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EXPERIMENTAL INVESTIGATION ON THE CONSOLIDATION OF POLYPROPYLENE-CLAY NANOCOMPOSITES FIBERS

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Abstract

Unidirectional composites were produced from hot-compaction of polypropylene and polypropylene nanocomposite fibers. Microscopic observations first revealed that satisfactory level of consolidation could be achieved. Characterization of the laminate structure by X-ray diffraction then indicated that the clay (001) axis (normal to the clay platelets plane) remained oriented normal to the fiber length as well as the chain crystalline axis (c-axis) of polypropylene in the machine direction (with some improvement due to annealing). Characterization of flexural modulus showed that the properties of the unidirectional polypropylene nanocomposite laminates were nearly two times those obtained from plates made from randomly oriented polypropylene fibers.

Introduction

Polymers like polypropylene lack sufficient mechanical properties to be used in many engineering applications. To improve their mechanical properties, two main approaches have traditionally been employed [1]. The first and most common approach consists in adding foreign fillers or fibers such as talc or glass fiber. More recently, nanoparticles of clay and carbon nanotubes have also been used to enhance the mechanical properties of polypropylene [2,3]. A second approach that can be used to improve the mechanical properties consists in producing parts from oriented fibers of a polymer. The production of such all-polymer composites has been shown to be successful for several polymer materials including polypropylene [4,5] and commercial applications can now be found [6,7].

Consolidation of polymer fibers into solid laminates can be achieved by partially melting the oriented fibers. By using this procedure, one fraction of the material remains oriented to provide good material properties, while the melted fraction becomes the matrix phase. The resulting laminate properties are therefore a combination of those of the oriented fibers and those of the recrystallized molten region [8]. To improve laminate properties, it is of great interest to optimize the fiber properties. In a previous work on the production of nanocomposite reinforced fibers [9], the presence of clay nanoparticles in polypropylene fibers was shown to increase the fiber modulus by up to 30%. Tensile strength did not, however, show sign of significant improvement. This latter effect was attributed to possible fiber defect related to clay particle heterogeneities. Such defect, if present, would create important stress concentration leading to early fracture as stress increase.

In this paper, the results of an experimental investigation on the consolidation of polypropylene (PP) and polypropylene nanocomposite (PPNC) fibers is presented. Two reinforcing effects were targeted by using polymer fibers reinforced with nanoparticles of clay. First, by carefully selecting the temperature, it should be possible to keep some of the orientation of the polymer chain in the composite. Secondly, the presence of nanoparticles is expected to increase the mechanical properties of the laminate. The alignment of these nanoparticles during the drawing process may also have an effect on the final mechanical properties.

Experimental

Material

The material used in this study was a polypropylene (PP1274) having a melt flow rate of 12 and a density of 0.902 g/cm^3 obtained from Basell Company. A polymer nanocomposite of the same polypropylene (designated PPNC) was produced using a twin-screw extruder from a master batch containing 10wt% of Cloisite 15A from Southern Clay with 10wt% of maleic anhydride grafted PP, of Eastman Chemical. Master batch was then diluted to 2wt% clay with the extruder. To produce fibers, PP and PPNC were extruded at 220°C through a 37.75 mm (1.25 in.) extruder, followed by a gear pump and fiber die. The die contained 150 holes having a diameter of 380 µm and spaced by 0.5 mm. A constant mass flow rate of 4 kg/hr was used. A draw down ratio of about 22 was used to orient the fibers in air at the exit of the die before collection.

Consolidation Procedure

Unidirectional composites were produced by hot compaction of PP and PPNC fibers. These composites were manufactured by aligning manually a specific mass

(42 grams) of continuous fibers in an aluminum mold of 152 x 152 mm^2 to produce 2-mm thick plates. During consolidation, fibers were heated to a temperature comprised between 160 and 167°C, held at this temperature for a period varying from 5 to 15 minutes and then cooled to room temperature at a rate of 10°C/min. A constant pressure of 2.4 MPa (350 psi) was applied during the entire molding cycle. Typical temperature profile measured during processing is shown in Figure 1. "Annealed" plates were also produced by dispersing randomly oriented fibers cut to a 25.4 mm length. These plates were then molded at 180°C for 15 minutes to remove any possible effect of orientation. Due to the relatively high temperature employed, a 2 mm-thick aluminum frame was used as spacer between the upper and bottom halves of the mold to prevent excessive flowing of the material outside of the mold during consolidation.

