Analysis on Abrasive Wear Rate of VGCF/Polyamide 6 Composite Fibers

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The tribological properties under abrasive wear conditions, the tensile properties, the thermal properties and the structure have been investigated on the polyamide 6 (PA6) fibers dispersed with vapor-grown carbon fibers (VGCF's) in order to analyze the effects of dispersing VGCF's on the wear resistance of PA6 fibers. The wear resistance of the fibers have been determined using a method previously proposed by the present authors. The coefficient of friction decreased by dispersing a small amount of VGCF's but increased with increasing VGCF fraction at large VGCF fractions. The wear resistance increased with increasing VGCF fraction. Under the experimental conditions adopted in this study, the dispersion of VGCF's more effectively increased the wear resistance of PA6 fibers than the heat treatment. These experimental results have been analyzed based on a model with which the coefficient of friction (μ) and the wear rate (W_s) have been related to the microhardness (H), the resistance against sliding (σ_s), the fracture probability (f) the shape factor (g) and a constant (k) as $\mu = g\sigma_s/(kH)$ and $W_s = gf/(kH)$.

Keywords: abrasive wear, wear rate, coefficient of friction, polyamide 6, VGCF, fiber, composite

1. Introduction

Polymeric materials are used under various tribological conditions in place of metals and ceramics on the occasion where characteristic properties of polymeric materials such as flexibility and good processability are of importance^{1,2)}. An example is the fiber used for paper-making belts which are exposed to severe abrasive conditions when they are in contact with other parts of the paper-making machine. In addition, this fiber needs to sustain large tension to drive the belts at a high speed. Although polyamide 6 (PA6) fibers are currently used for this purpose, it is desired to increase the resistance of the fibers against abrasive wear in order to increase the driving speed of the belts. The tensile modulus and strength of PA6 fibers can be increased by heat treatment and drawing as a result of the increases in the crystallinity and the molecular orientation³⁾. The increases in the tensile modulus and strength are favorable to increase the wear resistance. Our previous study^{4,5)}, however, showed that the wear resistance of PA6 fibers was decreased by heat treatment and drawing. This result has been attributed to the

decreases in the elongation at break and the shear strength against the force applied on the surface of the fiber, due to the increases in the crystallinity and the anisotropy of the structure, respectively.

It is expected that the wear resistance of PA6 fibers can be increased effectively by dispersing fillers. The effects of dispersing fillers on the wear resistance of polymers in the form of films and bulk specimens have been studied by many researchers. Based on the consideration that the wear resistance is in proportion to the product of the tensile strength and the elongation at break⁶⁻⁸⁾, the wear resistance of polymers dispersed with fillers has often been analyzed using the plots of wear volume against the product of the tensile strength and the elongation at break (Rantner-Lancaster plots)⁹⁻¹²⁾. Based on the model analysis by Lhymn showing that the wear resistance of polymer composites is in proportional to the tensile modulus or the hardness, the wear resistance of polymers dispersed with fillers has also been analyzed in relation with the tensile modulus and the hardness¹³⁾. The increase in the wear resistance of polymers by dispersing fillers has been attributed mainly to two factors: one being the changes in the polymer structure developed

during processing^{14,15)} and the other being the contribution of the mechanical properties of the fillers itself such as the high tensile strength, high tensile modulus and high hardness¹⁶⁻¹⁸⁾.

