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Mechanical Properties of PP/Clay Nanocomposites Prepared from Masterbatch: Effect of Nanoclay Loadings and Re-Processing

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Abstract. PP/clay nanocomposites samples of 1st and 2nd cycles (recycle) and different nanoclay loadings (i.e. 0, 5, 10, 15 wt%) samples were made by utilizing twin-screw extruder and injection molding machine. The samples were then characterized using a tensile test machine. The tensile tests results showed that modulus and tensile strength of the nanocomposites samples for both 1st and 2nd cycles were all higher than the neat PP, and increased with increasing nanoclay loadings. The enhancements of modulus of elasticity (as compared to the neat PP) for 1st cycle of the nanocomposites were about 38.08%, 49.33%, and 78.65% for NC-5-I, NC-10-I, and NC-15-I, respectively. Whereas, for the 2nd cycle of the nanocomposites were about 44.33%, 59.59%, and 84.69% for NC-5-II, NC-10-II, and NC-15-I, respectively. This indicated that the incorporation of 2 moclay in the PP matrix significantly increased mechanical properties, especially modulus of elasticity and tensile strength of the nanocomposites. Additionally, values of modulus of elasticity and tensile strength of 1st cycle and 2nd cycle of PP/clay nanocomposites were compared by plotting them in two graphs. The plots revealed that reprocessing of the nanocomposites did not significantly influence the mechanical properties of the nancomposites.

Introduction

Organoclay or organically modified nanoclay/layered silicates is one of the most widely used reinforcing nanofillers to fabricate polymer nanocomposites. Numerous literatures have reported that the addition of this nanomaterial could significantly improve mechanical properties, flame retardancy, gas permeability or barrier properties of the polymer matrix [1, 2]. In case of the polymer matrix, polypropylene is considered as one of the most widely used thermoplastic polymer. Therefore, fabrication and investigation of polypropylene/clay nanocomposites properties are very interesting topic of research [1].

Generally, there are three routes that can be followed to prepare polymer nanocomposites, which are: 1) solution-blending method; 2) melt blending method; and 3) In-situ polymerization method. Melt blending method is more preferable to prepare polymer/clay nanocomposites, because it gives better blending of clay and polymer if compared with the solution-blending method [3, 4]. additionally, this method does not need solvent, and thus environmentally friendly. Furthermore, compared to other methods, melt blending method is more simple, economical, and thus more feasible for mass production of polymer/clay nanocomposites. It is also the most compatible method with the current industrial machines, such as extrusion and compression/injection molding [1, 4].

In recent years, nanomaterial based masterbatch based nanomaterials have been widely produced. Masterbatch is polymeric materials filled with reinforcing nano-materials at high concentration. Since the nanomaterials are bound inside the polymer matrix, masterbatch is dust free and thus easy to handle and less health/safety hazards. Therefore, masterbatch based polymer nanocomposites can become a promising alternative route to produce polymer nanocomposites. Moreover, this masterbatch is very compatible with the melt blending method [2]. There have been limited research studies that investigate the properties of PP/clay nanocomposites fabricated from

masterbatch. Therefore, in this work, we has prepared PP/clay nanocomposites via melt blending method using masterbatch and investigate the effect of nanoclay loadings and reprocessing (i.e. recycle) on the mechanical properties of the nanocomposites.

Experimental

Materials and nanocomposites preparation. To prepare the nanocomposites we have melt blended the nanoclay masterbatch and polypropyler (PP) pellets utilizing a twin-screw extruder (TSE) (Farrell FTX-20, UK). The nanocomposites pellets from the TSE were fed into injection molding machine (Super Master Series SM 120, China) to make ASTM standard test samples. The nanoclay masterbatch (NanoMax®) was acquired from Nanocor (USA). The masterbatch contains nanoclay and PP (as carrier) at 50:50 weight ratio. The clay material is montmorillonite (MMT) type, which has been organically treated with dimethyl-dihydrogenated tallow ammonium. Whereas, the PP (as the carrier) has been functionalized with maleic anhydride (MA). The details fabrication process of the PP/clay nanocomposites, including the steps, processing conditions of the TSE and injection molding have been splained in our previous study [2].

Nanocomposites characterization. The surface morphology of the nanocomposites samples was analyzed using a Scanning Electron Microscopy (SEM), JEOL JSM-6360A, Japan. The samples were cryogenically fractured using liquid nitrogen to zero the originality of the nanocomposites structure morphology before fractured [2]. Whereas, mechanical properties of the nanocomposites zero investigated by analyzing nanocomposites samples using a Tensile Test machine, LYOD at cross-head speed of 500 mm/min. The reference used for the analysis was ASTM D-638 standard. The nanocomposites samples used were dumbbell-shape bars made by the injection molding machine. From the tensile tests, stress-strain curves were generated and from the curves, some mechanical properties have been derived, such as: modulus elasticity or tensile modulus (E), which associated to the stiffness nature of the nanocomposites, and yield stress or tensile strength.

