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Influence of Silane Coupling Agents on the Rheological Behavior of Hemp Fiber Filled Polyamide 1010 Biomass Composites in Molten State

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Abstract. In order to develop the new engineering materials such as structural materials and tribomaterials based on all plants-derived materials, the influence of silane coupling agent on the rheological properties of hemp fiber (HF) filled polyamide 1010 (PA1010) biomass composites in molten state was investigated for one step of the fabrication of these materials. PA1010 was made from sebacic acid and decamethylenediamine, which are obtained from plant-derived castor oil. Hemp fibers were surface-treated by two types of surface treatment: a) alkali treatment by NaOH solution and b) surface treatment by silane coupling agents with different concentrations. Three types of silane coupling agents: aminosilane, epoxysilane and ureidosilane were used for surface treatment. HF/PA1010 composites were extruded by a twin screw extruder and compression-molded. Rheological behavior in molten state were evaluated by oscillatory flow testing using a parallel plate type rheometer. It was found that the silane coupling agents remarkably influence on: 1) rheological properties such as storage modulus, loss modulus, loss tangent and complex viscosity in low angular frequency region in molten state, 2) temperature dependences of rheological properties, and 3) relationship between phase angle and complex modulus (van Gurp – Palmen plots). These rheological behavior were also strongly influenced by the type of silane coupling agents. The viscoelastic properties (both storage and loss moduli) of aminosilane and epoxysilane treated composites were lower, however, those of ureidosilane treated ones were higher than the moduli of only alkali treated composites. Ureidosilane treated composites were the least temperature sensitive in the surface treated composites investigated here.

Keywords: Rheological behavior, Biomass polymer composites, Polyamide 1010, Hemp fiber, Silane coupling agent
PACS: 81.05.Qk, 83.80.Sg

INTRODUCTION

Recently, biopolymers have been extensively interested not only as a solution to growing environmental threats but also as a solution to alleviating the uncertainty of the petroleum supply [1, 2]. In addition, supply of raw materials is unstable since many of biopolymers are made from edible biomass like as corn. In order to solve these problems, the new engineering materials based on all inedible plants-derived materials are strongly required. Meanwhile, the investigation of short natural (plant) fibers, which are banana, flax, hemp, ramie, sisal fiber and so on, reinforced biopolymer composites have attracted more and more in recent decades [3, 4]. These natural fiber have some ecological advantages over inorganic fibers such as carbon and glass fibers since they are renewable and can be incinerated. In previous studies, we conducted the studies on the mechanical and tribological properties of natural fiber reinforced biopolymer composites such as hemp fiber (HF) reinforced polyamide 1010 (PA1010) composites [5- 7]. PA1010 was made from sebacic acid and decamethylenediamine, which are obtained from plant-derived castor oil [8]. Since castor oil is not used for food, there is no competition with human food consumption. It was found that the mechanical and tribological properties of these composites are improved with the filling of hemp fibers and their surface-treatment by silane coupling agent. However, in order to achieve further higher performance in the short natural fiber reinforced biopolymer composites, there is a key issue that the rheological behavior of these biomass composites in molten state is very critical to understand process-ability, internal microstructures, their change and structure-property relationships of these materials [9]. The purpose of this study is to improve the performance of all inedible plants-derived materials mentioned above for new engineering materials such as structural materials and tribomaterials. The influence of surface treatment by silane coupling agent on the rheological properties of hemp fiber filled polyamide 1010 biomass composites in molten state under oscillatory flow

was investigated experimentally. Three types of silane coupling agent, which is aminosilane, epoxysilane and ureidosilane were used for the surface treatment of hemp fiber in this study.

