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Effect of Processing Sequence on the Dynamic Viscoelastic Properties of Ternary Biomass Composites (Hemp Fiber/ PA1010/ PA11E) in the Molten State

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Abstract. For developing the new engineering materials such as structural materials and tribomaterials based on all plants-derived materials, we investigated the effect of processing sequence on the dynamic viscoelastic properties of the ternary biomass composites: 5mm cut hemp fiber (HF) filled polymer blend of plants-derived polyamide 1010 (PA1010) and polyamide 11 elastomer (PA11E) composites in the molten state. PA1010 and PA11E, which contain the polyether groups as soft segment, were made from plant-derived castor oil. The composition of the polymer blend of PA1010 and PA11E was fixed with 60/40 weight fraction. HF was surface-treated by two types of treatment: alkali treatment by NaOH solution and surface treatment by ureido silane coupling agent. The volume fraction of HF in the composites was fixed with 20vol.%. Five different processing sequences: (1) HF, PA1010 and PA11E were mixed simultaneously (Process A), (2) Re-mixing (second compounding) of the materials prepared by Process A (Process AR), (3) PA11E was blended with PA1010 (PA1010/PA11E blends) and then these blends were mixed with HF (Process B), (4) HF was mixed with PA1010 (HF/PA1010 composites) and then these composites were blended with PA11E (Process C), and (5) HF were mixed with PA11E (HF/PA11E composites) and then these composites were blended with PA1010 (Process D) were attempted for preparing the ternary biomass composites (HF/PA1010/PA11E) composites. These ternary biomass composites were extruded by a twin screw extruder and compression-molded. Their dynamic viscoelastic properties in the molten state were evaluated by oscillatory flow testing using a parallel plate type rheometer. It was found that those properties of the ternary biomass composites in the molten state are influenced so much by processing sequence. This is attributed to the change of internal microstructure of these composites such as the distribution and dispersion of HF.

INTRODUCTION

There has been some scientific and practical interest in the biopolymers and biomass polymer composites for innovative materials in a wide range of industrial applications¹. Some of the reasons are the renewability, sustainability and environmentality. In addition, supply of raw materials is unstable since many of biopolymers are made from edible biomass like as corn. To solve these problems, the new engineering materials based on all inedible plants-derived materials are strongly required. In our previous studies, we investigated the rheological, mechanical

and tribological properties of natural fiber reinforced biopolymer composites such as hemp fiber (HF) reinforced inedible plants-derived polyamide 1010 (PA1010) biomass composites and the blend of these composites and plants-derived thermoplastic elastomers (bio-TPE) such as polyamide 11 elastomer (PA11E) and thermoplastic polyurethane elastomer (TPU)²⁻⁶. It was found that the rheological, mechanical and tribological properties of these composites are improved with the filling of hemp fibers, their surface-treatment by silane coupling agent and the addition of bio-TPE. However, in order to achieve further higher performance in these ternary biomass composites such as HF/PA1010/bio-TPE composites, it is necessary to control the morphologies, which are the internal structure such as phase structure, fiber dispersion and fiber localization of these ternary biomass composites. It is well known that the morphologies of multi-component composites are strongly influenced by the processing sequences at melt mixing by twin extruder. Several investigations have been conducted on the effect of processing sequences at melt mixing on the relationship between the morphology and the mechanical properties of ternary composites such as PA/Clay/SEBS⁷, CNF/PBT/TPE⁸ and CNF/PA/SEBS^{9, 10}. It was found that the influence of processing sequence on the mechanical properties of these ternary composites differs with each property. However, there is not enough knowledge of reliable relations between the internal structure and the rheological properties of ternary biomass composites. Because there is a key issue that the rheological behavior of these ternary biomass composites in molten state is very critical to understand process-ability, internal microstructures, their change and structure-property relationships of these materials. The objective of the present study is to develop the new engineering materials such as structural and tribolomaterials base on all inedible plants-derived materials mentioned above. The effect of processing sequence on the dynamic viscoelastic properties of the ternary biomass composites: 5mm cut hemp fiber (HF) filled polymer blends of plants-derived polyamide 1010 (PA1010) and plants-derived polyamide 11 elastomer (PA11E) composites in the molten state was investigated experimentally.