Results and Discussion

structure of nanocomposites is believed to play important role in tailoring the properties, e.g. mechanical properties of polymer nanocomposites. Good distribution and dispersion of nanomaterials in the polymer matrix could significantly enhance the mechanical properties of the polymer matrix. Therefore, the morphological structure of the nanocomposites is important to be investigated. Figures 1a and 1b shows the morphological structure of cryo-fractured nanocomposites samples of NC-5-I and NC-5-II, respectively. As shown in Fig. 1a the nanoclay materials (indicated by white needle-like) were well distributed in the PP matrix. Whereas, for nanocomposites at 2nd cycle, the SEM micrograph of NC-5-II shown in Fig. 1b also exhibited the similar result of the 1st cycle (i.e. NC-5-I). The nanoclay platelets were evenly distributed in the PP matrix. It is worth to note that SEM images of nanocomposites with higher nanoclay concentrations (i.e. NC-15-I and NC-15-II) were available and also exhibited similar results, but not shown in this paper. The effect of reprocessing was not clearly demonstrated in these SEM images. Whereas, the dispersion state of nanoclay were also not observable due to limitation of the SEM apparatus. Other microscopy techniques, such as Transmission Electron Microscopy (TEM) are needed to further study the dispersion state of the nanoclay.

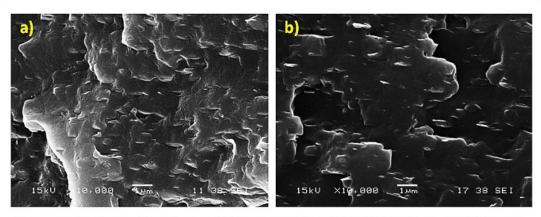


Fig. 1 SEM micrographs of cryo-fractured nanocomposites samples: a) NC-5-I and b) NC-5-II.

Fig. 2 shows that the stress-strain curves of PP/clay nanocomposites for 1st cycle and 2nd cycle. From these curves, two of important mechanical properties could be derived, which are modulus of elasticity and tensile strength. The modulus of elasticity or Young's modulus which associated to the material's stiffness, was determined as the slope of the initial stass-strain curve. Whereas, tensile strength, which associated to the amount of stress needed to break the sample, was determined as the peak of stress-strain curve. As seen in the figure, both the slope and peak of the stress-strain curves of the nanocomposites for both 1st and 2nd cycles were all higher than that of the neat PP.

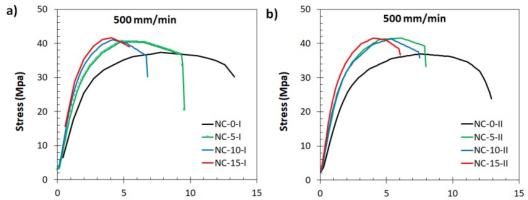


Fig. 2 Stress-strain curves of PP/clay nanocomposites for **a)** 1st cycle of nanocomposites and **b)** 2nd cycle of nanocomposites.

In order to clarify the influence of nanoclay loadings and reprocessing on the mechanical behavior of the nanocomposites, modulus of elasticity and tensile strength of the nanocomposites were derived from Fig. 2 and listed in Table 1. As seen in the table, and also already mentioned in the previous paragraph that both modulus flasticity and tensile strength of the nanocomposites samples for both 1st and 2nd cycles were all higher than the neat PP, and increased with increasing nanoclay loadings. The enhancements of the modulus of elasticity (compared to the neat PP) for 1st cycle of the nanocomposites were about 38.08%, 49.33%, and 78.65% for NC-5-I, NC-10-I, and NC-15-I, respectively. Whereas, for the 2nd cycle of the nanocomposites were about 44.33%, 59.59%, and 84.69% for NC-5-II, NC-10-II, and NC-15-I, respectively. Furthermore, the similar trend also occurred in the tensile strength of the nanocomposites. The enhancements of the tensile strength (compared to the neat PP) for 1st cycle of the nanocomposites were about 9.63%, 9.89%, and 11.76% for NC-5-I, NC-10-I, and NC-15-I, respectively. Whereas, for the 2nd cycle of the

nanocomposites were about 13.35%, 13.62%, and 13.35% for NC-5-II, NC-10-II, and NC-15-II, respectively.

Sample	Modulus elasticity, E (MPa)	Tensile strengh (MPa)	Sample	Modulus elasticity, E (MPa)	Tensile strength (MPa)
NC-0-I	1560 ± 36.7	37.4 ± 0.1	NC-0-II	1478.3 ± 27.5	36.7 ± 0.28
NC-5-I	2154.1 ± 112.3	41.0 ± 0.5	NC-5-II	2133.6	41.6
NC-10-I	2329.5 ± 73.1	41.1 ± 0.1	NC-10-II	2359.2 ± 35.3	41.7 ± 0.29
NC-15-I	2787 ± 83.5	41.8 ± 0.1	NC-15-II	2730.2	41.6

Table 1 Modulus elasticity and tensile strength of PP/clay nanocomposites for 1st and 2nd cycles.

