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Influence of Types of Alkali Treatment on the Mechanical Properties of Hemp Fiber Reinforced Polyamide 1010 Composites

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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 purpose of this study is to investigate the influence of types of alkali treatment on the mechanical and tribological properties of hemp fiber (HF) reinforced plants-derived polyamide 1010 (HF/PA1010) biomass composites. HF were surface-treated by four types of surface treatments: (a) alkali treatment by sodium hydroxide (NaOH) solution, (b) alkali treatment by sodium chlorite ($NaClO_2$) solution, (c) alkali treatment by NaOH solution and surface treatment by ureido silane coupling agent, and (d) alkali treatment by $NaClO_2$ solution and surface treatment by ureido silane. The volume fraction of hemp fiber in the composites was fixed with 20vol.%. HF/PA1010 composites were extruded by a twin screw extruder and injection-molded. Mechanical properties such as tensile, bending and tribological properties by ring-on-plate type sliding wear testing were evaluated. It was found that the effect of the types of alkali treatment on the mechanical and tribological properties of the composites differed for each property. The mechanical and tribological properties are improved with both alkali treatments by NaOH and $NaClO_2$ with or without the surface treatment by ureido silane coupling agent (A-1160). This may be attributed to the interfacial interaction and interphase adhesion between HF and PA1010 according to the type of these alkali treatments. The combination $NaClO_2$ and A-1160 is the most effect improvement for the mechanical and tribological properties of HF/PA1010 biomass composites. It follows from these results that it may be possible to develop the new engineering materials with sufficient balance between mechanical and tribological properties.

INTRODUCTION

The need for ecological alternatives to traditional petroleum-derived polymers has attracted recent interest in biomass composites, which are made from carbon neutral raw materials[1), 2)]. However, their low performances compared to traditional petroleum polymer have limited their applications, 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 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

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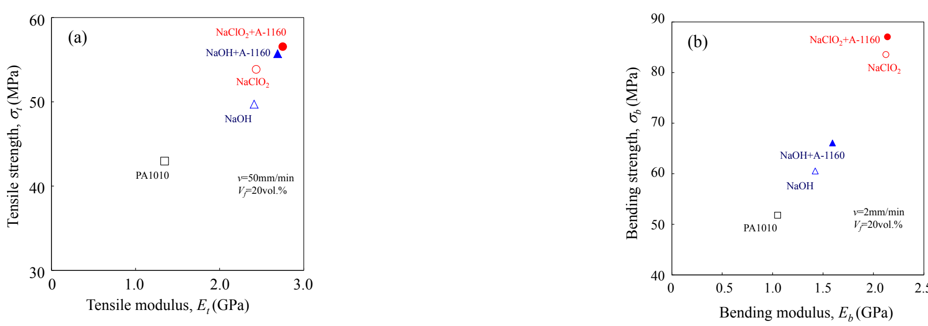
(HF) reinforced polyamide 1010 (PA1010) composites and the blends of these composites and plants-derived thermoplastic elastomers (bio-TPE) such as polyamide 11 elastomer (PA11E) and thermoplastic polyurethane elastomer (TPU) [3)-8)]. It was found that the mechanical and tribological properties of these composites are improved with the filling of hemp fibers (HF), their surface treatment by alkali and silane coupling agent and the addition of bio-TPE. Nevertheless, in order to achieve further higher performance in all plants-derived polymer based biomass composites, it is necessary to clarify of the effect of type of alkali treatment (mercerization) of natural fiber such as HF on the mechanical properties of all plants-derived biomass polymer composites. Alkali treatment is one of the chemical treatment of natural fiber, which is the most commonly used to reinforce thermoplastic and thermoset[9), 10)]. The important modification resulting from alkali treatment is the disruption of hydrogen bonding in the network structure, thereby increasing surface roughness. This treatment removes a certain amount lignin, hemicellulose, wax and oils covering the external surface of fiber cell wall, depolymerizes cellulose and exposes the short length crystallites. Therefore, a strong effect can be expected from the treatment. In order to develop the new engineering materials and tribomaterials based on all plants-derived materials, the purpose of this study is investigated the influence of types of alkali treatment on the mechanical and tribological properties of hemp fiber (HF) reinforced plants-derived polyamide 1010 (HF/PA1010) biomass composites experimentally.

