

고강도 초음파에 의한 PP/Woodfiber 복합체의 물성 강화

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Enhanced Properties of PP/Woodfiber Composites Assisted by High-Intensity Ultrasound

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Introduction

In the recent years, woodfiber thermoplastics composites have received considerable attention from the wood and plastic industries. Although woodfiber has been used as filler for thermosetting polymers for a long time, wood fibers or cellulosic fillers are being increasingly used nowadays to reinforce thermoplastics for the development of new applications. PWCs (Plastic Woodfiber Composites) take advantage of both wood and plastics. The advantage of wood include low density, relatively low cost, low equipment abrasiveness, non-hazardous, abundant ability, renewability, recyclability and good biodegradability. However, plastics provide PWCs with good moisture and decay resistance [1].

In spite of the advantages, the use of wood in thermoplastics has been plagued by the thermal stability limitation of wood and the difficulties in obtaining good filler dispersion and strong interfacial adhesion [2-3]. This is because of the natural incompatibility between the hydrophilic, polar woodfibers and hydrophobic, non-polar thermoplastics [4-6] such as PP(Polypropylene). Thus, in order to obtain a composite based in nonpolar thermoplastics with competitive final properties, it is necessary to achieve a good interphase between filler and matrix. Maleic anhydride grafted polymers, such as maleated polyethylene (MAPE) and maleated polypropylene (MAPP), are widely used as good compatibilizers to improve the mechanical properties.

In this study, its was investigated that the feasibility of eco-friendly new process to improve the compatibility between PP and woodfiber through the use of high-intensity ultrasound inducing macroradical generation. Exeperiments was performed under the variation of woodfiber contents and different woodfiber size.

The mechanical, thermal and rheological properties were performed for each composites. And the structure analysis and phase morphology observation were also performed by FT-IR, scanning electron microscope (SEM) respectively to confirm the effect of high-intensity ultrasound.

Experimental

PP resin used in this study was a commercial available homopolymer. It was

supplied in the form of palletized from Samsung Total Co., and melt index 3.3g/min (230℃, 2.16kg) and density 0.91 g/cm³. Commercial grade MAPP was also used in this study supplied from Honam petrochemical Co. and 50g/min (230℃, 2.16kg) and density 0.90 g/cm³ with grafted contents of maleic anhydride was 1 wt%. Two kinds of woodfiber were used in this study. They were classified by dominantly existed woodfiber size. It was supplied from JRS Co. and AWF. Woodfibers have relative moisture contents about 7~8% and density 0.9~1.5 g/cm³. For the reason of preventing deteriorated general properties, it was important to keep the relative moisture of woodfiber low. So, all woodfibers were dried at 80℃ for 24 hours in a convection oven before compounding.

PP and MAPP were compounded in a Haake Rheocord 90 with specially designed Rheomix 900 equipped with roller blades rotor at 170℃ for 5min / 10min at 50 rpm. After the addition of PP, the woodfiber filler was added as soon as the registered torque indicated that the polymer melt had reached a steady state. It took approximately 2 min. During the mixing procedure, high-intensity ultrasonic wave was embedded from the sonic wave horn to PP matrix and woodfiber.

Mechanical properties of PWCs were measured by Universal Testing Machine (UTM, LR-5K, Lloyd Co.) and Dynamic Mechanical Analyser (DMA, Q800, TA Instruments). Tensile strength test was performed by UTM with head speed 50mm/min and over than 8 samples were measured in each case.

DSC studies were performed on a MDSC-2910 of TA instruments to obtain the melting temperature, the heat of crystallization and onset point of cure exothermic peak. It was performed by two steps. The first step, the samples were kept at 180℃ for 5 min and then cooled down to 25℃ with the cooling rate was 10℃/min to measure the temperature of crystalline. The second step, the samples were kept in 25℃ for 5min and then scanned to 180℃ with the heating rate was 10℃/min for the melting temperature. All scans for each of samples were repeated at least twice to verify the reproducibility of the measurements. The thermal stabilities of the samples were also measured using a thermo gravimetric analyzer (TGA, TA Instruments Model 2950) in a nitrogen atmosphere at a heating rate of 20℃/min from room temperature up to 700℃.

The storage modulus, loss modulus and damping factor (*tand*) of cured specimen were measured with a Dynamic mechanical Analyzer (DMA) Q800 from TA Instruments from 30℃ up to 180℃ at a scan rate of 5℃/min. The dual cantilever beam test mode was used at a frequency of 1Hz and amplitude 50 μm.

Dynamic oscillatory mode were performed on a parallel plate rheometer ARES(TA Instruments) under strain-controlled conditions and stress-controlled Physica MCR-500 (Anton Paar) were also performed. Measuring condition of all samples were kept in the linear viscoelastic region (LVR). The plates' diameter is 25 mm and the gap between plates was adjusted to be 2.0 mm. Disc test samples having the same dimensions as the rheometer plates were produced by compression molding at 180℃ for 5min compression time. All samples were repeated at least three runs to verify the reproducibility of the

measurements. The strain amplitude of 0.1% in the LVR was chosen by a dynamic strain sweep within 0.01 - 10% strains at a fixed frequency of 10 rad/s, and the frequency sweeps were implemented within 0.1-100 rad/s. The shear viscosity at shear rates ranging from 10-2000 1/s was measured by Rheograph 2003 (Göttfert) equipped with a 0.5, 1.0, 1.5 mm diameter die with all constant L/D = 20 at the 180°C.