Characterization

Micrographs of polished cross-sections were used to determine the voids distribution. To produce convenient image quality, specimens were polished and then observed with an optical microscope. Flexural tests were performed at 23°C using a three point bending set-up. These tests were performed using a span-to-depth ratio of 16 on 12.5 mm wide specimen. Differential scanning calorimetric (DSC) experiments were conducted using a Perkin Elmer scanning apparatus at a rate of 20°C/min. The degree of crystallinity of each specimen was then determined from the melting enthalpy, ΔH_m, using the relation:

$$\%cristal\,lnity = (\Delta H_m / \Delta H_m^o) X 100 \qquad (1)$$

where ΔH_m^o is the enthalpy of fusion of 100% crystalline PP, 207J/g [10]. Structure of PP and PPNC fibers was evaluated using X-ray diffraction. The PP and clay crystalline axes orientation factors [11] were determined from wide-angle X-ray diffraction pole figures of using a Bruker AXS X-rays goniometer equipped with a Hi-STAR two-dimensional area detector. The generator was set up at 40 kV and 40 mA and the copper K_α radiation (λ=1.542 Å) was selected using a graphite crystal monochromator.

Results

A micrograph of a polished specimen molded from randomly oriented PPNC fibers is shown in Figure 2. From this picture we can observe that fiber pattern was erased during molding. Randomly distributed voids, originating from trapped air that could not be evacuated during molding, can also be observed. Although not shown here, similar observations were made for plates molded from PP fibers. Flexural modulus and maximum flexural stress of plates molded from randomly distributed PP and PPNC fibers were determined. Flexural modulus of 1.65 and 1.85 GPa were obtained for the PP and PPNC, respectively. This corresponds to an increase of 12% of the flexural modulus for the PPNC. For the maximum flexural stress, similar values of 60.1 and 61.5 MPa were obtained for the PP and PPNC. This is in good agreement with a previous study that showed no increase in strength for PPNC fibers when compared to PP fibers [9]. These results will be used as benchmark for the remainder of the study.

The influence of the molding parameters on the void distribution was investigated for PP and PPNC unidirectional plates. Polished micrographs of PP plates produced at 165°C for two different holding times are shown in Figure 3. For a holding time of 5 minutes, large porosities can be observed between fibers, indicating insufficient resin melting to fill the gaps between the fibers. For a holding time of 15 minutes, only small voids can be observed between fibers, indicating a significant improvement of the consolidation quality. Similar results were also observed for the influence of the molding temperature, since void content was seen to decrease with increasing temperature.

The influence of the holding time and forming temperature on the flexural properties measured in the longitudinal (LD) and transverse (TD) directions was determined. Results were obtained for holding times of 10 and 15 minutes, since observations performed for a holding time of 5 minutes showed only poor consolidation (Figure 3a). Results obtained for holding time of 10 minutes are shown in Figure 4. As shown in figure 4a, a sharp increase in flexural modulus is measured between low and high forming temperature for PPNC (Figure 4a). However, for PP, the flexural modulus remained nearly constant for the entire range of temperature under investigation. Further investigations are needed to explain this difference. As shown in Figure 4b, maximal flexural stress in the longitudinal direction (LD) is nearly two times superior to that measured in the transverse direction (TD). The lower strength obtained in the transverse direction can be attributed to the remaining voids observed between fibers; these voids are acting as defects to initiate failure. The variation of the flexural properties for holding time of 15 minutes is shown in Figure 5. By opposition to what was shown in Figure 4, a nearly constant flexural modulus is measured throughout the entire range of molding temperature investigated. Increasing the holding time therefore allow increasing the temperature processing window without reduction of the flexural modulus. As shown in Figure 5b, maximum flexural stress measured in the TD was seen to increase

from 40 to 50 MPa for holding time of 15 minutes compared to 10 minutes. This increase in maximum flexural stress in TD is believed to be attributed to the reduction of the void content.

Results obtained in flexion are summarized in Figure 6. Compared to the PPNC "annealed" plates, a significant increase in flexural modulus is obtained for PPNC unidirectional laminates (Figure 6a). If the flexural modulus of the PPNC "annealed plates" is taken as a reference, the increase in modulus is of approximately 70%. When the flexural modulus of PP unidirectional laminates are compared to the one of the PPNC unidirectional laminates, a significant increase of 15% is measured. This shows that PPNC fibers can be molded into laminates to produce composites with higher performance. Summary of the results obtained for the maximum flexural stress is shown in Figure 6b. In the longitudinal direction, maximum flexural stress is 30% higher than values obtained for the randomly oriented plates. In the transverse direction, the maximum stress is 15% lower than for the randomly oriented plates. Reduction of mechanical is thought to be related to consolidation of the materials, voids observed between the fibers acting as defects to initiate the failure.

