The Effect of Surface Modified Polytetrafluoroethylene on Polyacetal/Polytetrafluoroethylene Blends

WEN-YEN CHIANG* and CHI-YUAN HUANG

Department of Chemical Engineering, Tatung Institute of Technology, 40 Chungshan North Road, 3rd Sec., Taipei 10451, Taiwan, Republic of China

SYNOPSIS

Five kinds of blends: polyacetal (POM) and polytetrafluoroethylenes (PTFEs) [pure (PTFE), coupling agent coated (LZ-PTFE), chemical-treated (CPTFE, containing NaF salt), chemical-treated (WPTFE, no NaF salt), coupling agent coated WPTFE(LZ-WPTFE)] were prepared by mechanical blending. The PTFE presented in the blends, had good wear resistance properties. However, the adhesion interaction between the POM and the PTFE was poor, and increasing the PTFE content caused a decrease in the mechanical properties. Using the chemical surface treatment method to etch PTFE could cause treated-PTFE to homogeneously disperse in POM. This result caused the POM/treated-PTFE blends to have higher mechanical properties than those of the POM/PTFE blends. The NaF salt that adsorbed on the CPTFE surface acted as a coupling agent and offered a very strong adhesion interaction between the POM and the CPTFE. The free salt also acted as a nuclei to aid POM in crystallizing. As a result, the POM/CPTFE blends possessed the highest mechanical properties of all the blends and the best wear resistance property of POM/modified-PTFE(LZ-PTFE, LZ-WPTFE, WPTFE, CPTFE) blends. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Polyacetals are the first plastic with strength properties that approach those of the nonferrous metals, and in a real sense are metal-like. They are strong, hard, highly crystalline typical thermoplastics with a unique balance of mechanical, thermal, chemical, and electrical properties. These resins have a good balance of both long- and short-term predictable properties. In terms of abrasion resistance, the polyacetals are superior to most plastics and diecast aluminum. Therefore, they are used as polymeric material in slide application, where their frictional and wear characteristics are most important. These properties of polyacetals are coupled with the wear resistance and low coefficient of friction imparted by the PTFE,[1-7] carbon fiber,[8-14] oil,[15-18] aramide fiber,[19,20] mixer,[21-23] and others.[24-26] The PTFE incorporated in the polyacetals transfers to the op-

posite mating surface and extends wear life when parts are designed with the proper tolerances and finish.[4] At all speeds, the content of PTFE provides a solid-lubricated surface capable of sustaining high loads at elevated temperature. The bonding ability between the PTFE and the polymer was poor; therefore, the mechanical properties of POM/PTFE blends were poor though they possessed good wear resistance properties. The surface modified PTFE as added to POM to improve the bonding ability between the POM and the PTFE.

Many methods have been proposed for modifying the surface of PTFE to increase the adhesion interaction between the PTFE and the polymer. They include chemical surface treatment,[27,28] plasma surface treatment,[29,30] radiation surface treatment,[31,32] and physical surface treatment.[33] The popular method is the sodium etching method used in this study to treat the PTFE. This method is more widely used because of better stability and ease of handling. Several important properties of five kinds of blends (POM/PTFE, POM/LZ-PTFE, POM/LZ-WPTFE, POM/WPTFE, POM/CPTFE) were in-

vestigated. As the surface of PTFE was modified, the compatibility between the POM and the PTFE was increased. For this reason, the modified-PTFE (LZ-PTFE, LZ-WPTFE, WPTFE, CPTFE) could be dispersed in POM homogeneously. Therefore the mechanical properties of all blends were enhanced.

EXPERIMENTAL

Materials

Naphthalene (Wako) was used without previous purification. The ultra-pure reagent grade tetrahydrofuran (THF) of purity 99.7% (ALPS Chem. Co. Ltd., Taiwan) and sodium were also used as received. The coupling agent used was Neopentyl(dially)oxy, tri(dioctyl)pyro-phosphato zirconate made by American Kenrich Petrochemicals, Inc., trade name LZ 38.

The PTFE used in this study was a commercial product of the DuPont Mitsui Fluorochemical Co. Ltd. designated as TLP-10F-1. The POM used was a commercial product of the Polyplastic Co. Ltd., Japan, designated as Duracon M90-02, with the following characteristics: specific gravity = 1.41 g/cm^3, melt flow index = 8–10 g/10 min.

