Viscoelastic Properties of Wood Flour/Polypropylene/Glass Fiber Hybrid Nanocomposite Reinforced with Organoclay

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Abstract: Nanocomposites are a new class of composites that are particle-filled polymers for which at least one dimension of the dispersed particles is in the nanometer range. Recently, using nanoclay filler in wood plastic composite could represent a promising new approach to obtain better products. In this study, the effect of organomodified layered silicate on the viscoelastic properties of wood flour/glass fiber reinforced polypropylene hybrid composites. The nanocomposites samples were fabricated by melt compounding and then injection molding. The results indicated that storage modulus and loss modulus of hybrid composites increased with increase organoclay loading. Also, the X-ray diffraction tests clarify that the nanoclay in samples is not exfoliated and the dispersion is in need of improvement. Also, Morphological findings showed that samples containing 4phc of clay had higher order of intercalation and better dispersion.

Key words: Viscoelastic Properties · Organoclay · Reinforced · Hybrid Nanocomposite

INTRODUCTION

Polymer/clay nanocomposites are polymeric materials that are reinforced by nanoclay particles whose dimensions are in the sub-micron scale; the particles are composed of stacks of 1 nm thick mono-layers whose in-plane dimensions range from 100 nm to 1000 nm. The thickness of the stacks depends upon how well they are intercalated or exfoliated. For enhanced functional properties of nanocomposites, full exfoliation is desired [1]. The Toyota group was the first to achieve successful exfoliation of clay in nylon 6 through in situ polymerization. They have shown that inserting as little as 4.7 wt% clay into nylon 6 doubles both elastic modulus and strength. However, it is the functional properties of nanocomposites that are the main driving force in nanocomposite development. Functional properties such as barrier, flammability resistance and ablation performance are all greatly improved by the addition of small volume fractions of nanoclay. To find applications for this new class of materials their mechanical properties have to be sufficient to ensure mechanical reliability [2].

Nanoclays is the most commonly used layered silicate because of its natural occurrences and beneficial properties (high cationic exchange capacity, high surface area and large aspect ratio) [1-3]. Using nanoclay filler in WPC composite has been reported in many literatures [4-9]. Many efforts have been made in the formation of wood polymer nanocomposite to improve such properties so as to meet specific end-use requirements. Many efforts have been made in the formation of wood polymer composite (WPC), to improve such properties so as to meet specific end-use requirements. Both thermoplastic and thermosetting systems have been used and have achieved certain improvements in wood properties, but both showed limitations [1-3]. Nanotechnological preparation of WPCs could represent a promising new approach to obtain better products. In this study, the effect of nanoclay on the viscoelastic properties of wood flour/glass fiber reinforced polypropylene hybrid composites.

MATERIALS AND METHODS

Montmorillonite modified with a quaternary ammonium salt (trimethyl ammonium chloride) of bis-2-hydroxyethyl tallow as an organic modifier, having a cationic exchange capacity (CEC) of 90 mequiv/100 g clay, a density of 1.98 g/cc and a d-spacing of $d_{001}=18.5$ nm was obtained from Southern Clay Products Co. USA, with

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Table 1: Composition of the Studied Formulations

Polypropylene (Wt. %)	Wood flour (Wt. %)	Glass Fiber (Wt. %)	Nanoclay (phc)*	PP-g-MA (phc)
50	40	10	0	2
50	40	10	2	2
50	40	10	4	2
50	40	10	6	2

*Per hundred compound

the trade name Cloisite 30B. The E-glass fibers (GF) used in this study were supplied by Diba Glass Fiber Co (Iran). A silane coupling agent, 3-methacryloxypropyl trimethoxysilane, was coated on the glass fiber surface. Average glass fiber original lengths were 3mm length.

The polymer matrix, polypropylene (PP), was supplied by Arak Petrochemical Company, Iran, in the form of homopolymer pellets with a density of $0.92 g/cm^3$ and a MFI of 18 g/10min. The important mechanical characteristics of the PP, namely tensile strength, flexural modulus and notched izod impact strength are 33 MPa, 1550 MPa and 30 J/m respectively. The cellulosic material used as reinforcing filler in the composite was wood flour (WF) from beech tree (Fagus Orientalis Lipseky). Beech pieces were ground with a Thomas-Wiley mill to pass through a 100-mesh screen and then they were dried again and stored in sealed plastic bags prior to compounding. Maleic anhydride grafted polypropylene (PP-g-MA) provided by Solvay with trade name of Priex 20070 (MFI=64 g/min, grafted maleic anhydride 0.1 Wt. %) was used as coupling agent.