DSC experiments were conducted to measure the change in crystallinity due to the hot-compaction process. To determine the initial fraction of crystallinity, experiments were first performed on the PPNC and PP fibers. Results showed that the initial fraction of crystallinity was of 44% for both types of fibers. Similar experiments were then performed on the PPNC and PP unidirectional laminates. Results of the experiments gave crystallinity of 55% for both materials. This is similar to what was previously observed by Rojanapitayakorn *et al.* [12] for PET.

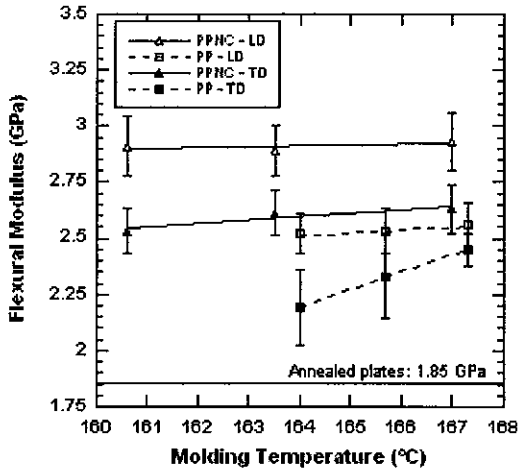
Finally, orientation of the PP crystalline reflections of (110) and (040) in PP and PPNC fibers and laminates as well as that of clay (001) axis (normal to the clay platelets plane) in the PPNC fibers and laminates were determined from X-ray diffraction pole figures and results are shown in Figure 7. Results on the orientation of the clay 001 axis (normal to the clay platelets plane), shown in Figure 7a, indicate that it is oriented in the normal direction in the PPNC fibers and that the orientation is maintained after hot-compaction. Figure 7 also shows that orientation of PP crystalline axes of PP is maintained after hot-compaction for PP and PPNC. PP crystalline orientation is actually seen to increase slightly as a result of recrystallization during the hot-compaction process.

Conclusions

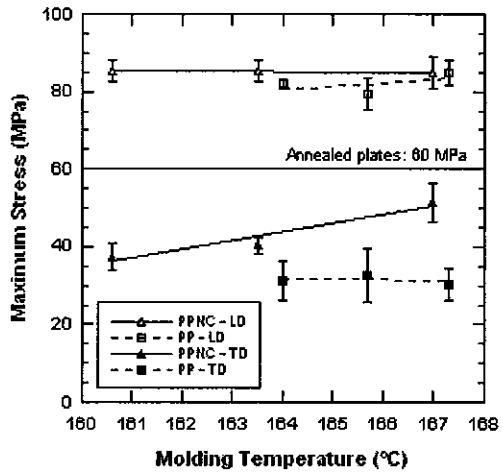
Composite laminates were produced from PP and PPNC fibers using hot-compaction process. Results of microscopic observations showed that acceptable level of consolidation can be achieved when appropriate processing parameters are used. Flexural modulus in the longitudinal direction (LD) was seen to result in a 70% improvement in performance, as compared to composites produced from randomly oriented fibers. Flexural modulus of unidirectional polypropylene nanocomposite laminates were also seen to be two times those obtained from plates made from randomly oriented polypropylene fibers. This shows the potential of PPNC fibers to produce high performance structural part with controlled anisotropy. Maximal flexural stress in the longitudinal direction (LD) was seen to be nearly two times superior to that measured in the transverse direction (TD). The lower strength obtained in the transverse direction can be attributed to the remaining voids observed between fibers, these voids acting as defects to initiate failure.