EXPERIMENTAL

The materials used in this study were hemp fiber reinforced plant-derived polyamide 1010 biomass composites (HF/PA1010). Polyamide 1010 (PA1010, Vestamid Terra DS16, DaicelEvonic Ltd., Japan) was used as the matrix polymer. PA1010 was made from sebacic acid and decamethylenediamine, which are obtained from plant-derived caster oil[11)]. Hemp fiber (HF, ϕ50-100μm, Hemp Levo Ink., Japan) was used as the reinforcement fiber. The volume fraction of fiber V_f was fixed with 20vol.%. Hemp fibers were previously cut into length of about 5mm, and were surface-treated by four types of surface treatments: (a) alkali treatment by sodium hydroxide solution (NaOH), (b) alkali treatment by sodium chlorite solution ($NaClO_2$), (c) alkali treatment by NaOH solution and surface treatment by ureido silane coupling agent (3-ureidopropyltrimethoxy silane, A-1160, Momentive Performance Material Inc., USA) (NaOH+A-1160), and (d) alkali treatment by $NaClO_2$ solution and surface treatment by ureido silane ($NaClO_2$+A-1160). Two types of alkali treatment aqueous solutions: sodium hydroxide solution (by NaOH) or and sodium chlorite solution ($NaClO_2$) ones were used as the mercerization agent. Alkali treatment by NaOH and $NaClO_2$ was employed as follows: a 5% solution of alkali agents 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 alkali agents sticking to the fibers. The alkali treated fibers were dried in air for 12h and in a vacuum oven at 80^{o}C for 5h. The surface treatment of hemp fibers with the concentration of 1wt.% ureido silane coupling agent (A-1160) 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 kept in air for 12h and in a vacuum oven at 80^{o}C for 5h. All the components which were dried for 12h at 80^{o}C in vacuum oven were dry blended in the small plastic bottle, subsequently melt mixed at 85 rpm and 220^{o}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 a pelletizer, and were dried again at 80^{o}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^{o}C, mold (cavity) temperature of 30^{o}C and the injection rate of 13cm^3/s. Mechanical 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. 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 the 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).

RESULT AND DISCUSSION

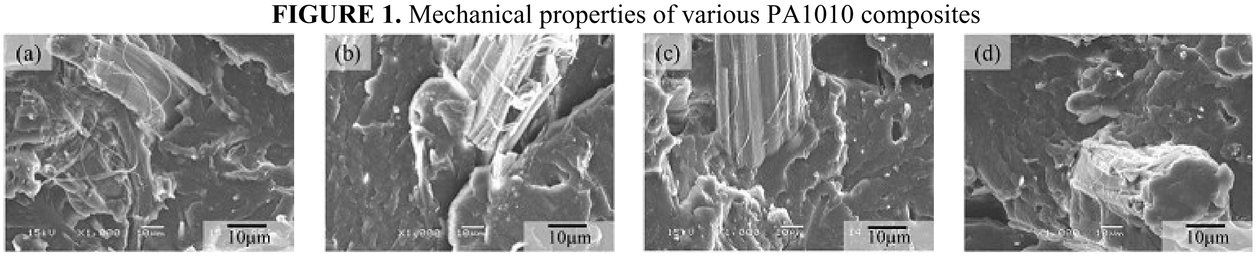
First, the influence of types of alkali treatments on the tensile and bending properties of hemp fiber reinforced plants-derived polyamide 1010 biomass composites (HF/PA1010 composites) is discussed. Fig. 1 shows the mechanical properties of various surface treated HF/PA1010 composites. In Fig. 1(a), the tensile strength σ_t is plotted against the tensile modulus E_t for pure PA1010 (100%) and HF/PA1010 composites with four types of surface treatments. σ_t and E_t of PA1010 improved with filling HF and their surface-treatment by alkali treatments and silane coupling agent, and increase in the following order: NaOH < $NaClO_2$ < NaOH+A-1160 < $NaClO_2$+A-1160. These results may be attributed to the improvement of the interphase adhesion and interaction between HF and matrix polymer. It is considered that the interaction between hemp fibers and polymer matrix is improved with surface treatment by silene coupling agent. The bending strength σ_b of various PA1010 composites is plotted against the bending modulus E_b in Fig. 1(b). σ_b and E_b of HF-S/PA1010 composites improve with filling HF and surface treatment, however the bending properties increase in the following: NaOH < NaOH+A-1160 < $NaClO_2$ < $NaClO_2$+A-1160. Thus, the influence of the types of alkali treatments on the mechanical properties differs with each property. These different tendencies are considered to be due to the testing mode of tensile and bending test such as testing speed, direction of deformation, fracture mechanism and so on. It is necessary to observe the internal structure of various surface treated HF/PA1010 biomass composites for understanding the relationship between the mechanical properties and the interphase adhesion between HF and PA1010. Fig. 2 shows SEM photographs of cryogenically fracture surface of various surface treated HF/PA1010 composites: (a) NaOH, (b) $NaClO_2$, (c) NaOH+A-1160, (d) $NaClO_2$+A-1160. The surfaces roughness of HF treated by $NaClO_2$ (Fig. 2(b) and Fig. 2(d)) are larger than those of NaOH (Fig. 2(a) and Fig. 2(c)). These observations are explained by the difference of attackability against HF with the type of alkali treatments. It is well known that the alkali treatment promotes the disruption of hydrogen bonding in the network structure of natural fiber, and removes the lignin and hemicellulose[11]. Therefore, this treatment not only increase the surface roughness resulting in better interlocking but also increases the amount of cellulose exposed on the fiber surface, and increasing the number of possible reaction site. From the comparison of the results in Fig. 2, it may be stated that the alkali treatment by $NaClO_2$ shows the lager amount of physical contact area between HF and PA1010 than that of NaOH. The morphologies of the composites surface treated by NaOH (Fig. 2(a)) and $NaClO_2$ (Fig. 2(b)) show the poor interaction between the hemp fiber and the PA1010. This indicates the poor chemical contact between fiber and polymer. On the other hand, the morphologies of the composites surface treated by both alkali treatment and silane coupling agent, show good interaction between fiber and matrix polymer, and fiber does not leave any voids on the fracture surface. This is attributed to the



