DOI 10.1007/s11029-016-9543-x
Mechanics of Composite Materials, Vol. 51, No. 6, January, 2016 (Russian Original Vol. 51, No. 6, November-December, 2015)

EFFECT OF NANOCLAY ON THE FLEXURAL CREEP BEHAVIOR OF WOOD/PLASTIC COMPOSITES

B. Kord,[1*] A. Sheykholeslami,[2] and A. Najafi[3]

Keywords: *wood/plastic composite, nanoclay, flexure, creep behavior, dispersion*

The effect of nanoclay on the short-term flexural creep behavior of polypropylene/wood flour composites was investigated. The results obtained showed that the flexural strength and modulus increased with contentt of nanoclay up to 3 phc and then decreased. The fractional deflection and relative creep decreased with increasing content of nanoclay. X-ray diffraction patterns and transmission electron microscopy revealed that the nanocomposites formed were intercalated. Morphological findings testified that the samples containing 3 phc of nanoclay had the highest degree of intercalation and dispersion.

1. Introduction

During the last few decades, thermoplastics have gained ever-increasing acceptance as an important family of engineering materials and are steadily replacing metals in a wide variety of applications. The commercial consumption of thermoplastics has constantly increased, and this trend is expected to continue despite the growth of their prices. This situation has created an impetus to cost reduction via composites by employing fillers in thermoplastics [1-2].

In the recent years, natural organic reinforcements, such as cellulose fibers, have slowly penetrated into this market, because they offer many advantages over the most common inorganic fillers. Cellulose fibers are abundantly available and have a lower cost and density. They lead to a reduced wear of processing equipment and are renewable, recyclable, nonhazardous, and biodegradable. The replacement of inorganic fillers with comparable cellulose fibers provides weight savings and decreases the cost without reducing the rigidity of the composites [3-4]. Wood fiber/plastic composites (WPCs) can be a cost-effective

[1]Assistant Professor, Department of Paper and Packaging Technology, Faculty of Chemistry and Petrochemical Engineering, Standard Research Institute (SRI), Karaj, P.O.Box: 31745-139, Iran
[2]Department of Wood and Paper Science and Technology, Chalous Branch, Islamic Azad University, Iran
[3]Department of Wood Science and Paper Technology Chalous Branch, Islamic Azad University, Iran
[*]Corresponding author; e-mail: b.kord@standard.ac.ir

Russian translation published in Mekhanika Kompozitnykh Materialov, Vol. 51, No. 6, pp. 1041-1048 , November-December, 2015. Original article submitted December 29, 2014.

alternative to many plastic composites or metals in terms of bending, stiffness, or weight [4]. Wood/plastic composites are becoming increasingly acceptable to consumers as a replacement for natural wood due to such their advantages as durability, permanent color, and reduced maintenance, in spite of their high price [1-4].

One of the most important characteristics affecting wood/plastic composite products is their time-dependent behavior. Generally, the time-dependent deformation of a material under a sustained load is referred to as creep. If the load is large and the duration is long, failure will occur [5]. Creep is one of the principal characteristics of WPCs resulting in their poor performance in certain applications. The consideration of creep and creep rupture (load-duration behavior) is essential if WPCs are meant for short and long-term loading applications. Wood and thermoplastics have been characterized as viscoelastic materials governed by the creep behavior [6-7]. The creep of these materials occurs as a combination of elastic deformation and viscous flow, commonly known as viscoelastic deformation [8]. It is reported that most of the materials respond differently depending on the time required to complete the mechanical test [5-7]. The creep behavior of wood/plastic composites depends on a variety of factors, including the stress level, composite formulation, temperature, and, last but not least, moisture content [6-10]. With recent advancements in the science and technology of WPCs and the parallel increasing industrial interests in advanced WPCs, such as in construction and building, the subject of load effect on the creep behavior of WPCs seems very important [6-7].

The technology of nanocomposites with layered silicate clays as an *in situ* reinforcement has been intensively investigated. Essential improvements of physical and mechanical properties, thermal stability, flame resistance, and barrier resistance have been observed for various thermoplastic and thermoset nanocomposites at a low silicate content [11-14]. The use of nanoclay fillers in WPC composites has been reported in [15-21]. Many efforts have been made in the formation of wood/polymer composites to improve their properties so as to meet the specific end-use requirements. The aim of this study was to investigate the effect of nanoclay on the flexural creep behavior of polypropylene/wood flour composites.

