and decreased elongation at break. On the contrary, when organoclays are present in the TPO elastomeric phase, they do not result in increases in TPO rigidity or strength and do not affect negatively their ductility.

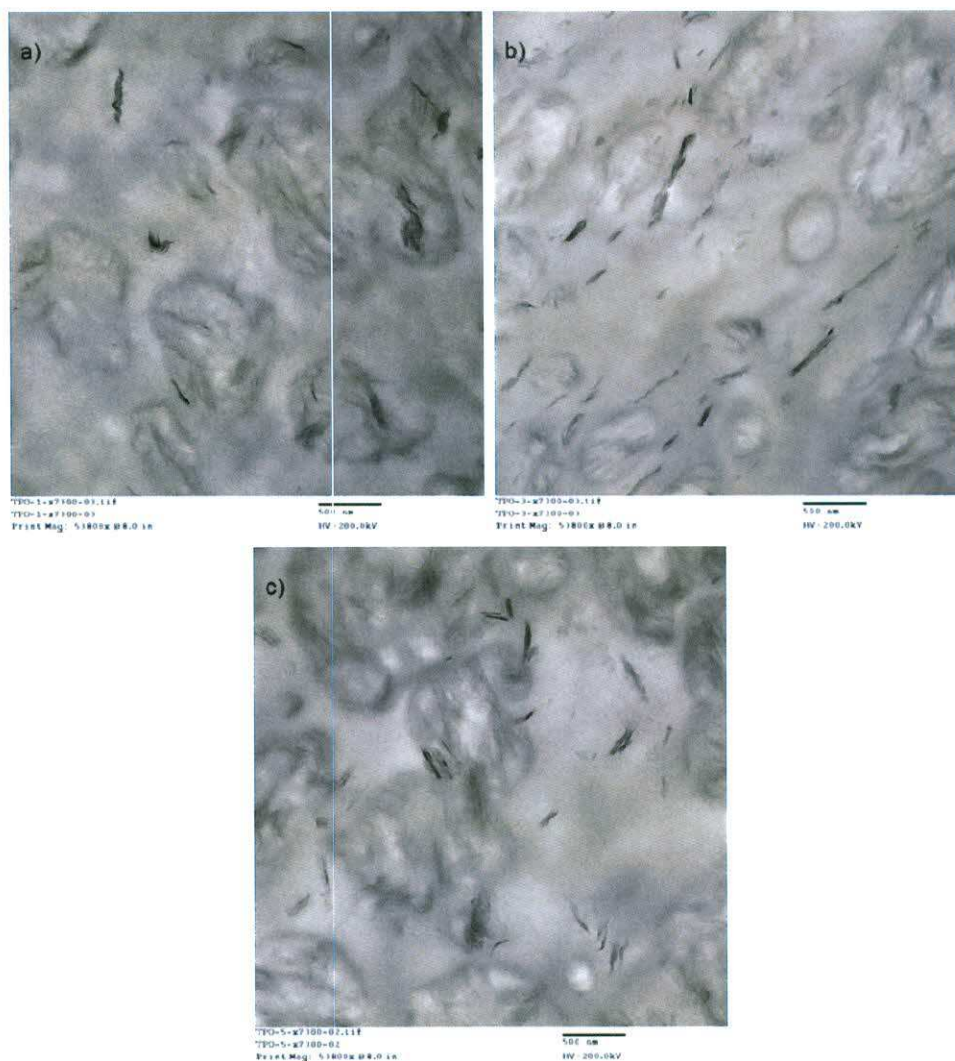


Figure 3. TEM micrographs at high magnification of the TPO nanocomposites: a) nTPO-A2, b) nTPO-B2, c) nTPO-AB2. Scale bars at bottom of pictures are for 500 nm.

Table 2. Tensile results of the TPO control and TPO nanocomposites. Results reported are average and standard deviations (in parentheses).

| Sample | Young's Modulus (MPa) | Yield Stress (MPa) | Yield Strain (%) | Elong. Break (%) |
|----------------------|-----------------------|--------------------------|--------------------------|------------------|
| TPO | 824 (22) | 14.1 (0.1) | 16.7 (0.8) | >500 |
| nTPO-A2 nTPO-A4 | 762 (24) 720 (13) | 13.2 (0.1) 12.5 (0.1) | 17.0 (0.9) 18.0 (0.2) | >600 >500-600 |
| nTPO-B2 nTPO-B4 | 890 (27) 914 (14) | 13.4 (0.1) 14.7 (0.1) | 14.5 (0.5) 15.8 (0.4) | 100-200 |
| nTPO-AB2 nTPO-AB4 | 882 (37) 878 (55) | 14.5 (0.1) 13.9 (0.1) | 14.4 (0.6) 15.6 (0.4) | 100-200 |

The notched Izod results at 23°C and multi-axial impact fracture results at -40°C are shown in Table 3. The notched Izod results indicate first that the TPO grade chosen indeed is above 600 J/m at room temperature. They also show that at room temperature notched Izod increased slightly by 3 to 10% upon organoclay addition, with the highest values obtained at 4% organoclay. While no clear trends could be extracted from these results with respect to organoclay presence in either TPO elastomeric phase or matrix, the strongest increases were noted on nTPO-AB, the TPO nanocomposite with both MB, i.e. with organoclay present in both phases.