(a) Relationship between tensile strength and tensile modulus of various PA1010 composites

(b) Relationship between bending strength and bending modulus of various PA1010 composites

FIGURE 1. Mechanical properties of various PA1010 composites



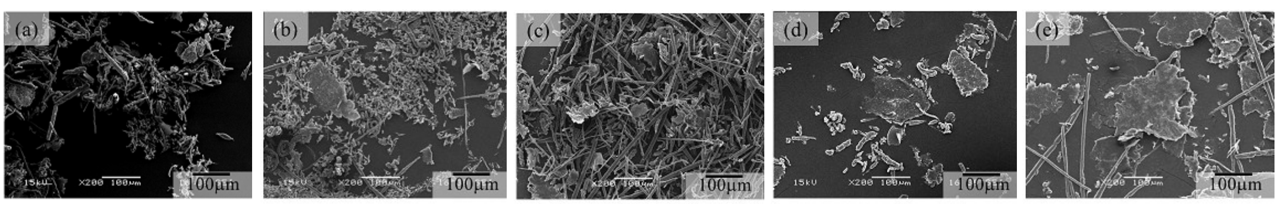
(a) NaOH (b) $NaClO_2$ (c) NaOH+A-1160 (d) $NaClO_2$+A-1160

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

chemical reaction between ureido group in silane coupling agent and possible reaction site on the fiber by $NaClO_2$ alkali treatment. These results are considered to be due to the good combination between $NaClO_2$ and A-1160 for improving the mechanical properties of HF/PA1010 biomass composites. These SEM photographs observations are in agreement with the mechanical properties such as tensile and bending results mentioned above.