2. Experimental

2.1. Materials

The polymeric matrix used in this study was polypropylene (PP) with a melt flow index of 18 g/10 min and a density of 1.2 g/cm^3 (supplied by Arak Petrochemical Co, Iran). The wood flour (WF) used as the reinforcing material was supplied from Cellulose Aria Co (Iran); the average size of wood flour particles was about 425 μm. A maleic anhydride-grafted polypropylene (PP-g-MA), provided by Solvay with the trade name Priex 20070 (MFI = 64 g/10 min, and grafted maleic anhydride = 1 wt.%) were used as the coupling agents. A nanoclay modified with a quaternary ammonium salt (methyl ammonium chloride) of bis-2-hydroxyethyl tallow and employed as an organic modifier, having a cationic exchange capacity (CEC) of 90 meq/100g clay, a density of 1.98 g/cc, and a *d*-spacing of d_{001}=18.5 Å, was obtained from Southern Clay Products Co, USA, with the trade name Cloisite 30B.

2.2. Preparation of composite

Before the preparation of specimens, WF was dried in an oven at (65 ± 2) °C for 24 hours. Composites consisting of PP and WF at 50% weight ratios, with various amounts of nanoclay (0, 3 and 6 per hundred compounds (phc)), were produced. The amount of coupling agent was fixed at 2 phc for all formulations. The mixing was carried out by a hake internal mixer (HBI System 90, USA). First, polypropylene was fed into the mixing chamber, and after melting of PP, the coupling agent and montmorillonite were added. At the 5th min, the wood flour was introduced, and the total mixing time was 13 min. The materials compounded were then ground using a pilot scale grinder (WIESER, WGLS 200/200 Model). The resulting granules were dried at 105°C for 4 h. Then test specimens were prepared by injection molding (Eman machine, Iran). Finally,

the specimens were conditioned at a temperature of 23°C and relative humidity of 50% for at least 40 h according to ASTM D 618 prior to testing.

2.3. Flexural properties

To determine the flexural properties of the composites prepared, flexural tests were performed according to ASTM D790, by using an Instron machine (Model 4486, England), at a crosshead speed of 5 mm/min. For each type of composite, five replicate samples were tested.

2.4. Creep tests

Short-term creep tests were performed on standard flexural specimens by using flexural creep equipment. The displacements at their midspan were measured by an extensometer. The total time of every test was 120 min. The stress level was 20% of the maximum bending one, which was held constant throughout the test. The fractional deflection and relative creep were determined and reported.

Fractional deflection. This is the ratio of total deflection (deflection within 120 min after loading) to the instantaneous one (deflection within 1 min after loading):

$$F_d = d_t / d_0,$$

where F_d, d_t, and d_0 are the fractional deflection, the creep deflection during a period t (min), and the instantaneous deflection (mm), respectively.

Relative creep. This is deflection expressed in terms of the initial elastic deflection:

$$R_c = (d_t - d_0)/d_0,$$

where R_c, d_t, and d_0 are the relative creep, the creep deflection during a period t (min), and the instantaneous deflection (mm), respectively.

3. Morphological Study

A wideangle X-ray diffraction (XRD) analysis was carried out on a Seifert-3003 PTS (Germany) apparatus with CuK_α radiation (λ = 1.54 nm, 50 kV, 50 mA) at room temperature; the scanning rate was 1°/min. The structure of the nanocomposites was investigated by a Philips (Model EM 208, Netherlands) transmission electron microscope (TEM) with an acceleration voltage of 100 kV. The ultrathin slides were obtained with a Leica Ultracut UCT device (Germany).

4. Statistical Analysis

A statistical analysis was conducted using the SPSS programming (Version 13) method in conjunction with the analysis of variance (ANOVA). The Duncan multiply range test (DMRT) was employed to determine the statistical significance at the $\alpha = 0.05$ level.