Surface Treatment

The sodium–naphthalene complex in THF was the commercially successful surface treatment for fluoropolymers. The naphthalene (0.1 mol) was first dissolved in THF (100 cm^3) and then the metallic Na (0.1 mol) was cut into slivers and added to the solution. After being stirred for 6–8 h, the dark green solution cooled to −40°C and then the PTFE was immersed in the fresh sodium solution for 3 and 5 min. Before treatment, the virgin PTFE powder was extracted with THF for 24 h and dried under vacuum

Table I   Abbreviation of Treated PTFE

Sample Code	Rinsed by Acetone	Rinse by D. Water[a]	Coated With Coupling Agent[b]
PTFE	X	X	X
LZ-PTFE	X	X	O
CPTFE	O	X	X
WPTFE	O	O	X
LZ-WPTFE	O	O	O

[a] Distilled water.
[b] Coupling agent made by American Kenrich Petrochemicals, Inc., trade name LZ38.

at 60°C to constant weight. After the desired time, the reaction solution was removed and the treated PTFE was rinsed by one of the following procedures: A, acetone; B, acetone, water, and then acetone. Treated PTFEs were then dried at reduced pressure. After procedure A, the material is abbreviated CPTFE. After procedure B, the material is abbreviated WPTFE. The WPTFE and PTFE coated with 0.5 wt % (vs. WPTFE and PTFE) coupling agent (LZ 38). The coated materials were abbreviated LZ-WPTFE and LZ-PTFE (Table I).

Melt Blending

All blends were made by melt blending in a single screw laboratory extruder (D = 1.78 cm; L/D = 20) and then pelletized. Prior to this step, powder of POM/PTFE were combined at the weight ratios of 100/0, 95/5, 90/10, 85/15, and 80/20, respectively, by a mechanical blender and dried in an air oven for 3 h at 82°C to remove sorbed water. The various heating zones for extrusion were set at 120, 170, 170, and 160°C. The screw speed was 15 rpm. The unblended POM was also processed under identical extrusion conditions to give a thermal history similar to that of the blend samples.

Mechanical Properties

Tensile properties were measured according to ASTM D638 using an Instron Universal Testing Machine, model 1130. The crosshead load was 500 kg, the speed was 5 cm/min, and the chart speed was 100 cm/min. All test specimens were prepared by compression molding (180°C) in a frame at 14.7 MPa for 8 min and then cooled by a water-cooling system. The molding was made of Mylar film. Dumbbell test pieces were made for mechanical testing. The thickness of the testing specimen was 3 ± 0.2 mm. The elastic modulus was determined from the initial part of the slope of the stress–strain curve in the linear section. The values were the average of five measurements.

Infrared Spectra

Infrared (IR) spectra were obtained from mixtures with KBr on a JASCO model A-202 spectrophotometer.

Taber Wear Factor

The Taber wear factor of each specimen was measured according to ASTM D1044 by Taber Machine model 5130. Taber resistance run with H-17V wheels under a load of 500 grams at 30°C. The Taber wear

factor was the loss of mass in milligram per one thousand cycles of abrasion. The unit of Taber wear factor was mg/1000 cycles.

SEM Micrographs

For examination of phase morphology, the circular extruded polymers were immersed in liquid nitrogen and fractured. The fracture surfaces were coated with gold. Then the center of circular extruded polymer (diameter = 3 mm) were viewed end-on by a Hitachi S-520 scanning electron microscope.

RESULTS AND DISCUSSION

Mechanical Properties

The variation in tensile strength, Young's modulus, and elongation with polytetrafluoroethylene concentration for these five materials are shown in Table II. The order of tensile strength at break and the Young's modulus of the blends were POM/CPTFE > POM/WPTFE, POM/LZ-WPTFE, POM/LZ-PTFE > POM/PTFE.

It is known that the adhesion interaction between the POM and the PTFE is very poor. On the other hand, the fine PTFE powder has a strong tendency to agglomerate. Thus, it is very difficult to disperse fine PTFE powder into highly viscous polymer melts. Therefore, nearly all actual composites contain more or less entrapped air, especially inside

particle agglomerates. Even small quantities of entrapped air have a great effect on the stress–strain behavior. At the same time, agglomerates are weak points in the materials and break fairly easily when a stress is applied to them. Particle agglomeration tends to reduce the strength of a material. For these reasons, the POM/PTFE blends possessed lowest tensile strength and Young's modulus of all blends.

