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Effect of Addition of Plants-Derived Polyamide 11 Elastomer on the Mechanical and Tribological Properties of Hemp Fiber Reinforced Polyamide 1010 Composites

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Abstract. For the purpose of developing the new engineering materials such as structural materials and tribomaterials based on all plants-derived materials, the effect of the addition of plant-derived polyamide 11 Elastomer (PA11E) on the mechanical and tribological properties of hemp fiber(HF) reinforced polyamide 1010 (HF/PA1010) composites was investigated. PA1010 and PA11E (except the polyether groups used as soft segment) were made from plant-derived castor oil. Hemp fiber was surface-treated by two types of treatment: alkali treatment by NaOH solution and surface treatment by ureido silane coupling agent. HF/PA1010/PA11E ternary composites were extruded by a twin screw extruder and injection-molded. Their mechanical properties such as tensile, bending, Izod impact and tribological properties by ring-on-plate type sliding wear testing were evaluated. The effect of the addition of PA11E on the mechanical and tribological properties of HF/PA1010 composite differed for each property. Izod impact strength and specific wear rate improved with the addition of PA11E although tensile strength, modulus, and friction coefficient decreased with PA11E. It follows from these results that it may be possible to develop the new engineering materials with sufficient balance between mechanical and tribological properties.

Keywords: Polyamide 1010, Hemp fiber, Polyamide 11 elastomer, Biomass composites, Mechanical properties.

PACS: 81.05.Qk, 81.40Pq,

INTRODUCTION

There has been a great interest in biopolymers which are plant-derived polymers because they have the possibility to solve some environmental problems such as uncertainty of the petroleum supply and global warming [1, 2]. However, the physical properties of biopolymers are lower than those of ordinary petroleum-derived polymers, and 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 inedible plants-derived materials are strongly required. In previous studies, we conducted the studies on the effect of surface treatment on the mechanical and tribological properties of hemp fiber (HF) reinforced polyamide 1010 (PA1010) composites [3-5]. PA1010 was made from sebacic acid and decamethylenediamide, which are obtained from plant-derived castor oil [6]. It was found that HF has a good reinforcing effect on the mechanical and tribological properties of the composites. And the surface treatment by silane coupling agent on HF significantly improved these properties. Especially, treatment by ureidosilane coupling agent was the most effective in various silane systems for enhancement of these properties of HF/PA1010 composites. However, in order to develop new tribomaterials with further higher performance using plant-derived polymer composite, it is necessary to investigate the effect of third component such as elastomer and other polymer on these properties, which is a method to use to polymer blend as the matrix material of the composite. The purpose of this study is to improve the performance of inedible plants-derived materials mentioned above for new engineering materials such as structural materials and tribomaterials. The effect of the addition of plant-derived polyamide 11 elastomer (PA11E) on the mechanical and tribological properties of HF/PA1010 composites was investigated. The influence of three types of PA11E with different hardness based on the chemical structure on the mechanical and tribological properties of these injection-molded composites was investigated experimentally.

EXPERIMENTAL

The materials used in this study were 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-L (PEBAX Rnew 35R53, D35, Arkema K.K.Japan), PA11E-M (PEBAX Rnew 55R53, D55), PA11E-H (PEBAX Rnew 72R53, D72), where D value means the Shore hardness (type D) of each materials, were used as the blending materials with HF/PA1010 composites. PA11E has two chemical structures, which are polyamide groups as the hard segment and polyether ones as soft segment. The hardness of PA11E is determined by the component ratio of these structures, and increases with increase of the volume of polyamide groups. 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 80/20 by weight fraction. Hemp fiber (HF, ϕ 50-100, 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 80°C 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 80°C 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 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/PA11E composites were cut by pelletizer, and were dried again at 80°C for 12h in vacuum oven. Various shaped samples for mechanical and tribological properties testing were injection molded (NS20-A, Nissei Plastic Industrial, Japan). The molding conditions were as follows: cylinder temperatures of 220°C, mold (cavity) temperature of 30°C and the injection rate of 13cm³/s. Mechanical (tensile, bending, and impact) and tribological properties were evaluated. Tensile testing was carried out with dog-bone samples on a Toyo Seiki testing machine V-10, in accordance to the JIS K 7161, at the cross-head speed of 50 mm/min. Three point bend testing was carried out with coupon specimens on the V-10, in accordance to the JIS K 7171, and at the cross-head speed of 2mm/min. Impact characteristics were determined by Izod impact test. Izod impact tests were conducted using coupon specimen with a notch depth of 2.5mm on a Toyo Seiki impact machine DG-IB at room temperature, in accordance to JIS K 7110. Tribological properties were measured by a ring on plate type sliding wear tester (EFM-3-EN, A&D Co. Ltd., Japan) under dry condition. A carbon steel (S45C) ring with the surface finished by No.240 and No.800 polishing paper was used as a counterpiece. Two types of tribological testing were carried out by constant normal load ($P=50N$) and sliding speed ($v=0.2m/sec$) testing, and limiting pv value testing by the step load method ($P_0=50N$, $P=25N/3min$, $v=0.3$, 0.4 and 0.5m/sec). The surface of samples fractured cryogenically in liquid nitrogen, transfer film on the counterface, worn surface and wear debris were observed by scanning electron microscope (SEM, VE-8800S Keyence Co. and JSM-6360LA. JEOL Ltd., Japan).