The importance of the large aspect ratio of the fillers to increase wear resistance has been recognized with the fillers such as carbon fibers and glass fibers¹⁹⁻²²⁾. This suggests that carbon nanofibers (CNF) having a large aspect ratio and a high tensile modulus are desirable fillers to increase the wear resistance of the polymer. A number of studies have been carried out on the tensile modulus and strength, the fracture toughness and the fatigue of the CNF dispersed polymers²³⁻²⁶⁾. As to the frictional properties and wear resistance, it has been shown that dispersion of a small amount of CNF's into polymers has large influences on these properties²⁷⁻³⁰⁾. The increase in the wear resistance of polymers by dispersing CNF's has been attributed to the bridging effect, reinforcement of the transfer films formed between the polymer and the counterface, self-lubrication, and the high thermal conductivity which contributes to release frictional heat³⁰⁾. Most of these studies focused on the adhesive wear of the films and the bulk specimens. It is worth while to study the influences of dispersing CNF's into polymers on the abrasive wear resistance of the fibers. It is considered that the difference in the molecular orientation between the films and the fibers, and the difference in the sizes of scars produced under the adhesive and abrasive wear will have a large difference in the effects of dispersing fillers on the wear resistance of polymers.

In this study, the abrasive wear resistance of PA6 fibers dispersed with vapor-grown carbon fibers (VGCF's) has been investigated in relation to other mechanical properties and the structure of the fibers. For determining wear rate of fibers, a method proposed by the present authors has been used⁵⁾.

2. Experimental

2.1. Materials

The extrusion and blow application grade PA6 (Unitika M1040) with the glass transition temperature at 48.5 °C and the melting temperature at 223 °C was used as the matrix polymer. VGCF's (Showa Denko, VGCF-S) about 150 nm in diameter and several micrometers in length with the aspect ratio of about 10 - 500 were used as the fillers.

The VGCF/PA6 composite fibers were prepared as follows: The compounds of PA6 containing 5 mass% VGCF's and the pellets of neat PA6 were dried at 80 °C for 24 h in a vacuum oven and blended so that the mass fraction of VGCF's in the blend varied between 0 and 5 mass%. The blends were hot-pressed at 250 °C into a film and immediately quenched by placing the film between two steel plates cooled with water at room temperature. The film was cut into small pieces and stirred in order to enhance dispersion of VGCF's in PA6. Then, the pieces

were hot-pressed into the film again with the same procedure as shown above. This film forming-cutting cycles were repeated and the films obtained at the third hot-pressing were used for melt spinning and measurements. The same process history was imposed on the neat PA6. The fibers were melt spun using a single hole spinneret with a diameter of 1.5 mm at a throughput rate of 1 g min⁻¹, a take-up velocity of 2 m min⁻¹, and an extrusion temperature of 250 °C. The fiber diameter was about 0.5 mm and the film thickness was about 0.3 mm. Some of the fibers and the films were heat treated under constant length at a temperature of 200 °C for 15 min in the air.

2.2. Crystallite structure

Wide-angle X-ray diffraction (WAXD) was measured on the aligned fibers using a diffractometer (Rigaku, CN4036A2), a position-sensitive proportional counter (PSPC), a proportional counter and a Ni filtered CuK α radiation. The equatorial diffraction profiles were measured with the PSPC in a manner that the incident beam, the specimen and the diffracted beam toward the center of the detecting window of the PSPC were in the symmetric transmission geometry. The azimuthal diffraction profiles were measured with the proportional counter by rotating the specimen keeping the symmetric transmission geometry.

2.3. Thermal properties

A differential thermal analysis (DTA) of the fibers was carried out using a TG-DTA apparatus (Rigaku, TG8120). Before the measurements, the fibers were dried at 80 °C for 24 h in a vacuum oven to eliminate absorbed water. The DTA measurements were carried out on the chopped fibers of about 5 mg using an aluminum cell under the nitrogen gas flow at a heating and cooling rate of 10 °C min⁻¹. The DTA curve of an Al₂O₃ standard was also measured in order to calculate the enthalpy change of the fibers from the area of the DTA curve.