The magnitude of the enhancement was quite high, which indicates that the incorporation of nanoclay in polypropylene matrix significantly increased modulus of elagority or stiffness of the nanocomposites. This improvement could be attributed to the good interaction between the nanoclay and the PP matrix, which then hindered the molecular mobility of the PP chains [2, 5, 6]. The enhancement of modulus of elasticity of the PP/clay nanocomposites was also reported in other research studies [1, 7, 8]. Additionally, Fig. 3a shows the comparison of modulus of elasticity between 1st cycle and 2nd cycle of PP/clay nanocomposites. As observed, the modulus of elasticity for both 1st and 2nd cycles were close one to each other. The same trend also applied for tensile strength (see Fig. 3b). These two figures (i.e. Fig. 3a and Fig. 20) clearly confirmed that the reprocessing or 2nd process/cycle did not significantly influence the modulus of elasticity and tensile strength of the nanocomposites.

Additionally, Figs. 4a and 4b show photographs of tensile test samples of PP/clay nanocomposites (after the break) for 1st cycle nanocomposites and 2nd cycle nanocomposite, respectively. As seen in the both of figures (i.e. Fig. 4a and 4b) all the nanocomposites samples exhibited low strain at break (%), which was indicated by the pattern of the broken samples (shown by the dashed-line). Whereas, for the neat PP, the strain at break was high, which was indicated by its pattern (shown by the solid-line). The neat PP street [11] first before it broke. The values of strain-at-break for all nanocomposites samples were not listed in Table 1, but from stress-strain curves in Fig. 2, it could be clearly observed that for both 1st and 2nd cycle nanocomposites, the strain-at-break decreased with increasing nanoclay loadings. It is well-known that strain-at-break property of materials is inversely proportional to the tensile strength, meaning that while the tensile strength increases the strain-at-break would decrease.

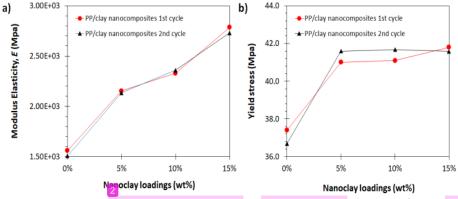


Fig. 3 Comparison of a) modulus of elasticity and b) Tensile strength between 1st cycle and 2nd cycle of PP/clay nanocomposites.

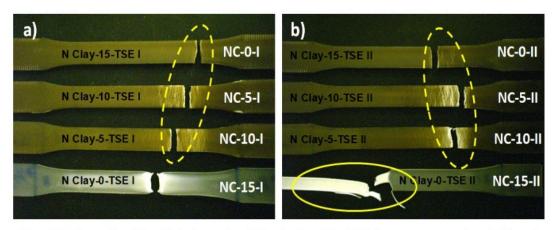


Fig. 4 Photographs of tensile test samples (after the break) of PP/clay nanocomposites a) 1st cycle nanocomposites and b) 2nd cycle nanocomposites

Conclusion

In this work, we have investigated the effect of nanoclay loadings and reprocessing on the mechanical properties of the PP/clay nanocomposites. The dumbbell-shape nanocomposites samples of 1st and 2nd cycles and different nanoclay loadings (i.e. 0, 5, 10, 55 wt%) were characterized by using a tensile test machine. The tensile test results showed that the modulus of asticity and tensile strength of the nanocomposites samples for both 1st and 2nd cycles were all higher than the neat PP, and increased with increasing nanoclay loadings. The enhancements of the modulus of elasticity (as compared for the neat PP) for 1st cycle of the nanocomposites were about 38.08%, 49.33%, and 78.65% for NC-5-I, NC-10-I, and NC-15-I, respectively. Whereas, for the 2nd cycle of the nanocomposites were about 44.33%, 59.59%, and 84.69% for NC-5-II, NC-10-II, and NC-15-I, respectively. The enhancements of the tensile strength (as compared for the neat PP) for 1st cycle of the nanocomposites were about 9.63%, 9.89%, and 11.76% for NC-5-I, NC-10-I, and NC-15-I, respectively. Whereas, for the 2nd cycle of the nanocomportes were about 13.35%, 13.62%, and 13.35% for NC-5-II, NC-10-II, and NC-15-II, respectively. In other hand, the strain-atbreak of the nanocomposites for both 1st and 2nd cycles decreased with increasing nanoclay loadings. Additionally, in general, the reprocessing did not significantly affect the mechanical properties of the nanocomposites.

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