

Crystallization Behavior of Natural Fiber-Reinforced Plastic Nanocomposite

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Abstract: The use of natural fibers as reinforcements for thermoplastics has received much attention from the international research community over the past decade. In the recent years, applications of wood plastic composites based on natural organic reinforcements have penetrated slowly into this market because they offer many advantages over most common inorganic fillers. Furthermore, the nanotechnological preparation of wood plastic composites could represent a promising new approach to obtain better products. The aim of this study was to investigate the effect of nanoclay on the clay dispersion and crystallization behavior of wood flour/ polypropylene composites. The mass ratio of wood flour to polypropylene was controlled at 50/50 for all formulations. The different levels of nanoclay include of 0, 2, 4 and 6 per hundred compounds (phc) were used. The amount of coupling agent was fixed at 2% for all formulations. The composites samples were fabricated by melt compounding and then injection molding. The results of statistical analysis indicated that the nanoclay loading had significant effects on the crystallization behavior of natural fiber-reinforced plastic composite. The crystallization temperature, crystallization enthalpy and crystallinity level of samples increased with increase of nanoclay loading. X-ray diffraction patterns show that with increasing of the nanoclay content the order of intercalation decreased.

Key words: Crystallization Behavior • Natural Fiber • Polypropylene • Nanocomposite

INTRODUCTION

Fiber-reinforced plastic composites usually show drastic increase in their mechanical properties compared to those of the base polymer. Glass fiber or carbon fiber-reinforced thermoplastic materials possess good mechanical properties, but they have environmental concerns and are relatively expensive. Bio-fibers have long been considered as a future candidate to replace glass fiber or carbon fiber in thermoplastic composites and thus help resolve environmental issues and take economic advantage over those artificial fibers. The use of natural fibers as reinforcements for thermoplastics has received much attention from the international research community over the past decade. The main advantages of natural fibers over glass fibers are their low cost, low density, high strength to weight ratio, resistance to breakage during processing, CO₂ neutral life cycle and recyclability [1].

In the recent years, natural organic reinforcements such as cellulosic fibers have penetrated slowly into this

market because they offer many advantages over most common inorganic fillers. Wood fiber/plastic composites (WPCs) can be a cost-effective alternative to many plastic composites or metals in terms of bending, stiffness or weight. WPCs are becoming increasingly acceptable to consumers as a replacement for natural wood due to advantages such as durability, permanent color and reduced maintenance, in spite of their high price [2].

Recently, to improve of the physical and mechanical properties of WPCs, some approaches such as: foaming [3], chemical treatments of wood fiber [4], hybridization with other fillers [5], etc have been considered by the researchers.

The impressive enhancement of material properties achieved with the inclusion of submicron-size fillers in plastics and elastomers has stimulated active research in polymer composites [6-8]. Clay nanocomposites, especially nanoclay/polymer composites, exhibit dramatic increases in modulus, strength, barrier properties, flammability resistance and heat resistance compared with conventional or microcomposites [9-12].

Many efforts have been made in the formation of wood polymer nanocomposite to improve such properties so as to meet specific end-use requirements [13-16]. Hetzer *et al.* reported; the addition of nanoclay to the wood polymer composites systems increased their thermal degradation and Young's modulus [16]. Lei *et al.* noted that the crystallization temperature, crystallization rate, crystallinity level, thermal conductivity and gas permeability of the of HDPE/pine composites nanocomposites decreased with an increase of the nanosilicate volume fraction [14].

The aim of this study was to investigate the effect of nanoclay on the clay dispersion and crystallization behavior of wood flour/ polypropylene 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 the trade name Cloisite 30B. The polymer matrix, polypropylene (PP), was supplied by Arak Petrochemical Company, Iran, in the form of homopolymer pellets with a density of 0.92g/cm³ 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 $(65 \pm 2)^{\circ}\text{C}$ for 24 hours. Then polypropylene, wood flour, nanoclay and PP-g-MA were weighed and papered for manufacture. The mass ratio of wood flour to polypropylene was controlled at 50/50 for all formulations. The different levels of nanoclay include of 0, 2, 4 and 6 per hundred compounds (phc) were used. 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 nanoclay were added. At the fifth minute, the wood flour 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 CuK α radiation ($\lambda=1.54$ nm, 50kV, 50mA) at room temperature; the scanning rate was 1° /min.

The crystallization behavior of the samples was measured using a differential scanning calorimeter (DSC 131, France). According to ASTM D 3418, the samples of 4 to 5 mg were placed in aluminum capsules and heated from 25 to 200°C at the rate of 5°C/min to eliminate the heat history before cooling at 10°C/min. From the crystallization curves that were recorded by computer, crystallization temperature, crystallization enthalpy and crystallinity level can be obtained.

The statistical analysis was conducted using SPSS programming (Version 16) method in conjunction with the analysis of variance (ANOVA) techniques. Duncan multiply range test (DMRT) was used to test the statistical significance at $\alpha = 0.05$ level.

