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Thermal Properties of Hemp Fiber Filled Polyamide 1010 Biomass Composites and the Blend of These Composites and Polyamide 11 Elastomer

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Abstract. The aim of this study is to improve the performance of all inedible plants-derived materials for new engineering materials such as structural materials and tribomaterials. Thermal properties of hemp fiber filled polyamide 1010 biomass composites and the blend of these composites and plants-derived TPE were investigated experimentally. These biomass composites were extruded by a twin screw extruder and compression or injection molded. Thermal properties such as dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of these biomass composites were evaluated. It was found that the addition of HF and the blend of bio-TPE with PA1010 have strong influence on the thermal properties such as DMA, TGA and DSC. In particular, HF has a good effect for the improvement of the thermal and mechanical properties. These properties of HF/PA1010/PA11E biomass composites are better than those of HF/PA1010/TPU ones.

Keywords: Thermal properties, Biomass polymer composites, Natural fiber, Plants-derived polyamide, Polymer blend.
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INTRODUCTION

Biopolymers and biomass polymer composites 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 in recent years[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. In our previous studies, we investigated the 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 (TPE) such as polyamide 11 elastomer (PA11E) and thermoplastic polyurethane elastomer (TPU) [3)-8)]. It was found that the 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 TPE. However, in order to achieve further higher performance in the natural fiber reinforced biopolymer composites, there is a key issue that the thermal properties of these biomass composites is very critical to understand heat resistance, internal microstructures, their change and structure-property relationships of these materials. The aim of this study is to improve the performance of all inedible plants-derived materials for new engineering materials such as structural materials and tribomaterials. Thermal properties such as dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA) and differential

scanning calorimetry (DSC) of hemp fiber filled inedible polyamide 1010 biomass composites and the blend of these composites and plants-derived TPE were 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 thermoplastic elastomers (bio-TPE). Polyamide 1010 (PA1010, Vestamid Terra DS16, Daicel Evonic Ltd., Japan) was used as the matrix polymer. Two types of plants-derived TPE (bio-TPE): PA11E (PEBAX Rnew 35R53, Arkema K. K., Japan) and TPU (PANDEX T-B190N, DIC Bayer Polymer Ltd., Japan) were used as the blending materials with HF/PA1010 composites. 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 TPE was fixed as 80/20 by weight fraction. Hemp fiber (HF, ϕ50-100, 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 80ºC for 5h. Ureido silane coupling agent was used as surface treatment agents. 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 80ºC for 5h. The volume fraction of fiber V_f in the composites was fixed with 20vol.%.

All the components which were dried for 12h at 80ºC in vacuum oven were dry blended in the small plastic bottle, subsequently melt mixed at 85 rpm and 220ºC 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 80ºC for 12h in vacuum oven. Various shaped samples for various experiments were injection molded (NS20-A, Nissei Plastic Industrial, Japan). The molding conditions were as follows: cylinder temperatures of 220ºC, mold (cavity) temperature of 30ºC and the injection rate of 13cm³/s. In addition, sheets of 2mm thickness were compression molded under the conditions of 220ºC, 5 min and 5MPa, and cut into 5mm x 40mm x 1mm shape specimen for measurement of dynamic mechanical analysis. To keep the drying conditions of specimens for all measurements, they were kept in accordance with JIS K 6920-2 for at least 24h at 23ºC in desiccators after molding.

Thermal properties such as dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were evaluated. The storage modulus, loss modulus and loss tangent (tan δ) of the composites were measured as function of temperature (from -100 to 200ºC) using a DMA equipment (RSA3, TA instrument Co. Ltd., USA) with a tensile fixture at a frequency of 1Hz. The thermogravimetric analysis (TGA) was carried out in a TGA equipment (Thermo plus EVO2, Rigaku Co. Ltd., Japan). The samples used for the TGA were cut from injection molded coupon specimen into a small piece having a weight of 10mg. TGA measurement was programmed for heating from 40 to 400ºC with a heating rate of 10ºC/min. The differential scanning calorimetry (DSC) was measured by DSC equipment (DSC-50, Shimadzu Co. Ltd., Japan). The samples used for the DSC were prepared like those for TGA (5mg). DSC measurement was scanned from -90 to 230 ºC with a constant heating rate of 10ºC/min.

RESULT AND DISCUSSION

First, the dynamic mechanical analysis of hemp fiber filled polyamide 1010 biomass composites (HF/PA1010 biomass composites) and the blend of these composites and plants-derived TPE (HF/PA1010/bio-TPE biomass composites) is discussed. The storage modulus E' and loss tangent tanδ are plotted as a function of temperature T for neat PA1010 (100%), HF-S/PA1010, HF-S/PA1010/PA11E and HF-S/PA1010/TPU composites in Fig.1 (a) (E' vs. T) and Fig.1 (b) (tanδ vs. T), respectively. E' of HF/PA1010 composites is higher than that of neat PA1010, indicating that HF has a strong reinforcing effect on the elastic properties of PA1010. On the other hand, E' of the ternary biomass composites (HF/PA1010/bio-TPE) decrease with blending of bio-TPE such as PA11E and TPU, and have the same level at that of neat PA1010. In particular, E' of HF/PA1010/PA11E biomass composites are slightly