In the Na/naphthalene/THF complex etching process, the fluorine was etched out by the alkali metals through a surface chemical reaction. The reaction mechanism was shown in the Scheme 1. It shows that each alkali atom was responsible for removing one fluorine atom from the chain. If the etching process continues to take place with the complete chain, $(CF)_n$[34] can be ultimately left in the ideal situation. Contrarily, Yoshino et. al.[35] report that Na/Naphthalene/THF complex-treated PTFE film obtained by a short reaction time should be $(CF)_x$ film heavily doped with alkali–fluoride. But after a long reaction time, the fluorine content decreases resulting in the formation of carbonized or graphite films. In Figure 1, the absorption at 1700 cm^{-1} was attributed to conjugated double bonds, respectively.[36] The absorption peaks in the range 1670–1720 cm^{-1} are due to $-CX=CX-CX-CX-$ and at 1733 cm^{-1} is the result of $-CF=CF-$.[37] The absorption at 1538 and 1754 cm^{-1} was attributed to terminal and internal double bonds.[37] Costello and McCarthy[38] tentatively assigned the absorption at 1722 cm^{-1} to $CF=CF$
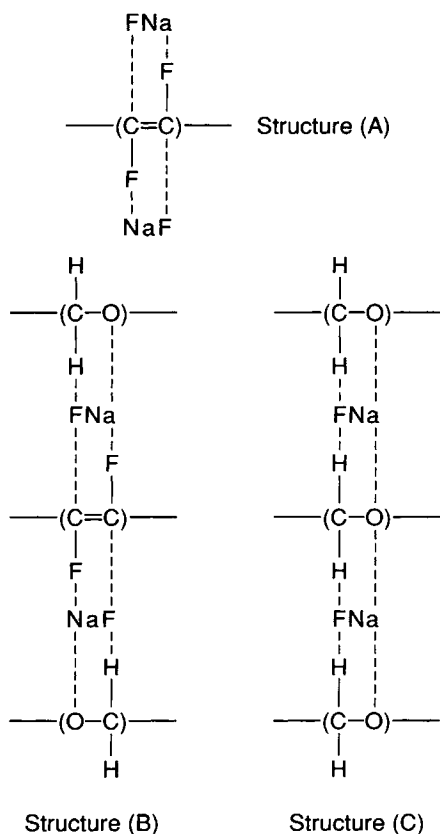
Table II   Variation of Mechanical Properties[a] with Polytetrafluoroethylene in Polyacetal for Five Kind of Blends

Properties	Wt %	PTFE	LZ-PTFE	CPTFE	WPTFE	LZ-WPTFE
Tensile strength	0	61.8	61.8	61.8	61.8	61.8
(MPa)	5	56.9	80.3	125.8	85.9	77.7
	10	55.4	72.3	122.8	67.7	71.7
	15	39.2	55.5	107.6	61.4	61.6
	20	30.9	45.2	100.5	56.2	56.7
Elongation (%)	0	45	45	45	45	45
	5	32	15.5	15	17	15
	10	31	15.5	12.5	13	14
	15	15	8	11	12	12
	20	13	7	10	10.5	12
Young's modulus	0	1.08	1.08	1.08	1.08	1.08
(GPa)	5	0.73	1.36	2.27	1.47	1.30
	10	0.69	1.25	2.32	1.26	1.26
	15	0.64	1.15	2.29	1.26	1.16
	20	0.55	1.09	2.40	1.17	1.12

[a] The deviation of all samples are ca. ±5% for tensile strength, ±10% for elongation, and ±6% for Young's modulus.

Reaction Mechanism of Na-Naphthalene Complex
Treated PTFE

1. $Na + C_{10}H_8 \longrightarrow (C_{10}H_8)^- ---- ^+Na$
2. $(C_{10}H_8)^- ---- ^+Na + —(CF_2CF_2)— \longrightarrow$
   $C_{10}H_8 + NaF +$
   a. Internal double bond
      $—(CF_2CF_2)_m—CF=CF—(CF_2CF_2)_n—$
   b. Terminal double bond
      $CF_2=CF------------CF=CF_2$
   c. Conjugate double bond
      $—(CF_2CF_2)_p—(CF=CF)_q—(CF_2CF_2)r—$

Structure (A)

Structure (B)   Structure (C)

Scheme 1

POM. The outward appearance of free NaF is shown
in Figure 2. In POM (M270)/CPTFE[39] blends, the
crystalline diffraction peak ($2\theta = 22°$ to $24°$) be-
comes weaker as the content of CPTFE increases.
However, the tip of the free NaF acted as a nuclei
to aid POM in crystallizing and the microstructure
would be formed as the structure (C).[40] In this case,
the free NaF acted as a kind of reinforcement. For
these reasons, the POM/CPTFE blends possessed
the highest mechanical properties of these five kinds
of blends. As a result, the tensile strength and the
Young's modulus of the POM/CPTFE blends were
more than twice as high as those of the POM.