RESULTS AND DISCUSSION

First, the effect of addition of plants-derived polyamide 11 elastomer (PA11E) on the mechanical properties such as tensile, bending, and Izod impact properties of surface-treated hemp fiber (HF-S) reinforced plant-derived polyamide 1010 (PA1010) biomass composites are discussed. Fig.1 shows the mechanical properties of various HF-S/PA1010/PA11E ternary composites. In Fig. 1(a), the tensile strength σ_t is plotted against the tensile modulus E_t for pure PA1010 (100%), HF-S/PA1010 composites and HF-S/PA1010/PA11E ternary composites with different hardness PA11E. Although σ_t of PA1010 improves with filling HF-S, the effect of the addition of PA11E on the σ_t and E_t of HF-S/PA1010 composites decreases with decreasing the hardness of PA11E in the following order: HF-S/PA1010/PA11E-H > HF-S/PA1010/PA11E-M > HF-S/PA1010/PA11E-L. The bending strength σ_b of various

PA1010 composites is plotted against the bending modulus E_b in Fig. 1(b). The influence of the addition of PA11E on the bending properties of HF-S/PA1010 composites has the same tendencies, however the decrease of bending properties with the hardness of PA11E is smaller than that of tensile properties. Fig.1(c) shows the Izod impact strength a_{iN} of various PA1010 composites. a_{iN} of HF-S/PA1010/PA11E ternary composites increases with decreasing the hardness of PA11E although that of PA1010 decreases with HF-S. To more clarify the effect of the addition of PA11E with different hardness on the mechanical properties of HF-S/PA1010 composites, Izod impact strength a_{iN} of various HF-S/PA1010/PA11E ternary composites as a function of bending modulus E_b is re-plotted Fig.2. This figure means that the higher the value is plotted in the upper and right side in this figure, the more sufficient balances with stiffness and toughness for engineering materials such as tribomaterials are shown. From the results on the mechanical properties obtained in this study, HF-S/PA1010/PA11E containing PA11E-L is thought to be the most suitable for engineering materials in the composites studied here.