EXPERIMENTAL

The materials used in this study were the surface treated hemp fiber reinforced polyamide 1010 biomass composites (HF/PA1010) and the blend of these composites and plant-derived polyamide 11 elastomers. Polyamide 1010 (PA1010, Vestamid Terra DS16, DaicelEvonic Ltd., Japan) was used as the matrix polymer. Polyamide 11 elastomers (PA11E, PEBAX Rnew 35R53, Arkema K. K., Japan). PA11E has two chemical structures, which are polyamide groups as the hard segment and polyether ones as soft segment. PA1010 and PA11E (except the polyether groups used as soft segment) were made from plant-derived castor oil. The composition of the polymer blend of PA1010 and PA11E was fixed as 60/40 by weight fraction. Hemp fiber (HF, ϕ 50-100 μ m, Hemp Levo. Ink., Japan) was used as the reinforcement fiber. Hemp fibers were previously cut into length of about 5mm, and were surface-treated by two types of surface treatment: a) alkali treatment by sodium hydroxide (NaOH) solution and b) surface treatment by ureido silane coupling agent (3-ureidopropyltrimethoxy silane, A-1160, Momentive Performance Material Inc., USA). 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 4h. 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 12h and in a vacuum oven at 80°C for 5h. Ureido silane coupling agent was used as a surface treatment agent. The treatment of hemp fibers with the concentration of 1wt.% ureido silane coupling agent was carried out in 0.5wt.% of acetic acid aqueous solution in which the pH of the solution was adjusted to 3.5 and stirred continuously for 15 min. Then, the fibers were immersed in the solution for 60 min. The surface-treated hemp fibers (HF-S) were removed from the solution and in air for 12h and in a vacuum oven at 80°C for 5h. The volume fraction of fiber V_f in the composites was fixed with 20vol.%. Prior to mixing, HF, PA1010 and PA11E were dried in a vacuum oven at 80°C for 12h. Five different processing sequences: (1) HF, PA1010 and PA11E were mixed simultaneously (Process A), (2) Re-mixing (second compounding) of the materials prepared by Process A (Process AR), (3) PA11E was blended with PA1010 (PA1010/PA11E blends) and then these blends were mixed with HF (Process B), (4) HF was mixed with PA1010 (HF/PA1010 composites) and then these composites were blended with PA11E (Process C), and (5) HF were mixed with PA11E (HF/PA11E composites) and then these composites were blended with PA1010 (Process D) were attempted for preparing the ternary biomass composites (HF/PA1010/PA11E). Fig.1 shows the schematic diagram of five different processing sequences for HF/PA1010/PA11E biomass ternary composites. These ternary biomass composites were 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/PA11E composites were cut by pelletizer, and were dried again at 80°C for 12 h in vacuum oven. The sheets of 1mm thickness were compression-molded, at the condition of 220°C, 5MPa and 3min, and cut

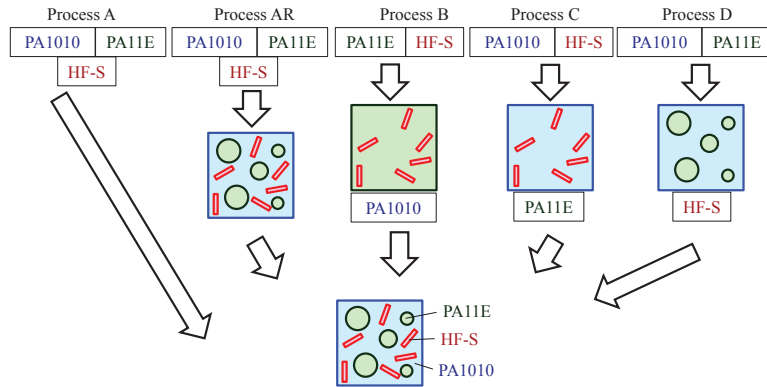


FIGURE 1. Schematic diagram of five kinds of processing method for HF/PA1010/PA11E composites

into $\phi 25\text{mm}$ disk shape for rheological properties measurements. The dynamic viscoelastic 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 $\phi 25\text{mm}$, 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 10^2rad/s , and the strain amplitude was set as 1%. These measurements were carried out at 210, 220 and 230 °C.

RESULT AND DISCUSSION

First, the effect of processing sequence on the morphologies of ternary biomass composites (Hemp fiber/PA1010/PA11E) ternary biomass composites to understand the internal structure formation is discussed. Fig.2 presents the SEM photographs of cryogenically fracture surface of HF/PA1010/PA11E ternary biomass composites prepared by various processing sequences. The dispersion of HF in these composites differs for each processing sequence. In particular, the morphologies of Process AR, Process B and Process C, which are twice mixing of HF by a twin screw extruder, are good distribution and dispersion of HF although those of Process A and Process D, which are once one, have some agglomerations of HF. In other words, the distribution and dispersion of HF correlate closely with the period of mixing time.