The melting temperature (T_m) and the crystallization temperature (T_c) were determined as the peak temperatures of the DTA curves measured during the first heating and the first cooling processes, respectively. The degree of crystallinity of PA6 (χ_c) was calculated according to the equation³¹⁾

$$\chi_c = \frac{\Delta H_m}{\Delta H_{m,o}(1-m)} \times 100 \quad (1)$$

where $\Delta H_{m,o}$ is the specific melting heat of PA6 crystal, ΔH_m is the specific melting heat of the VGCF/PA6 composite fiber and m is the mass fraction of VGCF's in the composite fiber. The values of $\Delta H_{m,o}$ for the α and γ phases are 241 and 239 J g⁻¹^{31,32)}, respectively, and the average value, 240 J g⁻¹ was used for $\Delta H_{m,o}$ in this study.

2.4. Tensile properties

Tensile tests were carried out on the single fibers using a tensile testing machine (Orientec, RTC-1350A).

Fig. 1 H of fibers versus H of films for untreated and heat-treated VGCF/PA6 composites fibers and films with various mass fractions of VGCF's

The gage length was 30 mm and the crosshead speed was 30 mm min^{-1} . The tensile modulus, the tensile strength and the work of fracture were determined from the initial slope of the stress-strain curve, the maximum load attained at the fiber break and the area under the stress-strain curve, respectively. For each specimen, 25 determinations were performed and the average value will be shown.

2.5. Microhardness

The microhardness measurements were carried out on the films and the fibers using a Vicker's microhardness tester (SHIMADZU, ENT-150). The measurements were carried out by applying the normal load of 0.5 N to an indenter for the indentation time of 15 s. The diagonal sizes of the scars after indentation were in a range from 50 to 100 μm . The microhardness (H) was calculated by dividing the applied load with the surface area of the scar of the indentation. For each specimen, 10 determinations were performed and the average value will be shown.

Fig. 1 compares H of the fibers with that of the films for all the neat and the composite fibers and films used in this study. Although the films and the fibers show almost the same values of H , the fibers show slightly higher values than the films. This is because the fibers presented smaller scars than the films due to the curvature of the fiber surface. Therefore, the value of H for the films will be used as the microhardness of the materials.

2.6. Coefficient of friction and wear rate

The fiber wear tests were performed by wearing one side of a single fiber using a fiber wearing apparatus as shown in Fig. 2. This apparatus consisted of a rotating drum, an abrasive paper covering the drum, a load cell to measure the tension of the fiber, a weight to apply tension to the fiber, and the nozzle and tube for pouring water. The drum was 100 mm in diameter and rotated at

Fig. 2 Schematic illustrations of fiber wearing apparatus and fiber cross section at worn portion

a speed of 150 rpm. The average sizes of the SiC abrasive particles on the abrasive paper were 50 and 14 μm , which are denoted as #320 and #800 (ISO 6344-1 and 6344-3), respectively. One end of the single fiber specimen was fixed to the load cell and the weight of 40 g was connected to the other end of the fiber. Then, the fiber was hung on the rotating drum for 60 s to wear the side of the fiber. During the wear tests, water at 20 $^{\circ}\text{C}$ was poured on the abrasive paper in order to keep the abrasive paper clean and remove the frictional heat. Fig. 3 shows the SEM images of the #320 and #800 abrasive paper before and after the wear tests of the untreated neat PA6 fibers under the tension of 0.39 N for 60 s. Although a few fine wear debris can be seen for #800 abrasive paper, most of the SiC particles are clearly seen on both abrasive paper. Neither the transfer film nor the

Fig. 3 SEM images of (a and b) #320 and (c and d) #800 abrasive paper (a and c) before and (b and d) after wear tests on PA6 fibers under tension of 0.39 N for 60 s

adhesion of the polymer by the melting due to frictional heat can be seen. This indicates that the water poured on the surface of the abrasive paper effectively cleaned the surface of the abrasive paper and removed the frictional heat.

After the wear test, the fiber was cut at the most worn cross section and the cross-section area lost by wear was measured with a profile projector (Nikon, 6CT2). The most worn portion of the fiber was always located within 3 mm from the point Q in Fig. 2.