higher than that of HF/PA1010/TPU ones in the temperature region higher than 50°C. Tanδ curves (Fig.1 (b)) exhibit two relaxation peaks. The first peak between at 40 and 60°C represents the grass transition temperature T_g of the composites, and the second one between at -80 and -60°C shows the relaxation arising from the hydrogen bonds between the PA1010 chains[9]. The relaxation peak at the high temperature region of HF/PA1010 composites decrease in comparison with neat PA1010 although those of ternary biomass composites such as HF/PA1010/PA11E and HF/PA1010/TPU are the same level at that of neat PA1010. On the other hand, the relaxation peak at the lower temperature region of neat PA1010 shifts toward the lower temperature with the addition of HF, however those of ternary biomass composites do not shift. In general, those of rigid fiber (or inorganic filler) filled polymer composites shift toward the higher temperature due to restricting the movement of the polymer chains[9]. In contrast, flexible fiber such as the natural fiber employed in this study show the contrary tendency. The mechanisms of how the addition of HF affects the relaxation peak at the low temperature region of composites needs to be studied further. In addition, tanδ curve of HF/PA1010/TPU biomass composites shows the small relaxation peak between at -50 and -30°C which may by derived from TPU.

Next, the thermogravimetric analysis (TGA) of various PA1010 biomass composites is discussed. Fig.2 shows TG curves (the weight as a function of temperature T) of various PA1010 biomass composites. The weight of neat PA1010 is higher than that of various HF filled PA1010 biomass composites over the whole range of temperature. TG curve of various PA1010 biomass composites shows the evidence of two weight loss processes, while that of neat PA1010 is only one weight loss process. The first weight loss process between 80 and 200°C is attributed to the dehydration of HF as well as the thermal degradation of lignin and hemicellulose[10], [11]. The second weight loss
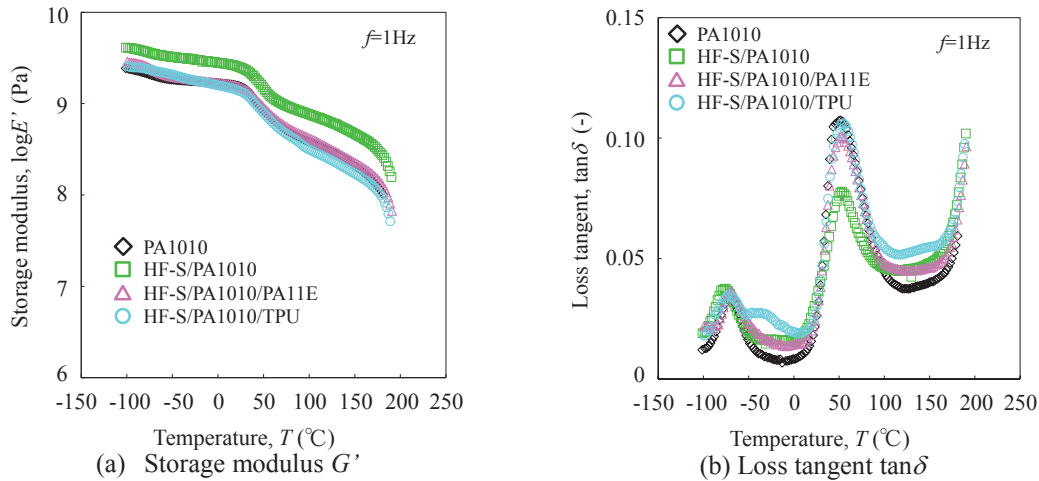

(a) Storage modulus G'

(b) Loss tangent tanδ

FIGURE1. Dynamic mechanical properties as a function of temperature for various HF/PA1010 composites
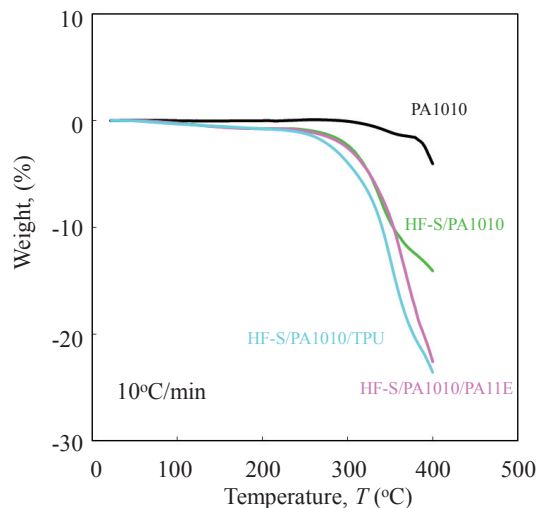

FIGURE2. Thermogravimetric curves of various HF/PA1010 biomass composites.

process at about 300°C is explained in terms of decomposing mostly of the cellulose in HF. In addition, TG curves of various PA1010 biomass composites decrease in the following order: HF/PA1010 > HF/PA1010/PA11E > HF/PA1010/TPU. This indicates that PA11E has more effective for the improvement of heat resistance of HF/PA1010 composites in the ternary biomass composites.