Second, the rheological properties of HF/PA1010/PA11E ternary biomass composites prepared by various processing sequences were evaluated by oscillatory flow behavior, which are considered to be strongly dependent on the internal microstructure formation of these composites. The effect of processing sequence on the dynamic viscoelastic properties of ternary biomass composites (Hemp fiber/PA1010/PA11E) in the molten state is plotted as a function of angular frequency ω in Fig.3 (a) (storage modulus G') and Fig.3 (b) (loss modulus G''), respectively. G' of HF/PA1010/PA11E ternary biomass composites prepared by various processing sequences shows the typical storage modulus G' of filled systems, indicating the “second rubbery plateau”, however the values of G' change with the types of processing sequences. The values of G' increase in the following order: Process AR < Process C < Process B < Process D < Process A. In short, G' of Process AR, B and C, which are twice mixing of HF, are smaller than that of Process A and D, which are once mixing. This can be explained by the change of internal microstructure according to the type of processing sequences. Thus, this tendency has closely relation with the distribution and dispersion of HF. On the other hand, loss modulus G'' of HF/PA1010/PA11E ternary biomass composites prepared by various processing sequences shows almost the similar behavior to G' , although the values of G'' of the composites prepared by Process AR, B and C, which twice mixing of HF, are different from that of G' . This may be due to the change of structure formation of matrix polymers, which is the polymer blend of PA1010 and PA11E. However, the detail

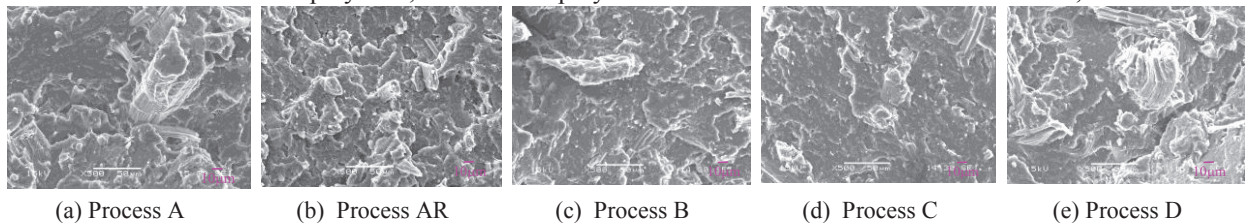
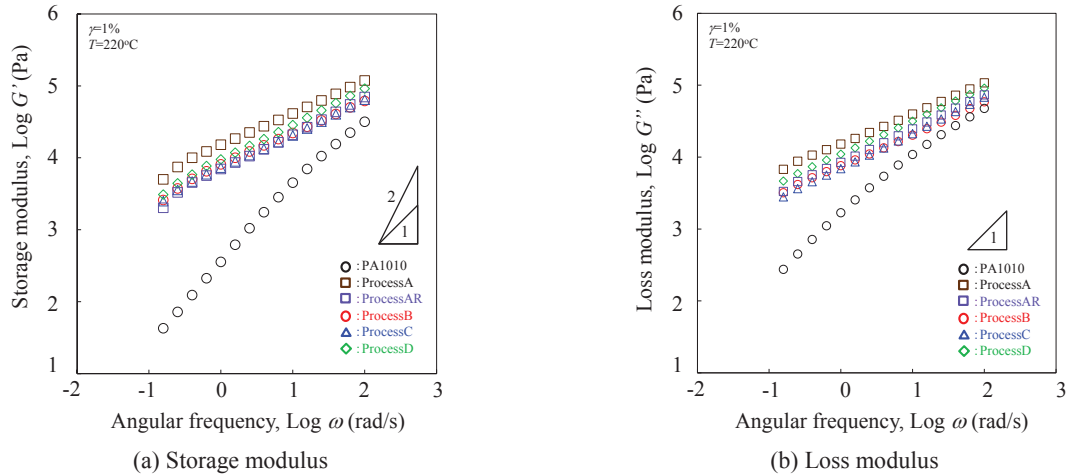


FIGURE 2. Image of SEM photographs of fracture surface of various HF/PA1010/PA11E composites



(a) Storage modulus (b) Loss modulus
FIGURE 3. Dynamic viscoelastic properties as a function of angular frequency for various processing sequences of HF/PA1010/PA11E ternary biomass composites.