The specific wear rate (W_s) is defined as

$$W_s = \frac{V}{FL} \quad (2)$$

where V is the volume lost by wear, F is the normal load applied on the wear surface and L is the sliding distance³³⁾. With the wear tests on bulk and film specimens using a pin-on-disk³⁴⁾ and a block-on-ring³⁵⁾ apparatus, the values of V and F can be directly measured. With the wear tests on fibers, however, direct measurements of these values are not easy. Using an analysis method proposed by the present authors⁵⁾, the wear rate of fibers can be determined as

$$W_s = \frac{1}{\omega T} \frac{dA}{dt} \quad (3)$$

where t is the wear time, A is the fiber cross-section area lost by wear, ω is the angular speed of the rotating drum and T is the fiber tension. The average specific wear rate ($\langle W_s \rangle$) during the wear test for the duration t can be obtained as

$$\langle W_s \rangle = \frac{1}{t} \int_0^t W_s dt = \frac{A}{\omega T t} \quad (4)$$

provided that the changes in ω and T during the wear test are small.

The coefficient of friction (μ) between the fiber and the abrasive paper during the wear test can be determined as^{36,37)}

$$\mu = \frac{1}{\beta} \ln \left(\frac{T_2}{T_1} \right) \quad (5)$$

where β is the angle between the radii OP and OQ shown in Fig. 2 and T_1 and T_2 are the fiber tension at points P and Q, respectively. In this study, β was π , T_1 was 0.39 N and T_2 which is equal to T in equation (4) was directly measured with the load cell.

3. Results and discussion

3.1. Structure and thermal properties

The equatorial WAXD profiles of the composite fibers are shown Fig. 4. The crystallization temperature, the melting temperature and the crystallinity of PA6 in the composite fibers determined with DTA are shown in Table 1.

The PA6 crystal exhibits polymorphism and forms α , β , γ and pseudohexagonal phases^{32,38,39)}. Thermodynamically stable phases are the α and the γ phases in which polymer chains take a fully extended

Fig. 4 Equatorial WAXD profiles of (a) untreated and (b) heat-treated VGCF/PA6 composite fibers with various mass fractions of VGCF's shown in the figure. Profiles have been shifted vertically to prevent overlap

Table 1 Crystallization temperature (T_c), melting temperature (T_m) and crystallinity (χ_c) of untreated and heat-treated VGCF/PA6 composite fibers with various mass fractions of VGCF's

Fraction of VGCF's (mass %)	Untreated fibers			Heat-treated fibers		
	T_c (°C)	T_m (°C)	χ_c (%)	T_c (°C)	T_m (°C)	χ_c (%)
0	188.1	217.8	24.9	189.3	218.9	33.3
0.5	191.6	218.5	23.2	192.1	218.8	28.5
1.0	191.2	218.3	23.4	191.3	219.2	30.2
2.5	191.8	219.2	22.2	191.0	218.9	33.4
5.0	194.6	219.3	23.8	192.7	219.0	27.1

Fig. 5 Azimuthal WAXD profiles of 200 diffractions from PA6 α phase for (A) untreated PA6 fiber and (B) untreated 5 mass% VGCF/PA6 composite fiber and that of 002 diffraction from VGCF's for (C) untreated 5 mass% VGCF/PA6 composite fiber. Azimuthal angle is 0° at equatorial direction. Profiles have been normalized with the maximum intensities

planar zigzag conformation and a twisted conformation, respectively. Thermodynamically instable phases are the β and the pseudohexagonal phases which are easily transformed into the α phase by the heat treatment. The γ and the pseudohexagonal phases produce similar WAXD peaks but are distinguishable based on the thermal stability³⁹⁾.