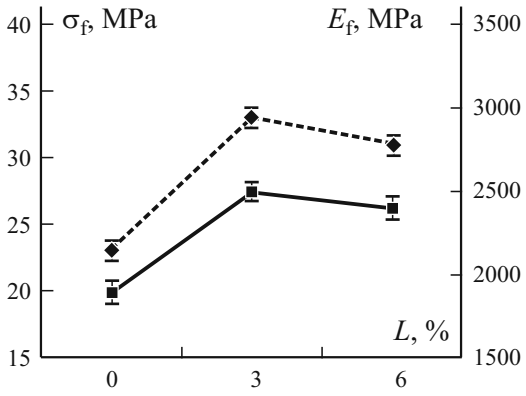

Fig. 1. Effect of nanoclay loading L on the flexural strength σ_f (♦) and modulus E_f (■) of polypropylene/wood flour composites.

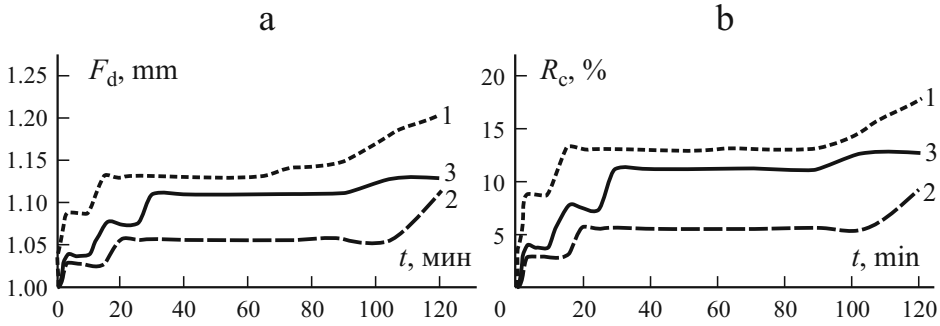

Fig. 2. Fractional deflection F_d (a) and relative creep R_c (b) vs. time t for polypropylene/wood flour composites with nanoclay loadings L = 0 (1), 3 (2), and 6 (3) phc.

5. Result and Discussion

The statistical analysis indicated that nanoclay had a significant influence on the flexural properties of polypropylene/wood flour composites.

From Fig. 1, it can be concluded that the flexural modulus and strength increased with increasing content of nanoclay up to 3 phc and then decreased. At low nanoclay loadings, the enhancement of properties is attributed to the lower percolation points created by the high aspect ratio of nanoclays. This enhancement may also be attributed to the formation of intercalated and exfoliated nanocomposite structures at these loadings of clay [15-21]. At higher loadings, the decrease in flexural characteristics may be caused by the formation of agglomerated clay particles [15-21]. Also, the reinforcing efficiency of the nanoparticles is balanced by two opposite phenomena. The negative affect is attributed to the migration of nanoparticles into the interface of wood-plastic. At 6 phc of nanoclay, the agglomeration of nanoparticles could decrease the reinforcement of clay. The dispersion of nanoclay, as a positive effect, could increase the modulus and strength; therefore it can be concluded that at 3 phc of nanoclay in the hybrid composite, the former phenomenon was dominant and therefore the flexural modulus and strength increased.

The fractional deflection F_d of wood/plastic nanocomposite specimens is illustrated in Fig. 2. As seen, the fractional deflection decreased with increasing nanoclay loading. The lowest fractional deflection was observed at 3 phc of nanoclay. This implies the decrease in deflection resulting from the addition of nanoclay, which in turn indicates that the creep deflection depends on the modulus of the wood/plastic composite. So, we can expect that the improvement in the flexural modulus is

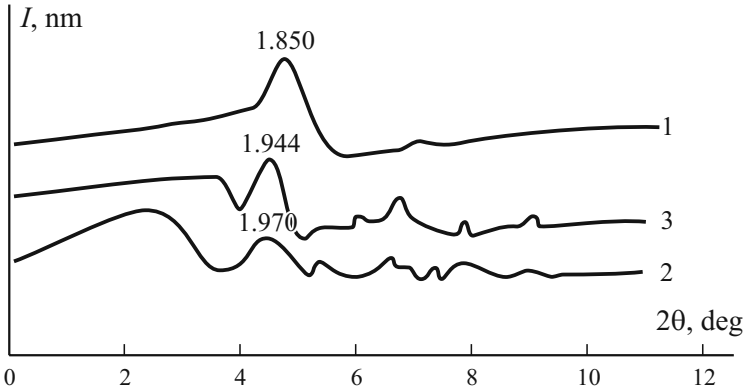

Fig. 3. XRD patterns of composites with L = 0 (1), 3 (2), and 6 (3) phc of nanoclay.