EXPERIMENTAL

The materials used in this study were various surface treated hemp fiber filled polyamide 1010 biomass composites. Polyamide 1010 (PA1010, Vestamid Terra DS16, Daicel-Evonik Ltd., Japan) was used as the matrix polymer. PA1010 was made from sebacic acid and decamethylenediamine, which are obtained from plant-derived castor oil. Hemp fiber (HF, ϕ 50-100 μ m, Hemp Levo Ink. Japan) was used as reinforcement fiber. The volume fraction of fiber V_f was fixed with 10 and 20 vol. %. Hemp fibers were previously cut into the length of about 50mm, and were surface-treated by two types of surface treatment: a) alkali treatment by sodium hydroxide (NaOH) solution and b) surface treatment by silane coupling agents. Alkali treatment by NaOH was employed as follows: a 5% solution of NaOH was taken in a stainless beaker. The chopped hemp fibers were added into the beaker and stirred well. This was kept at room temperature for 4 hours. The fibers were then washed thoroughly with water to remove the excess of NaOH sticking to the fibers. The alkali treated fibers (HF-A) were dried in air for 12 hours and in a vacuum oven at 80 °C for 6 hours. Three types of silane coupling agents: aminosilane (S1, 3-(2-aminoethylamino) propyltrimethoxy silane, A-1120, Momentive Performance Materials Inc., USA), epoxysilane (S2, 3-glycidoxypropyltrimethoxy silane, A-187) and ureidosilane (S3, 3-ureidopropyltrimethoxy silane, A-1160) were used as the surface treatment agents. The treatment of hemp fibers with the concentration of 1 wt.% of the chosen silane coupling agent was carried out in deionized water (for S1) or 5 wt.% of acetic acid aqueous solution (for S2 and S3, where pH of the solution was adjusted to 3.5) and stirred continuously for 15 min. Then, the fibers were immersed in the solution for 45 min. After treatment, fibers were removed from the solution and dried in oven at 80 °C for 5 hours. The volume fraction of HF in the composites was fixed at 20vol.%. All the components which were dried for 12 hours at 80 °C in vacuum oven were dry blended in the small plastic bottle, subsequently melt mixed at 85 rpm and 220 °C on a twin screw extruder (TEX-30, Japan Steel Works, Ltd., Japan). After mixing, the extruded strands of various HF/PA1010 composites were cut by pelletizer, and were dried again at 80 °C for 24 hours in vacuum oven. The sheets of 1mm thickness were compression-molded, at the condition of 220°C, 5MPa and 3min, and cut into ϕ 25mm disk shape for rheological properties measurements. The rheological properties in molten state were evaluated by oscillatory flow testing using a parallel plate type rotational rheometer (ARES, Rheometric Scientific Co., USA). The diameter of the parallel plate was ϕ 25mm, and the gap between the two plates was fixed at 1mm. Under such a gap condition, a test specimen was slightly compressed in the molten state. The angular frequency was varied from 10^{-1} to 10^2 rad/s, and the strain amplitude was set as 1%. These measurements were carried out at 200-240 °C.

RESULTS AND DISCUSSION

The rheological properties of hemp fiber filled polyamide 1010 biomass composites (HF/PA1010) in molten state were evaluated by oscillatory flow behavior. The dynamic viscoelastic properties of various surface treated HF/PA1010 composites (HF content is 20vol.%) are plotted as a function of angular frequency ω in Fig.1(a) (storage modulus G') and Fig.1b (loss modulus G''), respectively. G' of neat PA1010 (100%) increases with increasing ω agreeing with the linear dynamic viscoelastic model that G' is proportional to ω^2 ($\log G' \propto 2\log \omega$) [10-12]. G' of various HF/PA1010 composites shows the typical storage modulus G' of hilly filled systems, indicating the “second rubbery plateau”, however the value of G' changes with the types of silane coupling agents. G' of aminosilane (HF- S1/PA1010) and epoxysilane (HF-S2/PA1010) is lower than that of untreated (HF/PA1010) in wide ω region.

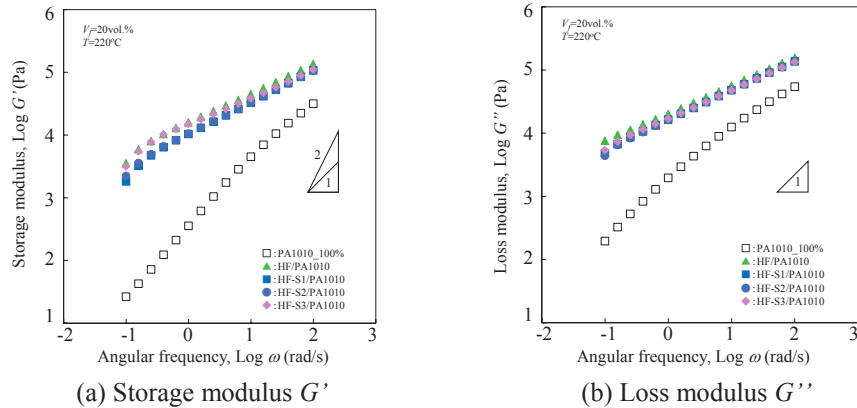


FIGURE 1. Dynamic viscoelastic properties as a function of angular frequency for various HF/PA1010 composites.

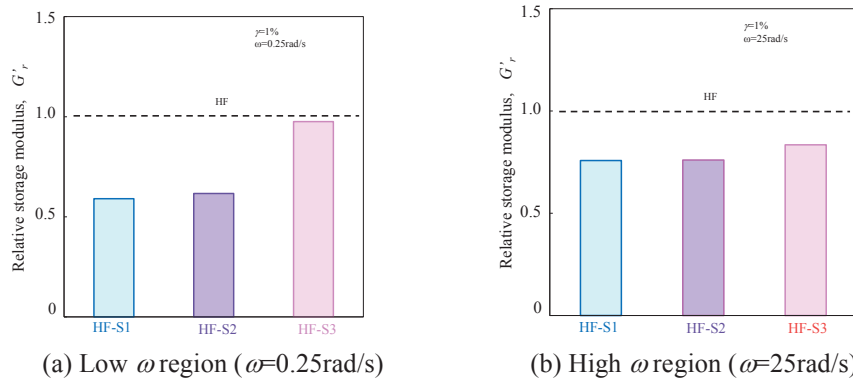


FIGURE 2. Influence of type of silane coupling agent on the relative storage modulus of HF/PA1010 composites.