In the diffraction profiles shown in Fig. 4, the peaks at the scattering angles (2θ) of 20.5° and 24.0° are respectively the 200 diffraction and the overlap of the 002 and the 202 diffractions from the α phase. In the diffraction profile of the untreated neat PA6 fiber, the peak at 2θ of $21^\circ - 22^\circ$ is the 001 diffraction from the pseudohexagonal phase since this diffraction was not produced after the heat treatment and the diffraction from the α phase was produced alternatively. Fig. 4 shows that the pseudohexagonal phase has been developed in the untreated neat PA6 fibers while the α phase has been developed in the heat-treated neat PA6 fibers and the composite fibers. It is known, therefore, that VGCF's work as the nucleation agent to form the α phase during the cooling process from the molten state. Reflecting the nucleation effect, the crystallization temperature of PA6 under the existence of VGCF's is higher than that of the neat PA6 as shown in Table 1. By dispersing VGCF's, the melting temperature is slightly increased while the crystallinity is not increased. By the heat treatment of the composite fibers, the crystallinity is markedly increased while the melting temperature is not changed. The nucleation effect to form the PA6 α phase has also been reported with multi-walled carbon nanotubes^{24,31)}.

In the diffraction profiles of the composite fibers

shown in Fig. 4, the peak at 2θ of 26.0° is the 002 diffraction of the carbon layer stacks in VGCF's. The intensity of this peak increases as the VGCF content increases.

Fig. 5 shows azimuthal WAXD profiles of the 200 diffractions of the PA6 α phase at 2θ of 20.5° for the untreated neat PA6 fiber and the untreated 5 mass% VGCF/PA6 composite fiber and the profile of the 002 diffraction of VGCF's at 2θ of 26.0° for the untreated 5 mass% VGCF/PA6 composite fiber. The background intensity from PA6 has not been removed from the profile of VGCF's shown in this figure. With the untreated 5 mass% VGCF/PA6 composite fiber, the orientation of the VGCF's is much higher than that of the PA6 α phase. The low orientation of the PA6 α phase results from the small spinning stress during the melt spinning carried out at a low take-up velocity. On the other hand, a large aspect ratio of VGCF's helps them to align in parallel to the fiber axis. The orientation of VGCF's does not influence the orientation of the PA6 α phase as is known by comparing the azimuthal diffraction profiles of the neat and the composite fibers.

Fig. 6 Tensile stress-strain curves for untreated and heat-treated PA6 fibers and 5 mass% VGCF/PA6 composite fibers

3.2. Tensile properties

Typical tensile stress-strain curves of the neat PA6 fibers and the composite fibers are shown in Fig. 6. The tensile modulus, tensile yield stress, tensile strength, elongation at break and work of fracture for the composite fibers are plotted against the VGCF fraction in Fig. 7(a) to (e). By the heat treatment, the tensile modulus and strength increase but the elongation at break decreases irrespective of the VGCF fraction. It has been reported that the tensile modulus and strength of PA6 fibers are increased by the change of the crystal form from the pseudohexagonal phase to the α phase³⁹⁻⁴¹⁾, the increase in the crystallinity and the increase in the crystallite orientation but significantly

Fig. 7 (a) Tensile modulus, (b) tensile yield stress, (c) tensile strength, (d) elongation at break and (e) work of fracture versus mass fraction of VGCF's for untreated and heat-treated VGCF/PA6 composite fibers

decreased by the absorption of water⁴²⁾. The increase in the crystallinity by the heat treatment at any VGCF fractions is considered to be the cause of the increases in the tensile modulus and strength, and the decrease in the elongation at break. The transformation of the crystal form from the pseudohexagonal phase to the α phase is considered to give an additional contribution to the increase in the tensile modulus and strength by the heat treatment of the neat PA6 fiber.