The crystal form of the polymer has a strong influence on the mechanical properties of the polymer composites. The differential scanning calorimetry (DSC) was employed to evaluate the effect of HF and the blends of these composites and bio-TPE on the crystallization behavior of PA1010. Fig. 3 shows DSC 1st heating (Fig.3 (a)) and 2nd heating (Fig.3 (b)) curves obtained at 10°C/min rate, respectively. DSC 1st heating curves in Fig.3 (a) show a melting peak, although DSC 2nd heating curves in Fig.3 (b) have two melting peaks. This may be explained by the following mechanisms: in DSC run, it was pointed out recently by Li et. al. [12] that the appearance of multiple melting peaks is probably due to rearrangement of the lamellae since the polyamide crystals can be easily thicken by annealing. It is considered that the same phenomenon occurs for PA1010 used in this study. T_{m1}, which is the melting point in the lower temperature side, is attributed to the thin lamellae formed during cooling, and T_{m2}, which is in the higher ones, is attributed to the melting of the thickened crystals during heating and annealing process. Parameters such as the melting point T_m, T_{m1} and T_{m2}, the cooling point T_c and the heat of fusion ΔH_f calculated from DSC curves for various PA1010 biomass composites are listed in Table 2. T_m in 1st heating curves shifts to lower temperature with the HF and bio-TPE, while ΔH_f increases with HF in spite of decreasing with blending the bio-TPE. On the other hand, T_{m1} does not change in 2nd heating curves except of HF/PA1010/TPU composites, however T_{m2} and ΔH_f shift to lower temperature. These results indicate that HF has a good effect for the improvement of mechanical properties.

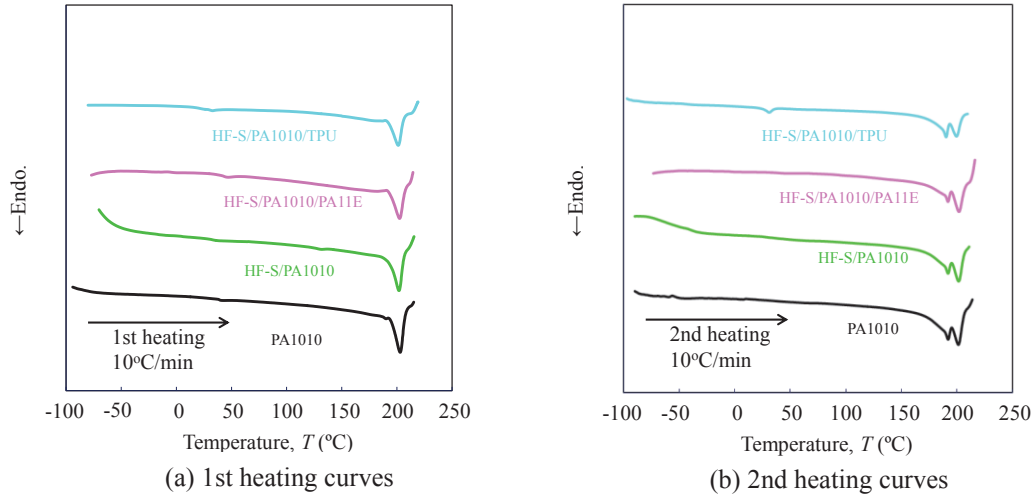(a) 1st heating curves　　　　(b) 2nd heating curves

FIGURE3. DSC curves of various HF/PA1010 biomass composites

TABLE1. Glass transition temperature and melting temperature of various HF/PA1010 composites

	1st heating		1st cooling	2nd heating		
	T_m (°C)	ΔH_f (J/g)	T_c (°C)	T_{m1} (°C)	T_{m2} (°C)	ΔH_f (J/g)
PA1010	203.0	18.5	177.7	192.2	203.3	36.0
HF-S/PA1010	201.8	21.0	178.3	192.0	201.6	31.4
HF-S/PA1010/PA11E	202.5	16.1	178.0	192.0	201.8	25.3
HF-S/PA1010/TPU	201.3	14.9	176.0	190.3	199.6	25.1

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CONCLUSION

The aim of this study is to improve the performance of all inedible plants-derived materials for new engineering materials such as structural materials and tribomaterials. Thermal properties such as DMA, TGA and DSC of hemp fiber filled polyamide 1010 biomass composites and the blend of these composites and plants-derived TPE were investigated experimentally. It was found that the addition of HF and the blend of bio-TPE with PA1010 have strong influence on the thermal properties such as DMA, TGA and DSC of PA1010. In particular, HF has a good effect for the improvement of the thermal and mechanical properties. These properties of HF/PA1010/PA11E biomass composites are better than those of HF/PA1010/TPU ones.

ACKNOWLEDGMENTS

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