Table 3. Notched Izod results at 23°C and multi-axial impact fracture results at -40°C of the TPO control and TPO nanocomposites. Results reported are average and standard deviations (in parentheses).

| Sample | Notched Izod at 23°C (J/m) | Multi-axial Impact at -40°C (J) | |
|----------------------|----------------------------|---------------------------------|--------------------------|
| | | at Max Load | Total |
| TPO | 628 (12) | 25.8 (0.8) | 59.4 (1.2) |
| nTPO-A2 nTPO-A4 | 646 (10) 671 (11) | 24.4 (1.3) 27.0 (0.8) | 58.8 (2.7) 62.6 (1.5) |
| nTPO-B2 nTPO-B4 | 655 (11) 655 (14) | 26.1 (0.9) 28.4 (1.1) | 61.1 (1.1) 63.7 (1.2) |
| nTPO-AB2 nTPO-AB4 | 665 (11) 693 (16) | 26.5 (0.9) 26.0 (2.7) | 58.3 (2.7) 62.8 (1.3) |

Results of multi-axial impact at -40°C, also shown in Table 3, confirm the trends observed from notched Izod, i.e. that impact resistance of the various TPO nanocomposites prepared in this study, even at low temperatures (under T_g), is maintained and even increased with respect to TPO control. While standard deviation are larger relatively to the impact values obtained, modest but significant increases (5-7%) were indeed obtained for nTPO-A, nTPO-B and nTPO-AB, again for 4% organoclay. In general, nTPO-B showed the best impact resistance, slightly above both nTPO-A or nTPO-AB, suggesting that having organoclays dispersed in the TPO matrix increases impact resistance more effectively.

Discussion

This study focused on different compatibilization strategies from master batch mixing using a twin-screw extruder with various coupling agents for high impact TPO nanocomposites based on a synthetic organically-modified clay. A first masterbatch was produced by mixing TPO, organoclay and a blend of two coupling agents (grafted maleic anhydride homopolymer PP and impact PP copolymer). A second masterbatch was produced by mixing TPO, organoclay and an ethylene-propylene ethylidene norbornene rubber grafted with maleic anhydride. Two different nanocomposites were obtained from each masterbatch diluted with TPO and a third from blending each masterbatch and TPO dilution.

Results in this study showed that using grafted maleic anhydride homopolymer PP and impact PP copolymer or ethylene-propylene ethylidene norbornene rubber grafted with maleic anhydride as coupling agents in organoclay-based TPO nanocomposites led to quite high levels of organoclay intercalation. TEM observations even suggested that organoclays could be guided to the matrix or elastomeric phase of TPO by using either the coupling agent mix of homopolymer PP and impact PP copolymer or the ethylene-propylene ethylidene norbornene rubber grafted coupling agent, respectively. The resulting mechanical properties of the TPO nanocomposites were obviously influenced by organoclay presence in the matrix or elastomeric phase of TPO.

When the compatibilization strategy led to organoclay presence in the elastomeric phase of TPO, slightly reduced tensile results in terms of Young's modulus and strength, with, however, maintained elongation at break, and only slightly improved impact resistance, both at room temperature and at -40°C , were obtained. When organoclays were present in the TPO matrix, Young's modulus, tensile strength, and impact resistance increased with respect to TPO control. Highest mechanical properties, obtained for 4%wt organoclay TPO nanocomposite compatibilized with the coupling agent mix of homopolymer PP and impact PP copolymer, were 11% increase in Young's modulus, 5% in tensile strength (yield stress), 5% also in notched Izod strength at 23°C and 7-9% increase in multi-axial impact strength at -40°C . To the knowledge of the authors, these results are the first to show increases in Young's modulus and tensile strength as well as impact resistance, especially at low temperatures, at the same time in a high impact polymer like TPO.

While these mechanical improvements are significant, a detailed knowledge of the TPO composition would permit to perform a better coupling agent(s) selection, without a doubt leading to higher TPO performance.

Conclusions

Using different combinations of coupling agents for enhanced compatibility between organoclays and specific polymer phases in TPO, it is possible to effectively disperse and guide organoclays in either or both the elastomeric domains or matrix of TPO. The mechanical properties of the resulting TPO nanocomposites can therefore be modulated for specific requirements. Improvements in Young's modulus, tensile strength and impact strength at room and low temperature could be obtained. A detailed knowledge of TPO chemistry is however necessary for optimal improvements in mechanical properties.

Acknowledgments

GM Corporation and Chemtura are gratefully acknowledged for respectively donating the TPO and the coupling agents based on maleic anhydride-grafted homopolymer PP and on ethylene-propylene ethylidene norbornene rubber used in this study.

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Key Words: TPO nanocomposites, organoclay, coupling agent, compatibilization, tensile properties, impact properties.