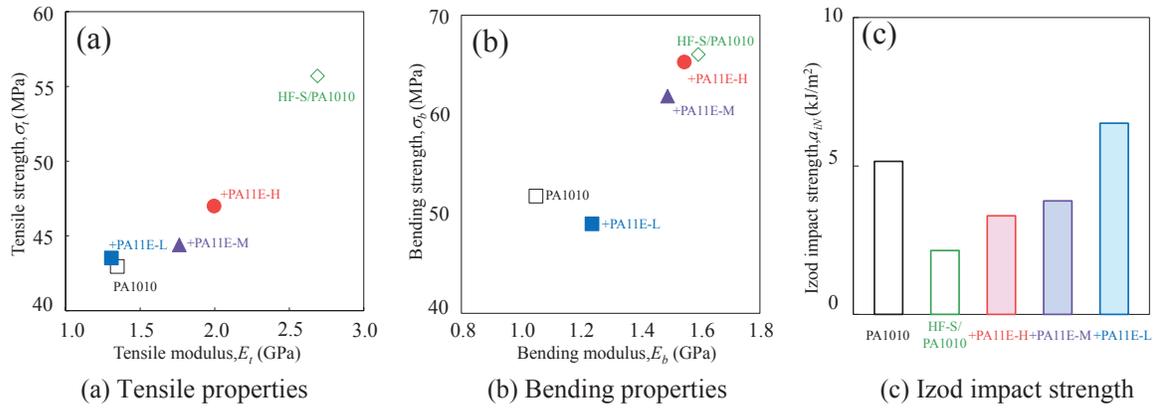


FIGURE 1. Mechanical properties of various PA1010 composite

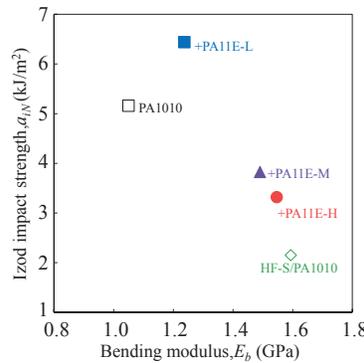


FIGURE 2. Relationship between Izod impact strength and bending modulus

The tribological properties of HF-S/PA1010/PA11E ternary composites by constant normal load and sliding speed testing using a ring-on-plate type sliding wear tester are discussed. Fig. 3(a) and Fig. 3(b) show the frictional coefficient μ and specific wear rate V_s of various PA1010 composites, respectively. Both μ and V_s of pure PA1010 improve with the filling of HF-S, and the effect of the addition of PA11E on the μ does not appear remarkably. To the contrary, V_s is highly influenced by the addition of PA11E, and these effects decrease in the following order: HF-S/PA1010/PA11E-H > HF-S/PA1010/PA11E-M > HF-S/PA1010/PA11E-L. In short, HF-S and PA11E have a good improvement effect for the tribological properties of PA1010. These results may be attributed to the change in the mode of wear mechanism by the filling of HF-S and PA11E. Because the tribological behavior of polymer composites are strongly influenced by their ability to form a transfer film on the counterface, it is essential to observe this factor for understanding the mechanisms of tribological behavior [7, 8]. Fig.4 presents SEM photographs of on the surface of metallic counterface (S45C) before (Fig.4 (a)) and after sliding wear testing against various HF-S/PA1010/PA11E composites. The morphology after sliding wear test of pure PA1010 (Fig.4 (b)) shows thick transfer film surface overall, although that of HF-S/PA1010 (Fig.4 (c)) composites shows thin ones overall. To the contrary, that of HF-S/PA1010/PA11E-H (Fig.4 (d)) shows thin ones with shallow grooves in a direction

orthogonal to sliding direction. On the other hand, that of HF-S/PA1010/PA11E-M (Fig.4 (e)) and HF-S/PA1010/PA11E-L (Fig.4 (f)) is formed with much thin smooth film, and several wear debris are observed on the transfer film surface. The thickness of the transfer film on the counterface against HF-S/PA1010/PA11E composites differs according to the hardness of PA11E in the following order: PA1010 > HF-S/PA1010 > HF-S/PA1010/PA11E-H > HF-S/PA1010/PA11E-M > HF-S/PA1010/PA11E-L. This is attributed to the difference of the amount of soft segment (polyether groups), which behaves like a rubber more. In ternary composites with PA11E, PA11E melts earlier than PA1010 by frictional heat since the melting point of PA11E is lower than that of PA1010. Thus, the transfer film containing preferentially PA11E (or soft segment of PA11E) is formed. These differences in the formation of transfer films on the counterface are considered to change the tribological properties of HF/PA1010 composites with the addition of PA11E. However, it is necessary for further clarification of the above mechanisms to carry out detailed observations of structural changes of frictional surface of various PA1010 composites such as the wear debris and worn surface. The SEM photographs of them after sliding wear testing will be reported at the Conference presentation.