By dispersing VGCF's, the tensile modulus increases but the tensile strength and the elongation at break decrease for both the untreated and the heat-treated composite fibers at the VGCF fractions larger than 0.5 mass%. The increase in the tensile modulus with increasing VGCF fraction is considered to be the contribution of the high tensile modulus of VGCF's having a large aspect ratio and a preferential orientation in the fiber axis direction. There may be an additional contribution from the change of the crystal form from the pseudohexagonal phase to the α phase with the untreated fibers at a low VGCF fraction. The increase in the tensile modulus by the dispersion of VGCF's indicates that the stress applied to the composite fibers can be transferred effectively to the VGCF's through filler/matrix interfacial bonding. The decrease in the tensile strength by the dispersion of VGCF's suggests that the filler/matrix interfaces are debonded during the composite fibers are stretched beyond the elastic region up to the strain at fiber break and the debonded VGCF's work as the defects.

3.3. Tribological properties and microhardness

Fig. 8 shows the SEM images of the wear surfaces of the composite fibers worn with #320 and #800 abrasive paper under the tension of 0.39 N for 60 s. The surfaces worn with #800 abrasive paper present smoother and shallower scars as compared with the surfaces worn with #320 abrasive paper. The composite fibers and the heat-treated neat PA6 fibers present smoother wear surfaces as compared with the untreated neat PA6 fibers. The VGCF's lying on the wear surface, bridging the banks of scars can be observed in Fig. 9.

The neat PA6 fibers and the composite fibers used in this study showed the variations of the coefficient of friction (μ) and the wear rate (W_s) with the wear time similar to those reported in a previous paper⁵⁾. The value of μ reached almost a constant value in less than 10 s after showing initial rise and overshoot. The values of W_s also reached a steady value after showing initial anomalous wear. The anomalous wear of the PA6 fibers at the very beginning of the wear tests has been attributed to the change of the surface roughness from that of the unworn surface to that of the slightly worn surface, and not to the formation of the transfer films nor the wear debris.

The microhardness (H) and the average values of μ and W_s during the initial 60 s of the wear tests under the tension of 0.39 N for the composite fibers are plotted against the VGCF fraction in Fig. 10(a) to (c). In this

Fig. 8 SEM images of wear surfaces for (a-d) neat PA6 fibers and (e-h) 5 mass% VGCF/PA6 composite fibers worn with (a, c, e and g) #320 and (b, d, f and h) #800 abrasive paper under tension of 0.39 N for 60 s. Wear surfaces of (a, b, e and f) untreated and (c, d, g and h) heat-treated fibers are presented

figure, the values of H and $\langle W_s \rangle$ are shown in the units of MPa for convenience of comparison with other mechanical properties. The units often used for these values in the literature are kgf m^{-2} for the vickers hardness and $\text{mm}^2 \text{N}^{-1}$ for the wear rate. These units can be converted as $1 \text{ MPa} = 0.102 \text{ kgf m}^{-2}$ and $1 \text{ Pa}^{-1} = 1.0 \times 10^6 \text{ mm}^2 \text{N}^{-1}$. It is found in Fig. 10 that H increases and $\langle W_s \rangle$ decreases as the VGCF fraction increases. The value of μ decreases by the dispersion of 0.5 - 1 mass% VGCF's while it increases by the dispersion of a larger

Fig. 9 SEM images of the VGCF's on worn surfaces of (a and b) untreated 5 mass% VGCF/PA6 composite fiber

Fig. 10 (a) H , (b) μ and (c) $\langle W_s \rangle$ versus mass fraction of VGCF's for untreated and heat-treated VGCF/PA6 composite fibers. Fibers were worn with #320 and #800 abrasive paper

amount of VGCF's. The heat treatment also reduces $\langle W_s \rangle$, whereas the dispersion of VGCF's more effectively reduces $\langle W_s \rangle$ under the present experimental conditions. The abrasive particle size clearly influences μ and $\langle W_s \rangle$.