Results and Discussion

We also the thermal and mechanical properties of PWCs using DMA. Storage modulus and $\tan\delta$ curves from DMA for 50wt% woodfiber of 140mesh size filled PP resin are shown in Fig. 1. As we see in Fig. 1. (a), storage modulus curves well agreed with the tensile strength results. But in the region of above normal temperature, storage modulus of sonicated PWCs shows a little bit low values. And in Fig. 1. (b), in the range of temperature analyzed, the $\tan\delta$ curve of neat PP exhibits two relaxations located in the vicinity of 10°C and 100°C. The lower temperature peak corresponds to the glass-rubber transition of the amorphous portions and the temperature of the maximum is taken as the glass temperature. The location of the lower temperature transition is shifted to lower temperatures with the additions of woodfiber. This results could be explain from the previous results of Díez-Gutiérrez et al. in talc-filled polypropylene composites [7]. They observed that the talc acted as nucleating agent, leading to a faster crystallization of the PP.

Fig. 2 shows thermal analysis which is the DSC cooling scanning curves of selected samples. We selected the sample to verifying the effect of ultrasonic wave with different sonication time and the contents of MAPP. We observed that there were opposite tendencies between sonicated PWCs and MAPP treated ones. This results certified that the mechanisms of enhancing the compatibility between woodfiber and matrix PP resin followed different pathway.

We performed the dynamic oscillatory measurements of PWCs for the reason of investigating the influence of woodfiber concentration on the complex viscosity and storage modulus. As we see in Fig. 3, and Fig. 4, it can be seen that both the complex viscosity and storage modulus increase with increasing the filler content. In case of sonicated PWCs, it showed a little difference of viscosity and storage modulus to simply mixed PWCs. But going into the more detailed shape, we could find the different trend of viscosity and storage at the low frequency regions for complex viscosity and storage modulus. Simply mixed PWCs exhibited the non-Newtonian behaviors. On the other hand, we can find a trend of reduction of non-Newtonian behavior in case of sonicated PWCs.

The capillary measurements are also shown in Fig. 3, in the high shear region. We used data from capillary for the application of Cox-Merz rule. It is clearly seen that only the neat PP obeys the Cox-Merz rule. The PWCs do not follow this rule and show a deviation expressed in much higher dynamic viscosity compared to the steady shear viscosity. The reason of invalidity of the Cox-Merz rule in case of PWCs is probably due to the strain amplitude viscosity dependence at low frequencies and wall slip in the capillaries.

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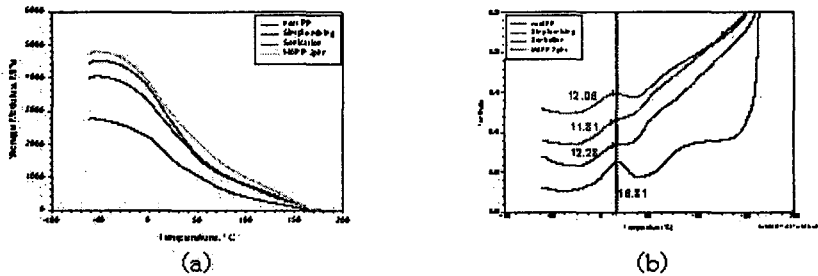


Fig. 1. Storage modulus and $\tan \delta$ of 50wt% filled PP resin (140 mesh)

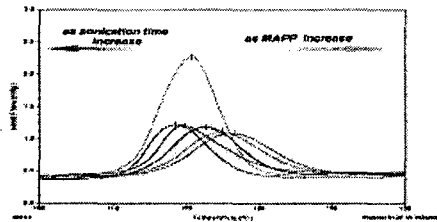


Fig. 2. T_c curves obtained from DSC under cooling $10^\circ\text{C}/\text{min}$ for neat PP and PWC(50wt% filled) with sonication time and contents of MAPP

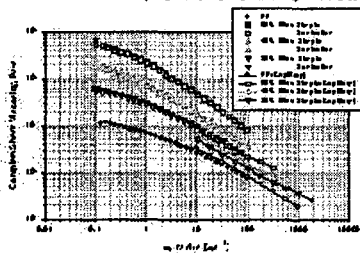


Fig. 3. Viscosity vs Frequency of wood filled PP under 0.1% strain

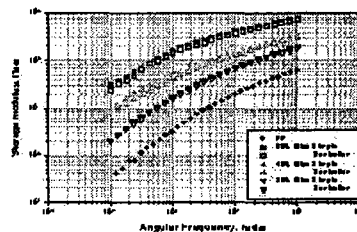


Fig. 4. Storage modulus vs Frequency of wood filled PP under 0.1% strain