Before preparation of samples, wood flour was dried in an oven at $(65 \pm 2)°C$ for 24 hours. Then polypropylene, wood flour, glass fiber, nanoclay and PP-g-MA were weighed and bagged according to formulations given in Table 1. According to Table 1, the mass ratio of fillers (include of wood flour and glass fiber) to polypropylene was controlled at 50/50 for all formulations. The concentration was varied from 0 to 6 per hundred compounds for nanoclay and from 0 to 15% for glass fiber, individually. The amount of coupling agent was fixed at 2% for all formulations. The mixing was carried out with a HAAKE internal mixer (SYS 9000 model, USA). First the polypropylene was fed to mixing chamber. After melting of the PP, the coupling agent and nano filler were added. At the fifth minute, the wood flour and glass fiber fed and the total mixing time was 13 min. The compounded materials were then ground using a pilot scale grinder (WIESER, WGLS 200/200 Model). The resulted granules were dried at 105°C for 4 hours. Test specimens were prepared by injection molding (Eman machine, Iran). The specimens were stored under

controlled conditions (50% relative humidity and 23°C) for at least 40 hours prior to testing.

For characterization of clay dispersion in composites, the wide angle x-ray diffraction analysis was carried out with a Seifert-3003 PTS (Germany) with CuKα radiation (λ=1.54 nm, 50kV, 50mA) at room temperature; the scanning rate was 1° /min.

A Du Pont 983 DMA instrument was used to characterize the viscoelastic properties of the material at different temperatures. The viscoelastic properties were studied in fixed frequency mode at a frequency of 1 Hz and strain amplitude of 0.2 mm. The samples were heated in the temperature range from - 40 to +160°C at a heating rate of 10°C/min.

RESULT AND DISCUSSION

Characterization of the morphological state of the composites was accomplished using X-ray diffraction. To verify a homogeneous dispersion of nanoclay (so-called intercalation and exfoliation) in a polymer matrix, the interlayer spacing in nanoclay (Bragg's law) and the relative intercalation (*RI*) of the polymer in nanoclay were quantified using the following equations,

$$n \lambda = 2d \sin \theta \qquad (1)$$

$$RI = [(d - d_0) \div d_0] \times 100 \qquad (2)$$

Where *n* is the integer number of wavelength ($n = 1$), λ is the wavelength of the X-rays, *d* is the interlayer or d-spacing of the clay in the nanocomposite, θ is half of the angle of diffraction and d_0 is the spacing of the clay layers in the pristine clay.

The d-spacing and relative intercalation of the clay in the nanocomposites calculated from equations (1) and (2) is listed in Table 2. This table shows that the order intercalation of samples increased with increase of nanoclay content up to 4phc and then decreased. The peaks appearing at 4.77° correspond to powdered nanoclay with d_{001} = 18.5 nm. In the sample with the addition of 2 phc nanoclay, the peak was shifted to a

Table 2: X-ray diffraction data of organoclay loading in samples

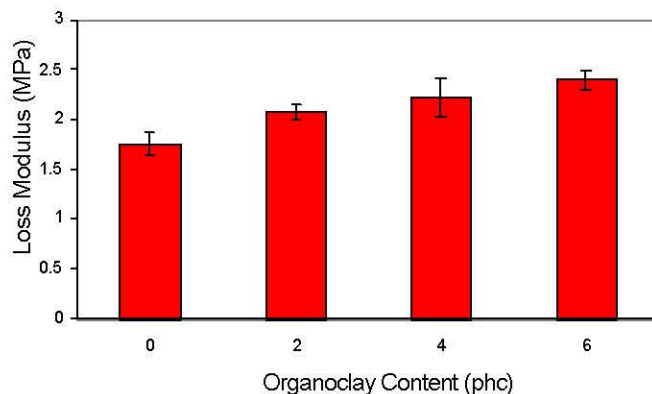| Samples	2θ (°)	D-spacing (nm)	Relative Intercalation (%)
Pure nanoclay	4.77	18.50	-
Composite with 2 phc nanoclay	3.98	22.18	19.89
Composite with 4 phc nanoclay	3.39	26.06	40.86
Composite with 6 phc nanoclay	3.46	25.49	37.78

Fig. 1: Effect of organoclay loading on loss modulus of samples
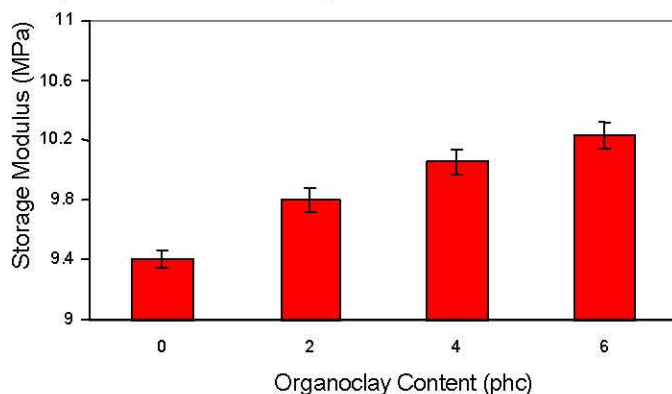