To the contrary, G' of ureidosilane (HF-S3) treated composites is the same level of that of untreated one in low ω region although this is lower than that of untreated in high ω region. The slope of G' in low ω region decreases in the following order: untreated < ureidosilane (HF-S3) < epoxysilane (HF-S2) < aminosilane (HF-S1). This may be attributed to the change of interfacial interaction between HF and PA1010 according to the type of silane coupling agent. These behavior are different from the dynamic viscoelastic properties of the polymer composites such as glass fiber reinforce polypropylene composites (GF/PP), in which G' of surface treated GF/PP by silane coupling agent is higher than that of untreated [13, 14]. In general, the influence of surface treatment by coupling agents on the dynamic viscoelastic properties of the polymer composites is complex. This is because the surface treatment by coupling agents plays some multiple roles simultaneously, as a coupling agent which improves the adhesion between the fiber and the polymer, a lubricant which reduce the friction, a plasticizer which helps to make the fiber and the polymer softer, a wetting agent which reduces the agglomeration of fibers and an additive to make deformation of fiber assembly easier and lower the viscoelastic properties of the matrix polymer. It is thought that the mechanisms mentioned above do not occur separately, and therefore it is very difficult to distinguish a particular type as the factor of coupling agent influenced on the viscoelastic properties. On the other hand, loss modulus G'' of various HF/PA1010 composites is higher than that of pure PA1010, however the effect of surface treatment by silane coupling agent on G'' of HF/PA1010 composites does not differ by the type of silane coupling agent. This is because G' is a more sensitive rheological function to the structural change of the internal structure of polymer composites than G'' . That is, G' is considered to be a sensitive indicator for the quantitative analysis of morphological change in the composites.

To more clarify the effect of surface treatment by silane coupling agent on the rheological properties of HF/PA1010 composites, the relative storage modulus G'_r of various surface treated HF/PA1010 composites is shown in Fig.2(a) ($\omega=0.25$ rad/s) and Fig.2(b) ($\omega=25$ rad/s), respectively. Here, the relative storage modulus is given by the values of surface treated HF/PA1010 composites divided by that of untreated ones. The values of G'_r in low ω region (Fig.2(a), $\omega=0.25$ rad/s) differ according to the type, and G'_r of aminosilane (HF-S1) and epoxysilane (HF-S2) remarkably decreases although that of ureidosilane (HF-S3) is almost as the same level of that of untreated

HF/PA1010 composites. On the other hand, G' of all HF/PA1010 composites in high ω region is lower than that of untreated, and slightly decreases in the flowing: ureidosilane (HF-S3) > epoxysilane (HF-S2) > aminosilane (HF-S1). Thus, it was found that the effect of type of silane coupling agent on the storage modulus of HF/PA1010 composites changes with the difference in frequency region. It is well known that the storage modulus in low ω region is influenced by the strong interaction of fiber-matrix polymer and/or fiber-fiber, and the microstructure formation by the fibers, and, to the contrary, this value in high ω region is generally dominated by the polymer matrix. From the results shown above, it is concluded that the various silane coupling agents decrease the storage modulus, and silane coupling agents used in this study play the role of the lubricant, the wetting agent or the plasticizer, supported by the fact of Fig. 2(a) and 2(b). However, only ureidosilane (HF-S3) may have the strong role of the coupling agent which improves the interaction of fiber and matrix polymer since G' of ureidosilane (HF-S3) is higher than those of other systems. This trend was the same tendency as for the mechanical and tribological properties of these composites [7].

The influence of temperature on the viscoelastic properties of surface treated HF/PA1010 composites will be discussed here. The complex viscosity $|\eta^*|$ of various HF/PA1010 composites is plotted against the reciprocal of the absolute temperature $1/T$ at the angular frequency ω of 25 rad/s in Fig.3. $|\eta^*|$ of all surface treated HF/PA1010 composites is lower than that of untreated ones, and the difference of the value increases with increasing temperature. The influence of temperature on $|\eta^*|$ of HF/PA1010 composites differs for each surface treatment by silane coupling agent. It is found that epoxysilane (HF-S2) is the most temperature sensitive, and ureidosilane (HF-S3) is the least ones. From the slope of $|\eta^*|$ versus $1/T$ plots, the apparent activation energy E_a for flow can be calculated from the following Andrade's equation:

$$\eta = A \exp\left(\frac{E_a}{RT}\right) \quad (1)$$

where A is the constant value, R is the gas constant, and η was replaced by $|\eta^*|$ [15]. The apparent activation energy E_a of various HF/PA1010 composites is listed in Table1. It is found that E_a increases in the following order: ureidosilane (HF-S3) < untreated (HF) < aminosilane (HF-S1) < pure PA1010 < epoxysilane (HF-S2). It can be said that the fluidity of the materials increase with increasing E_a . In short, epoxysilane (HF-S2) with the highest value of E_a indicate the high sensitivity to temperature change. In other words, ureidosilane (HF-S3) with the lowest value of E_a has the stable flow processability in wide temperature region for HF/PA1010 composites studied here.

Fig.4 shows the phase angle δ ($=\arctan G''/G'$) is plotted against the absolute value of the complex modulus $|G^*|$ of various HF/PA1010 composites. This is known as van Gorp – Palmen plot [16], which has attracted attention recently as a method for another representation of the internal microstructures and their change. This plot is considered to be a sensitive indicator for the time-temperature superposition, the presence of long chain branch of the polymer, the gelation behavior, rheological percolation of the polymer nanocomposites and so on [17,18]. This is because the change of the rheological properties, which is hard to understand the angular frequency dependence (G' - ω , G'' - ω , $\tan \delta$ - ω curves), is emphasized in this δ - $|G^*|$ plot. As seen in Fig.4, the δ - $|G^*|$ curve of pure PA1010 .

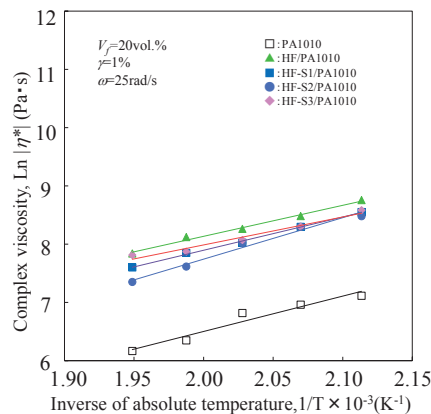


FIGURE 3. Temperature dependences of complex viscosity for various HF/PA1010 composites.

TABLE 1. Apparent activation energy of flow for various HF/PA1010 composites

Code	PA1010	HF/PA1010	HF-S1/PA1010	HF-S2/PA1010	HF-S3/PA1010
E_a (kJ/mol)	50.5	44.2	47.5	59.1	39.9

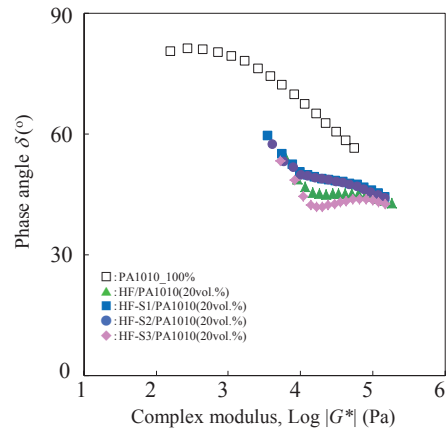


FIGURE 4. Phase angle versus absolute value of the complex modulus plots for various HF/PA1010 composites. approaches 90° at the low complex modulus $|G^*|$, indicating the flow behavior of viscous fluid. On the other hand, the $\delta|G^*|$ curves of various HF/PA1010 composites show the complex behavior, however these has the minimum value. In particular, ureidosilane (HF-S3), which is considered to play the strong role as the coupling agent to improve the interfacial interaction between the fiber and the polymer, has the minimum value clearly and is the lowest among the other surface treated systems. To the contrary, the other ones, which play weak role as the coupling agent, do not show the minimum values. Thus, this $\delta|G^*|$ plot may be able to become an indicator for the effect of surface treatment of polymer composites.

CONCLUSION

The purpose of this study is to improve the performance of all non-edible plants-derived materials based composites for new engineering materials such as structural materials and tribomaterials. The influence of surface treatment by silane coupling agent on the rheological properties of hemp fiber filled polyamide 1010 composites in molten state was investigated experimentally. It was found that the silane coupling agents remarkably influence on: 1) rheological properties such as storage modulus, loss modulus, loss tangent and complex viscosity in low angular frequency region in molten state, 2) temperature dependences of rheological properties, and 3) relationship between phase angle and complex modulus (van Gurp - Palmen plots). These rheological behavior were also strongly influenced by the type of silane coupling agents. The viscoelastic properties (both storage and loss moduli) of aminosilane and epoxysilane treated composites were lower, however, those of ureidosilane treated ones were higher than the moduli of only alkali treated composites. Ureidosilane treated composites were the least temperature sensitive in the surface treated composites investigated here.

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