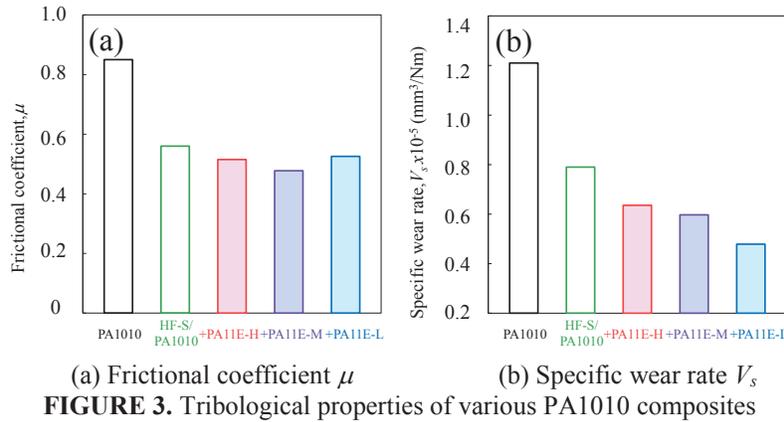


FIGURE 3. Tribological properties of various PA1010 composites

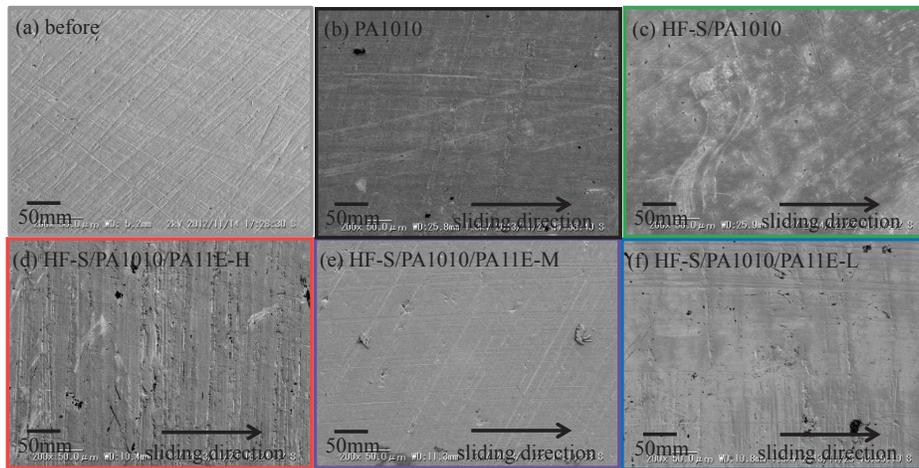
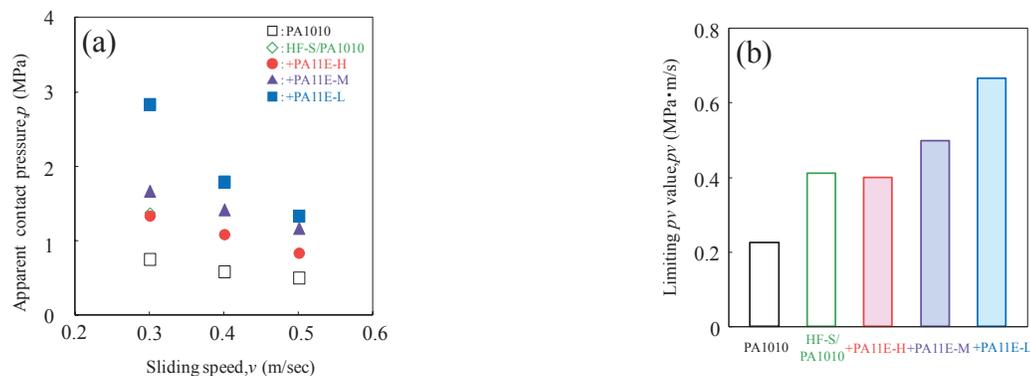


FIGURE 4. Image of SEM photographs of counterface of various PA1010 composites

The limiting $p\nu$ value testing results by the step load method of various HF/PA1010 composites, which is more severe than constant load and speed testing are discussed. Apparent constant pressure p is plotted against sliding speed ν in Fig.5 (a), which is called as $p\nu$ curves. p of all materials increases with decreasing ν , and the slope of $p\nu$ curves against ν increase with the addition of HF-S and PA11E according with the amount of soft segment. Fig.5 (b) shows the limiting $p\nu$ values of various HF/PA1010 composites. The limiting $p\nu$ values have the same tendencies as those of $p\nu$ curves. This result suggests the following mechanisms for the improvement of the limiting $p\nu$ value of various PA1010 composites: the ability of supporting the load increases with the filling of HF, and the transfer film containing preferentially PA11E is formed as above mentioned.



(a) Relationship between apparent contact pressure p and sliding speed v

(b) Limiting pv value

FIGURE 5. The limiting pv values of various PA1010 composites

CONCLUSIONS

We investigated the effect of the addition of plants-derived polyamide 11 elastomer (PA11E) on the mechanical and tribological properties of hemp fiber reinforced polyamide 1010 composites. It was found that the effect of the addition of PA11E on the mechanical and tribological properties of the composites differed for each property. Izod impact strength and specific wear rate improved with the addition of PA11E although tensile strength, modulus, and friction coefficient decreased with PA11E. The mechanical and tribological properties were strongly influenced by the types of PA11E. In particular, PA11E-L, which has the most polyether groups (soft segment), has the strongest effect for the improvement of mechanical and tribological properties. It follows from these results that it may be possible to develop the new engineering materials with sufficient balance between mechanical and tribological properties.

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