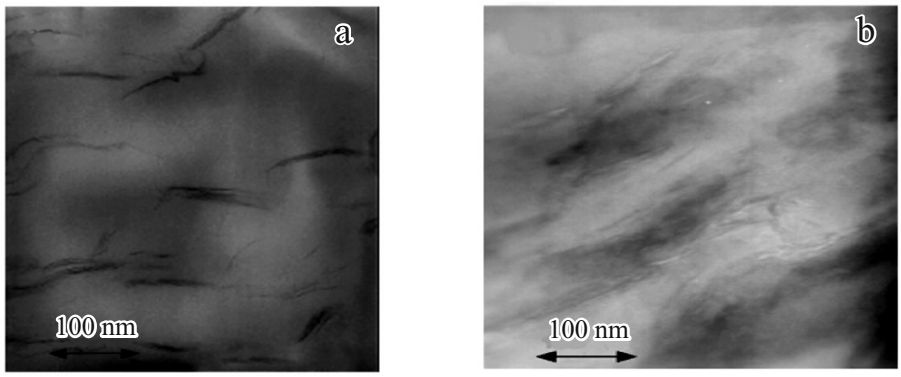

Fig. 4. TEM micrographs of polypropylene/wood flour nanocomposites with 3 (a) and 6 phc (b) of nanoclay.

related to the high aspect ratio of nanoclay due to the reduction of fractional deflection. Ebrahimi et al. [9] concluded that the creep behavior of wood/plastic composites is mainly controlled by the elastic modulus of composite. This means that the rate at which creep increases with time is almost the same for different composites, whereas the instantaneous creep is higher for lower-modulus materials. Najafi and Kazemi-Najafi [10] showed that a lower modulus leads to higher deflections regardless of creep rate.

The effect of nanoclay on the relative creep of polypropylene/wood flour composites is shown in Fig. 3. The relative values of creep C decreased with increasing loading of nanoclay up to 3 phc and then increased. This decrease can be attributed to the same reasons as for the fractional deflection.

The X-ray scattering intensities I for composites with different levels of nanoclay loadings are illustrated in Fig. 4, where the quantity 2θ (equal to 4.76º) refers to a neat clay with a basal spacing of 1.85 nm. In the sample with a 3-phc concentration of nanoclay, the peak was shifted to a lower angle (2θ = 4.48º, d-spacing = 1.970 nm), which implies the formation of a intercalation morphology. The (001) peak of the 6-phc nanoclay appeared at 2θ = 4.54º, with a d-spacing of 1.944 nm. These data show that the degree of intercalation was higher at the 3 phc than 6 phc of nanoclay concentration.

Figure 5 shows the dispersion state of nanoclay in the composites considered, as it was made evident by the TEM. The dark line represents the intersection of silicate layers, while the white background corresponds to the polypropylene matrix. When the loading level of nanoclay in the PP/WF composite was 3 phc (Fig. 5a), nanoclay exhibited better dispersion of clay layers in the polymeric matrix than at 6 phc of nanoclay (Fig. 5b). With increase in the level of nanoclay to 6 phc, the size of dispersed nanoclay particles became larger or even aggregated in part (as confirmed by the decreased d-spacing found from the XRD, see Fig. 4).

Conclusions

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

1. The flexural strength and modulus increased with increase in the content of nanoclay up to 3 phc and then decreased.

2. The fractional deflection and relative creep decreased with increase in the content of nanoclay. The lowest creep was observed at 3 phc of nanoclay.

3. Morphological findings showed that the composite containing 3 phc of nanoclay had the highest degree of intercalation and dispersion.