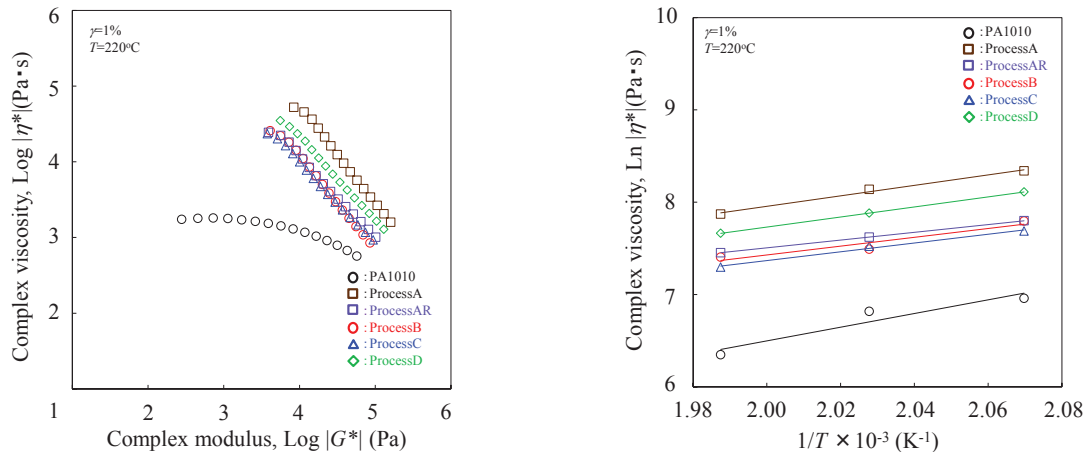


FIGURE 4. Relationship between the complex viscosity and complex modulus for various processing sequences of HF/PA1010/PA11E composites.

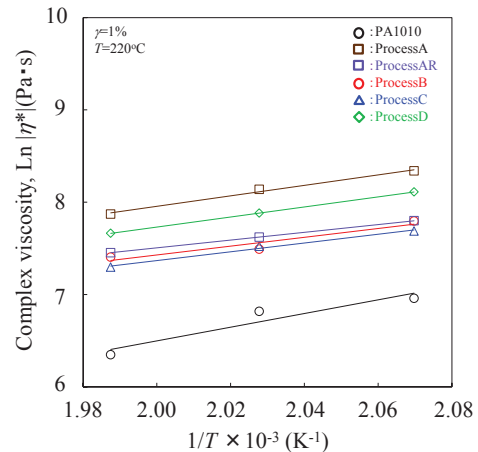


FIGURE 5. Temperature dependence of complex viscosity for various processing sequences of HF/PA1010/PA11E composites.

reasons are unknown at this time. For better understanding these phenomenon, it is necessary to observe the morphology of structure formation of matrix polymer region. These observation will be reported at the Conference presentation.

Next, the complex viscosity $|\eta^*|$ is plotted against the complex modulus $|G^*|$ of HF/PA1010/PA11E ternary biomass composites prepared by various processing sequences. $|\eta^*|$ decreases rapidly with increasing $|G^*|$, and $|\eta^*|$ - $|G^*|$ curves are typical high content particle and short fiber filled systems^{(11), (12)}. It can be estimated from these curves that there are apparent yield values. On the other hand, the effect of processing sequences on the $|\eta^*|$ - $|G^*|$ curves of these composites is shifted to lower left side according to the type of processing sequences. Specially, those curves of Process AR, B and C, which are twice mixing of HF, are shifted to the lower left side. The reason for such behavior can be considered as follows: The viscoelastic values such as $|G^*|$ and $|\eta^*|$ of the composites by Process AR, B and C are smaller than those by Process AR and D, because Process AR, B and C have better distribution and dispersion of HF in the composites. Therefore, the viscoelastic values of HF/PA1010/PA11E ternary biomass composites correlate closely with the internal structure formation of these composites. Finally, the effect of temperature on the complex viscosity of various processing sequences for HF/PA1010/PA11E ternary biomass composites is discussed. The complex viscosity $|\eta^*|$ of these composites is plotted against the reciprocal of the absolute temperature $1/T$ at the angular frequency ω of 25 rad/s in Fig.5. The effect of temperature on $|\eta^*|$ of these composites differs for each

TABLE 1. Apparent activation energy of flow for various processing sequences of HF/PA1010/PA11E composites

Code	PA1010	ProcessA	ProcessAR	ProcessB	ProcessC	ProcessD
E_a (kJ/mol)	50.5	45.8	31.0	36.0	34.2	42.5

processing sequence. From the slope of $|\eta^*|$ versus $1/T$ plot, the apparent activation energy E_a for flow can be calculated from the Andrade's equation. The detail of this calculation method are omitted here since it is noted in the previous report⁴. E_a of various processing sequences for these composites is listed in Table 1. E_a decreases in the following: Process A > Process D > Process B > Process C > Process AR. Therefore, Process AR with the lowest value of E_a has the stable flow processability in a wide temperature region for various processing sequences of HF/PA1010/PA11E ternary biomass composites in this study.

CONCLUSION

The objective of the present study was to develop the new engineering materials such as structural and tribomaterials base on all inedible plants-derived materials. The effect of processing sequence on the dynamic viscoelastic properties of the ternary biomass composites: 5mm cut hemp fiber (HF) filled polymer blends of plants-derived polyamide 1010 (PA1010) and plants-derived polyamide 11 elastomer (PA11E) composites in the molten state was investigated experimentally. It was found that dynamic viscoelastic properties of the ternary biomass composites in the molten are influenced so much by processing sequence. This is attributed to the change of internal microstructure of these composites such as the distribution and dispersion of HF.

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