Fig. 2: Effect of organoclay loading on storage modulus of samples

lower angle (2θ = 3.98°, d_{001} = 22.18 nm), which implies formation of the intercalation morphology. The increase of the interlayer distance and relative intercalation might result from the stronger shear during processing when wood flour was introduced. These data show that the order of intercalation was higher for 4 phc of nanocaly (2θ = 3.39°, $d00_1$= 26.06 nm). Also, the clay was not exfoliated, since the peak still obviously existed. In other words, formation of the intercalation morphology and better dispersion was shown in 4phc of nanoclay, because the peak of that was shifted to a lower angle. It seems; this is because of the limited value of coupling agent in the nanocomposites. It is well known, through the improvement of the compatibility between neat polypropylene and clay (using MA), the polymer chains could be well diffused into the clay layers and the basal spacing of clay layers might be increased [4-9]. In the case

of polymers containing polar functional groups, alkyl ammonium surfactant modified nanoclay is adequate to promote nanocomposite formation. However, in the case of polypropylene, it is frequently necessary to use a coupling agent, such as maleic anhydride polypropylene (MAPP) [6-8].

The effect of organoclay loading on viscoelastic properties of wood flour/polypropylene/glass fiber hybrid composites is shown in Figures 1 and 2. As can be seen, the storage and loss modulus values were increased with increase of the nanoclay loading. The viscoelastic properties of the nanocomposite materials are related to the properties of the components, the morphology of the system and the nature of the interface between the nanofiller and polymer matrix. When nanoclay is added to a matrix to form a polymer nanocomposite, an interphase is created. This interphase is very sensitive to the surface

modification of nanofiller, such as the compatibility between the nanoclay and the matrix [10]. Based on the results of this study, we can see that the storage and loss modulus was improved considerably. This improvement was, however, more obvious for the surface of organocaly.

CONCLUSION

The following conclusions could be drawn from the results of the present study:

- The storage and loss modulus of wood flour/polypropylene/glass fiber hybrid composites increased with increase organoclay loading.
- The X-ray diffraction tests clarify that the nanoclay in samples is not exfoliated and the dispersion is in need of improvement. Also, Morphological findings showed that samples containing 4phc of clay had higher order of intercalation and better dispersion.

REFERENCES

1. Viswanathan, V., T. Laha, K. Balani A. Agarwal and S. Seal, 2006. Challenges and advances in nanocomposite processing techniques; a review, Journal of Material Science and Engineering, 54: 121-285.
2. Tjong, S.C., 2006. Structural and mechanical properties of polymer nanocomposites; A review, Journal of Material Science and Engineering, 53: 73-197.
3. Ray, S. and M. Okamoto, 2003. Polymer/layered silicate nanocomposites; a review from preparation to processing, Journal of Program Polymer Science, 28: 1539-1641.
4. Wu, Q., Y. Lei, C.M. Clemons, F. Yao, Y. Xu and K. Lian, 2007. Properties of HDPE/clay/wood nanocomposites, Journal of Plastic Technol., 27: 108-115.
5. Lei, Y., Q. Wu, C.M. Clemons, F. Yao and Y. Xu, 2007. Influence of nanoclay on properties of HDPE/wood composites, Journal of Applied Polymer Sci., 18: 1425-1433.
6. Samal, S.K., S. Nayak and S. Mohanty, 2008. Polypropylene nanocomposites; Effect of organo-modified layered silicates on mechanical, thermal and morphological performance, Journal of Thermoplastic Composite Material, 8: 243-263.
7. Han, G., Y. Lei, Q. Wu, Y. Kojima and S. Suzuki, 2008. Bamboo-fiber filled high density polyethylene composites; effect of coupling treatmentand nanoclay. Journal of Polymer Environment, 21: 1567-1582.
8. Hetzer, M. and D. Kee, 2008. Wood/ polymer/ nanoclay composites, environmentally friendly sustainable technology; a review, Journal of Chemical Engineering, 16: 1016-1027.
9. Zhao, Y., K. Wang, F. Zhu, P. Xue and M. Jia, 2006. Properties of poly (vinylchloride) /woodflour/ montmorillonite composites: Effects of coupling agents and layered silicate, Journal of Polymer Degradation and Stability, 91: 2874-2883.
10. Mishra, J.K., K.J. Hwang and C.S. Ha, 2005. Preparation, mechanical and rheological properties of thermoplastic polyolefin (TPO) /organoclay nanocomposites with reference to the effect maleic anhydride modified polypropylene as a compatibilizer, Polymer, 46: 1995-2002.