References

1. B. Alckock, N.O. Cabrera, N.M. Barkoula, J. Loos and T.J. Peijs. Composites: Part A, **37**, 716 (2006).
2. Tan. F. Perrin-Sarazin, T-M Ton-That, M.N. Bureau and J. Denault. Polymer, **28**, 11624 (2005).
3. A. Chatterjee and B.L. Deopura. Composites: Part A, **37**, 813 (2006).
4. P.J. Hine, I.M. Ward and J. Teckoe. Journal of Materials Science, **33**, 2725 (1998).
5. T. Amornsakchai, D.C. Basset, R.H. Olley, P.J. Hine and I.M. Ward. Journal of Applied Polymer Science, **78**, 787 (2000).
6. I. Verpoest, W. Broeckaert and T. Czarnecki. 27th Sampe Europe International Conference, 83 (2006).
7. S. Nathan. Process Engineering, **84**, 19 (2003).
8. P.J. Hine, I.M. Ward and J. Teckoe. Journal of Applied Polymer Science, **91**, 2223 (2004).
9. A. Ajji, J. Denault, D. Côté, M.N. Bureau and D. Trudel-Boucher. International Polymer Processeing, **4**, 368 (2007).
10. H. Bu, S.Z.D. Cheng and B. Wunderlich. Makromol. Chem. Rapid Comm. **9**, 75 (1988).
11. K.C. Cole, and A. Ajji, Chap. 3. Solid Phase Processing of Polymers. I.M. Ward, P. Coates and M.M. Dumoulin Ed., Hanser Munich, 33 (2000).
12. P. Rojanapitayakorn, P.T. Mather, A.J. Goldberg and R.A. Weiss. Polymer, **46**, 761 (2005).

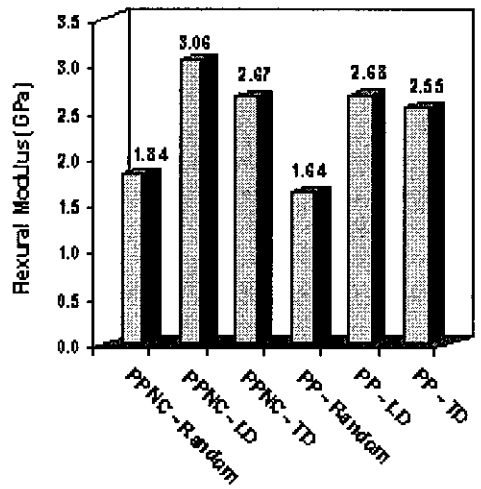


(a)

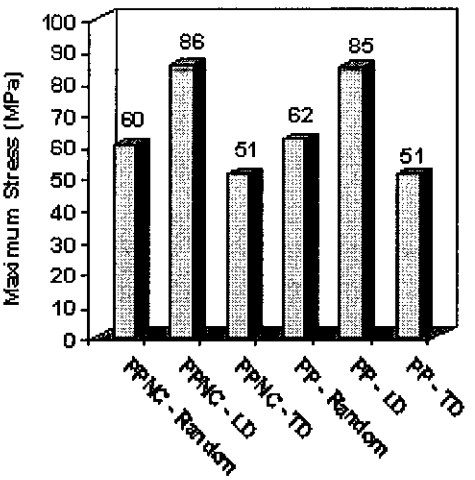


(b)

Figure 5. Variation of (a) the flexural modulus and (b) the maximum flexural stress for unidirectional composite molded using a holding time of 10 minutes.

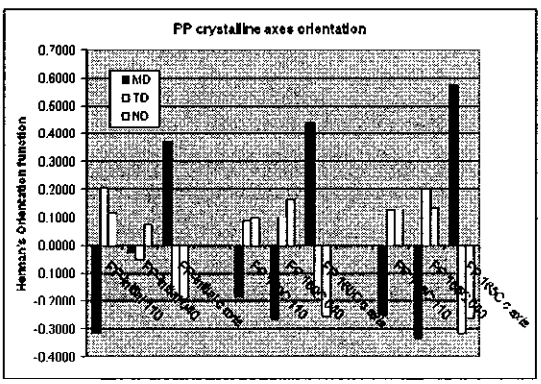


(a)



(b)

Figure 6: Flexural properties obtained from unidirectional and randomly oriented plates: (a) flexural modulus and (b) maximum flexural stress.



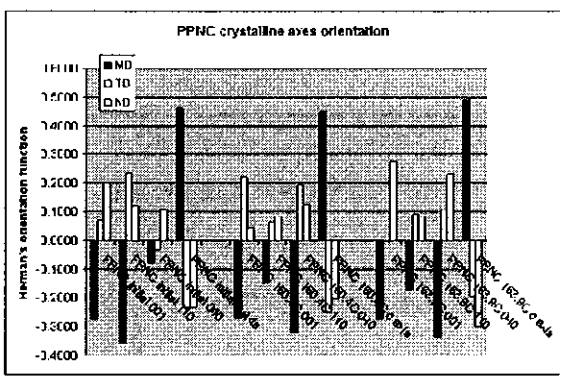


Figure 7: Herman orientation factor calculated from ref [11] for PP reflections (110) and (040) in PP fibers and laminates and in PPNC as well as clay (001) reflection in PPNC.

Key Words: Nanocomposite, Polypropylene, Fibers, Consolidation, orientation, Hot-compaction.