RESULTS AND DISCUSSION

The results of statistical analysis indicated that the nanoclay loading had significant effects on the crystallization behavior of natural fiber-reinforced plastic composite. The influence of nanoclay content on the crystallization temperature, crystallization enthalpy and crystallization level was shown in Figures 1-3, respectively. As can be seen, the crystallization temperature, crystallization enthalpy and crystallinity level increased with increase of nanoclay loading. Crystallization behavior of polymers with nanoclay has been studied extensively. Many studies have shown a nucleating effect of nanoclay for different polymers [17-19]. This effect can be used to enhance the thermal behavior of the polymer. These increases indicated the nucleating effect of the nanofiller in the crystallization of the HDPE/rice husk composite. On the other hand, the nucleation efficiency and the crystallinity of composite can be improved by the presence of the nanofiller as a nucleating agent.

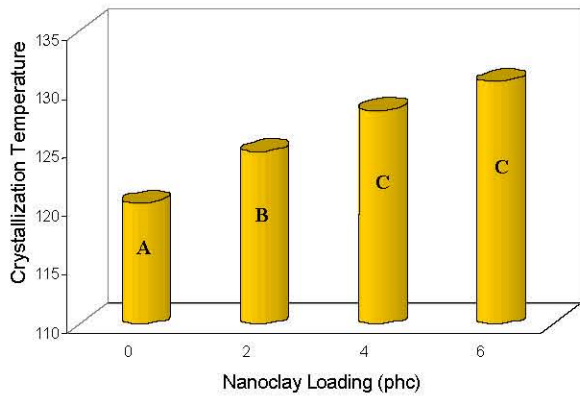


Fig. 1: Effect of nanoclay loading on crystallization temperature of natural fiber-reinforced plastic composite

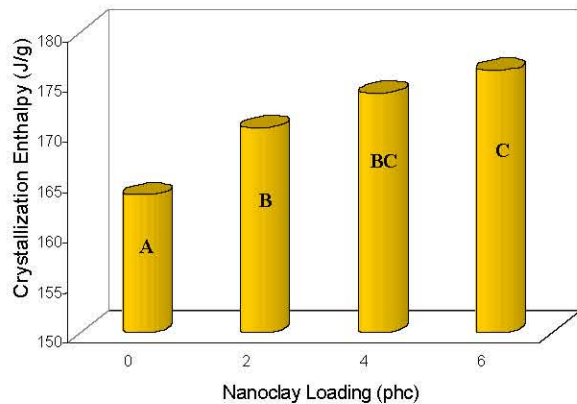


Fig. 2: Effect of nanoclay loading on crystallization enthalpy of natural fiber-reinforced plastic composite

Characterization of morphological state of the natural fiber-reinforced plastic composite has been accomplished using x-ray diffraction. The x-ray scattering intensities for pure nanoclay and hybrid composites with different levels of nanoclay are demonstrated in Figure 4. This figure shows that, with increasing of the nanoclay content the order of intercalation decreases. In other words, formation of the intercalation morphology and better dispersion was shown in 2phc concentration of nanoclay, because the peak of sample with 2phc concentration of nanoclay was shifted to a lower angle. It seems; this is because of the limited value of MA 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 [20]. In other words, the MA in lower concentration of clay has higher efficiency to d-spacing of the layers.

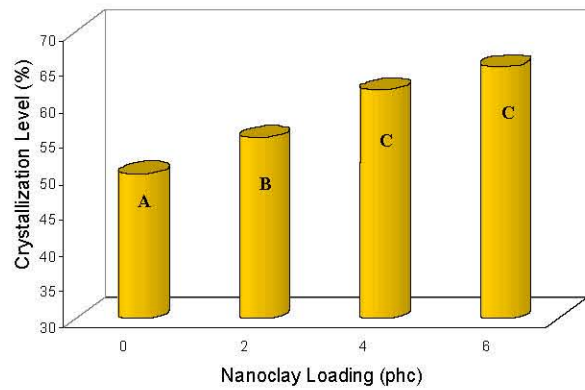


Fig. 3: Effect of nanoclay loading on crystallization level of natural fiber-reinforced plastic composite

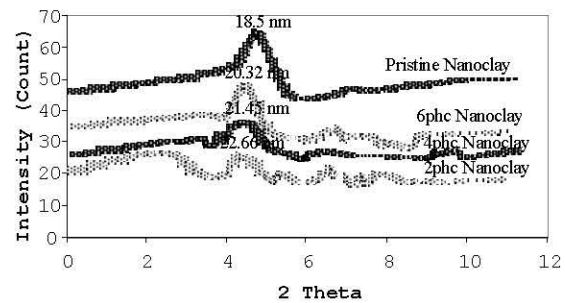


Fig. 4: XRD patterns of nanoclay loading in natural fiber-reinforced plastic composite

CONCLUSION

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

- Statistical analysis indicated that the nanoclay loading had significant effects on the crystallization behavior of wood plastic nanocomposite.
- The crystallization temperature, crystallization enthalpy and crystallinity level of natural fiber-reinforced plastic composite increased with increase of nanoclay loading.
- X-ray diffraction patterns show that with increasing of the nanoclay content the order of intercalation decreased.

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