Next, the tribological properties of various surface treated HF/PA1010 biomass composites using a ring on plate type sliding wear tester are discussed. Relationship between specific wear rate V_s and frictional coefficient μ of the composites by constant normal load and sliding speed testing is shown in Fig. 3. μ of pure PA1010 improve with the filling of HF and their surface treatment by alkali treatments and silane coupling agent. And μ of various surface treated composites decrease in the following order: PA1010 < NaOH < $NaClO_2$ < NaOH+A-1160 < $NaClO_2$+A-1160. On the other hand, V_s is highly influenced by the types of alkali treatments with or without the surface treatment by ureido silane coupling agent (A-1160). And V_s of various surface treated HF/PA1010 biomass composites shows the different behavior from that of μ, and decreases in the following: NaOH < PA1010 < $NaClO_2$ < NaOH+A-1160 < $NaClO_2$+A-1160. Although V_s of NaOH is bigger than that of pure PA1010, that of $NaClO_2$ is smaller than that of pure PA1010. This result may be attributed to the poor interaction between the hemp fiber and the matrix polymer caused by the difference of attackability against HF with the type of alkali treatments. To the contrary, V_s of HF/PA1010 biomass composites with surface treatment both alkali treatment and ureido silane coupling agent improves remarkably according to the type of alkali treatments. Especially, the combination of $NaClO_2$ and A-1160 have the best improvement effect for the tribological properties of HF/PA1010 biomass composites. These results may be attributed to the change in the mode of wear mechanism by the types of alkali treatments caused by the good interaction and interphase adhesion between fiber and matrix polymer. Because the tribological properties of polymer composites are strongly influenced by their ability to form the worn debris, it is essential to observe this factor for understanding the mechanism of tribologial properties. Fig. 4 presents SEM photographs of wear debris of various surface treated HF/PA1010 biomass composites. The shape and size of wear debris change with the type of alkali treatments with or without silane coupling agent: first, the shape and size of wear debris of pure PA1010 (Fig.4 (a)) is filamentary and granular particles. Second, that of NaOH treated composite (Fig. 4(b)) is some flaky, filamentary and many small granular ones. Third, that of $NaClO_2$ treated one (Fig. 4(c)) is many long thin filamentary ones. Forth, that of NaOH+A-1160 (Fig. 4(d)) is big flaky and small granular ones. Fifth, that of $NaClO_2$+A-1160 (Fig. 4(e)) is big flaky and long filamentary ones. These tendencies mentioned above are thought to effect on the tribological properties of these biomass composites.

Finally, the limiting pv value testing results by the step load method of various surface treated HF/PA1010 biomass composites, which is more severe than constant load and speed testing are discussed. Apparent constant pressure p is plotted against sliding speed v in Fig. 5, which is called as pv curve. p of all materials increases with



(a) PA1010 (b) NaOH (c) $NaClO_2$ (d) NaOH+A-1160 (e) $NaClO_2$+A-1160

FIGURE 4. Image of SEM photographs of fracture surface of various PA1010 composites

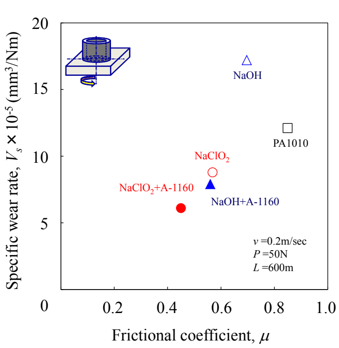


FIGURE 3. Relationship between V_s and μ of various PA1010 composites

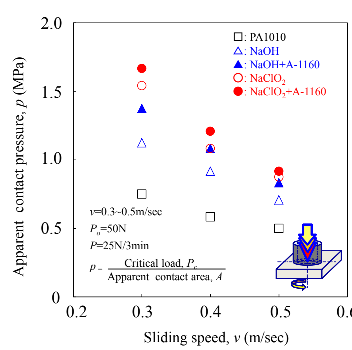


FIGURE 5. Relationship between apparent contact pressure p and sliding speed v

decreasing v, and the slope of pv curves against v increases in the following order: PA1010 (0.23) < NaOH (0.34) < NaOH+A-1160 (0.41) < $NaClO_2$ (0.43) < $NaClO_2$+A-1160 (0.46). Here, the values in the brackets are the limiting pv values calculated from Fig. 5, and their units are MPa･m/s. The limiting pv values have the same tendencies as bending properties. This indicates that pv values are closely related to the load carrying ability. The results shown above suggest that the combination $NaClO_2$ and A-1160 is the most effective treatment method to improve the tribological properties of HF/PA1010 biomass composites.

CONCLUSION

In order to develop the new engineering materials and tribomaterials based on all plants-derived materials, the purpose of this study is to investigate the influence of types of alkali treatment on the mechanical and tribological properties of hemp fiber reinforced plants-derived polyamide 1010 (HF/PA1010) biomass composites experimentally. It was found that the effect of the types of alkali treatment on the mechanical and tribological properties of the composites differs for each property. The mechanical and tribological properties are improved with both alkali treatments by NaOH and $NaClO_2$ with or without the surface treatment by ureido silane coupling agent (A-1160). This may be attributed to the interfacial interaction and interphase adhesion between HF and PA1010 according to the type of these alkali treatments. The combination $NaClO_2$ and A-1160 is the most effective treatment for the improvement of the mechanical and tribological properties of HF/PA1010 biomass composites. 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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