The relationships among the microhardness, the coefficient of friction, the specific wear rate and other mechanical properties are analyzed based on a simple model as follows: It is assumed that the tip of an abrasive particle indenting the material has a cross section area A_i in the plane of undeformed material surface and a projection area A_s on the plane perpendicular to the sliding direction. The shape factor (g) is defined as

$$g = \frac{A_s}{A_i} \quad (6)$$

If the tip of the abrasive particle is a cone with an angle ζ from the sliding direction, then g is given by $(\tan \zeta)/\pi$. It is assumed that the force (P) in parallel to the sliding direction which is required to apply to the abrasive particle for sliding the particle is in proportion to A_s . That is

$$P = \sigma_s A_s \quad (7)$$

where σ_s is a proportional constant representing the resistance against sliding. The force (F) perpendicular to the material surface which is required to apply to the abrasive particle for making the indentation with an area of A_i is given by

$$F = \sigma_i A_i = k H A_i \quad (8)$$

where σ_i is a proportional constant representing the resistance against indentation. This parameter is in proportion to the microhardness (H) with the proportional constant (k) of 1.08. From equations (6) to (8), the coefficient of friction (μ) is derived as

$$\mu = \frac{P}{F} = \frac{g \sigma_s}{k H} \quad (9)$$

This equation differs from the equation derived by Ernst et al.⁴³⁾ in which g appears as an additional term. It is assumed that the volume lost by wear (V) is in proportion to the volume swept by the tip of the particle in sliding. That is

$$V = f A_s L \quad (10)$$

where L is the sliding distance and f is a proportional constant representing the probability that the material is removed or plastically deformed forming a scar per one sweep of the abrasive particle. The parameter f , which will be called fracture probability, is zero for a completely elastic material with sufficiently large strain at fracture and reaches unity as the material is getting weaker. From equations (8) and (10), the wear rate (W_s) is given by

Fig. 11 (a) Tensile yield stress, (b) $kH\mu$ (c) $kH < W_s >$ and (d) $\mu / < W_s >^{-1}$ versus H for untreated and heat-treated VGCF/PA6 composite fibers with various mass fractions of VGCF's. Fibers were worn with #320 and #800 abrasive paper

$$W_s = \frac{V}{FL} = \frac{gf}{kH} \quad (11)$$

A similar equation has already been derived⁴⁴⁾ for a special case in which $f=1$ and the abrasive particle has a cone-shape tip. Equations (9) and (11) indicate that μ and

W_s are determined as a function of H , σ_s , f and g . Conversely, relative variations in σ_s and f for a constant value of g can be estimated using the equations.

$$g\sigma_s = kH\mu \quad (12)$$

$$gf = kHW_s \quad (13)$$

The tensile yield stress of the composite fibers is plotted against H in Fig. 11. The values of $kH\mu$ and $kH < W_s >$ which correspond to the average values of $g\sigma_s$ and gf , respectively, are also shown in this figure.

It is expected that the tensile yield stress, H and σ_s are closely related to each other since all these parameters represent the resisting stress against deformation. As shown in Fig. 11(a), the tensile yield stress is actually in proportion to H with a proportional constant of about 0.5. The negative correlation between the tensile strength and H known by comparing Figs. 7(c) and 11(a) is considered to be due to the fact that the tensile strength reflects the properties of the defects rather than the average fiber properties.

The dependence of $g\sigma_s$ on H shown in Fig. 11(b) can be attributed mainly to the variation of the material parameter σ_s since the dependence of the shape factor of the abrasive particle, g , on H is considered to be small. It is known that the resistance σ_s is an increasing function of H .

On the other hand, the dependence of $g\sigma_s$ on the abrasive particle size can be attributed mainly to the variation of g . Fig. 11(b) indicates that the difference of g with the abrasive particle size is very small at large values of H and about 20% at small values of H . If the tip of the abrasive particle has some special shape such as a cone, g is independent of the indentation depth. With some other shapes, however, g depends on the indentation depth. Therefore, even if the wear tests are carried out under the same contacting force, the indentation depth varies depending on the hardness of the material and the shape and the size of the abrasive particles. This causes the dependences of g on H and the abrasive particle size. This can be the reason for the variation of $g\sigma_s$ with the abrasive particle size at small values of H .