REFERENCES

1. R. T. Woodhams, G. Thomas, and D. K. Rodgers, "Wood fibers as reinforcing fillers for polyoefins," J. Polym. Eng. Sci., **24**, 1166–1171 (1984).
2. A. K Bledzki and J Gassan, "Composites reinforced with cellulose based fibers," J. Polym. Sci., **24**, 221-274 (1999).
3. R. M. Rowell, A. R. Sandi, D. F. Gatenholm, and R. E. Jacobson, "Utilization of natural fibers in plastic composites: Problem and opportunities in lignocellulosic composites," J. Compos. Mater., **18**, 23-51 (1997).
4. K. Oksman and M. Sain, "Wood Polymer Composites," Woodhead Publ. Ltd, Great Abington, Cambridge, UK, 2008.
5. K. J. Fridley, "Design for creep in wood structures," For. Prod. J., **42**, 23–28 (1992).
6. B. D. Park, and J. Balatinecz, "Short term flexural creep behavior of wood fiber/polypropylene composites," Polym. Compos., **19**, 377–382 (1998).
7. S. Y. Lee, H. S. Yang, H. J. Kim, C. S. Jeong, B. S. Lim, and J. N. Lee, "Creep behavior and manufacturing parameters of wood flour filled polypropylene composites," Compos. Struct., **65**, 459–469 (2004).
8. M. Sain, J. Balatinecz, and S. Law, "Creep fatigue in engineered wood fiber and plastic composites," J Appl. Polym. Sci., **77**, 260–268 (2000).
9. G.H. Ebrahimi, R.H. Falk, and M. Tajvidi, "Short-term creep behavior of natural fiber/polypropylene composites," In: Proc. of the 2nd Int. Conf. on Wood Mechanics, STFI, Stockholm, Sweden, 2003.
10. A. Najafi, S.K. Najafi, "Effect of load levels and plastic type on creep behavior of wood sawdust/HDPE composites," J. Reinfor. Plast. Compos., **28**, 2645-2653 (2009)
11. S. C. Tjong, "Structural and mechanical properties of polymer nanocomposites; A review," J. Mater. Sci. Eng., **53**, 73-197 (2006).
12. L. A. Utracki, M. Sepehr, and E. Boccaleri, "Synthetic layered nanoparticles for polymeric nanocomposites (PNCs); A review," J. Polym. Addit. Technol., **8**, 1-37 (2007).
13. V. Viswanathan, T. Laha, K. Balani, A. Agarwal and S. Seal, "Challenges and advances in nanocomposite processing techniques; A review," J. Mater. Sci. Eng., **54**, 121-285 (2006).
14. M. Alexandre and P. Dubois, "Polymer-Layered silicate nanocomposites: Preperation, properties and use of a new class of materials; A review," J. Mater. Sci. Eng., **28**, 1-63, (2000).
15. Y. Lei, Q. Wu, C.M. Clemons, F. Yao, and Y. Xu, "Influence of nanoclay on properties of HDPE/wood composites," J Appl. Polym. Sci., **18**, 1425-1433 (2007).
16. Y. Zhao, K. Wang, F. Zhu, P. Xue , and M. Jia, "Properties of poly (vinylchloride)/ woodflour/montmorillonite composites: effects of coupling agents and layered silicate," J. Polym. Degrad. Stabil., **91**, 2874-2883 (2006).
17. G. Han, Y. Lei, Q. Wu, Y. Kojima, and S. Suzuki, "Bamboo–fiber filled high density polyethylene composites; Effect of coupling treatment and nanoclay," J. Polym. Envir. **21**, 1567-1582 (2008).
18. A. Hemmasi, H. Khademieslam, M. Talaiepoor, B. Kord, and I. Ghasemi, "Effect of nanoclay on the mechanical and morphological properties of wood polymer nanocomposite," J. Reinfor. Plast. Compos., **29**, 964-971 (2010).
19. M. Hetzer, and D. Kee, "Wood/polymer/nanoclay composites, environmentally friendly sustainable technology; A review," J. Chem. Eng., **16**, 1016-1027 (2008).
20. B. Kord, A. Hemmasi, and I. Ghasemi, "Properties of PP/wood flour/ organomodified montmorillonite nanocomposite," Wood. Sci. Technol., **45**, 111-119 (2011).
21. I. Ghasemi and B. Kord, "Long-term water absorption behavior of polypropylene/wood flour/organoclay hybrid nanocomposite," Irani. Polym. J., **18**, 683-691 (2009).