The dependences of fg on H and the abrasive particle size shown in Fig. 11(c) can be attributed mainly to the variation in f since the variation of g is small as shown above. The values of fg is of the order of 10^{-3} , and so is the fracture probability f . This means that permanent scars are produced after the material is swept with the abrasive particles 1000 times. The work given to the material in the sliding path of the abrasive particle, per unit volume and per one sweep of the abrasive particle, is equivalent to σ_s . Therefore, the total work given to the material in the sliding path until it is deformed, broken and eventually removed as wear debris, per unit volume is given by σ_s/f . Part of the work given to the material causes plastic deformation while some other part of the

work is once stored elastically, turns into kinetic energy and eventually released as a heat. The material of unit volume is removed as wear debris when the total work given to the material reaches σ_s/f . Thus σ_s/f is a measure of the toughness of the material against abrasive wear. The value of σ_s/f can be obtained with the equation

$$\frac{\sigma_s}{f} = \frac{\mu}{W_s} \quad (14)$$

As shown in Fig. 11 (d), σ_s/f increases with increasing H , indicating that the toughness against abrasive wear increases with increasing VGCF fraction. It is suggested that dispersion of VGCF's enhances the ability of the material to return to the undeformed shape after each sweep of the abrasive particles.

Fig. 11(d) shows that the toughness, σ_s/f , is smaller with the larger abrasive particle. This result can be interpreted similarly to the size effect in the strength. The strength of a material generally decreases with the increase in volume since the probability that the material contains defects increases. In the case of abrasive wear, the volume of the stressed region under each abrasive particle increases as the particle size increases and the fracture probability increases correspondingly.

The dependences of μ and W_s on the VGCF fraction, the fiber structure and the abrasive particle size reflect the variations in H , σ_s , f and g so far shown. The values of

Fig. 12 (a) μ and (b) $\langle W_s \rangle$ versus $1/H$ for untreated and heat-treated VGCF/PA6 composite fibers with various mass fractions of VGCF's. Fibers were worn with #320 and #800 abrasive paper

μ and $\langle W_s \rangle$ are plotted against $1/H$ in Fig. 12. If σ_s is completely in proportion to H , then μ takes a constant value. The deviation of the relationship between σ_s and H from the proportionality produces the minimum of μ in Fig. 12(a). If f is almost independent of the VGCF fraction but depends on the abrasive particle size, then $\langle W_s \rangle$ is in proportion to $1/H$ with a slope depending on the abrasive particle size. This feature can be seen in Fig. 12(b).

4. Conclusion

The tribological properties under abrasive wear conditions, the tensile properties, the thermal properties and the structure have been investigated on the polyamide 6 (PA6) fibers dispersed with vapor grown carbon fibers (VGCF's) in order to analyze the effects of dispersing VGCF's on the wear resistance of PA6 fibers. The VGCF's worked as the nucleation agent to form the α phase during the melt spinning process. The crystallinity was increased by the heat treatment. With increasing VGCF fraction, the tensile modulus and the tensile yield stress increased while the tensile strength and the elongation at break decreased. The coefficient of friction (μ) and the wear rate (W_s) could be related to the microhardness (H), the resistance against sliding (σ_s), the fracture probability (f) and the shape factor (g) as $\mu = g\sigma_s/H$ and $W_s = gf/H$. The analysis based on these equations showed that for the composite fibers with varying VGCF fractions, tensile yield stress is in proportion to H , σ_s is an increasing function of H where its variation decreases as H decreases, f is roughly independent of H but depends on the abrasive particle size and g is roughly independent of H and the abrasive particle size. Reflecting the variations of these parameters, the coefficient of friction decreased by dispersing a small amount of VGCF's but increased with increasing VGCF fraction at large VGCF fractions. The wear resistance increased with increasing VGCF fraction. Under the experimental conditions adopted in this study, the dispersion of VGCF's more effectively increased the wear resistance of PA6 fibers than the heat treatment.

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