Table II showed that the tensile strength and the
Young's modulus of POM/WPTFE blends were
higher than those of the POM/PTFE blends. SEM
showed that the WPTFE dispersed in POM ho-
mogeneously and the particle size of agglomerative
WPTFE as also smaller than those of agglomerative
PTFE. Therefore, the entrapped air and weak points
(agglomerates) in agglomerative WPTFE that dis-
persed in POM were lower than those of agglom-
erative PTFE that dispersed in POM. On the other
hand, the surface tension, polarity, wettability, and
bondability (adhesion) of fluoropolymer were in-
creased by the surface treatment.[41-43] Figure 1
showed that the surface structure of WPTFE pos-
sessed a lot of $CF=CF$ double bond. The adhesion

stretch. As a result, the surface structure of WPTFE
possessed a lot of $CF=CF$ double bonds. Therefore,
the authors suggested that the surface structure of
etched-PTFE may be formed as the structure in
Scheme 1. The NaF salt that was produced in the
etching procedure adsorbed on the surface of etched
PTFE that contained the $CF=CF$ double bond for
the reason of polarity and formed the structure (A)
(CPTFE). As the CPTFE was added to POM, the
structure of the POM/CPTFE blends were formed
as the structure (B). In this case, the NaF acted as
a good coupling agent and offered a very strong
bonding force between the etched PTFE and the

Figure 1 Infrared spectra of (A) PTFE, (B) CPTFE,
and (C) WPTFE.
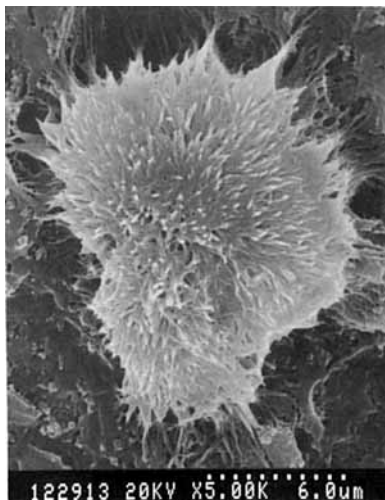
Figure 2 Scanning electron micrograph of NaF salt in POM.

interaction between POM and WPTFE was higher than the adhesion interaction between POM and PTFE for the reason of polarity. For the above reasons, the tensile strength and the Young's modulus of POM/WPTFE blends were higher than those of the POM/PTFE blends.

The morphology of POM/LZ-WPTFE blend was similar to that of POM/WPTFE blend. Because LZ-WPTFE dispersed in POM homogeneously and the particle size of agglomerative particles of LZ-WPTFE were smaller than those of agglomerative PTFE, the entrapped air and weak points (agglomerates) in agglomerative LZ-WPTFE that dispersed in POM were less than those of agglomerative PTFE that dispersed in POM. Therefore, the mechanical strength of POM/LZ-WPTFE blends were very similar to that of POM/WPTFE blends. In this case, the coupling agent did not markedly increase the adhesion interaction between POM and WPTFE. The adhesion interaction between the POM and the PTFE was poor. Addition of the coupling agent results in improved mechanical properties for any portion of LZ-PTFE, as would be expected because of better POM-coupling agent modified PTFE interface bonding in the presence of a coupling agent. Furthermore, the LZ-PTFE could be dispersed in POM homogeneously. Hence, the tensile strength and the Young's modulus of the POM/LZ-PTFE were drastically higher than those of the POM/PTFE blends.

In Table II, it was found that the elongations at break of POM/modified-PTFE blends were smaller than that of POM/PTFE blends. This result showed

that the adhesion between POM and modified PTFE was better than that of POM and PTFE.

Taber Wear Factor

It is known that[44] below 19°C the PTFE molecules are in the form of a 13/6 helix and at higher temperatures they untwist slightly into 15/7 helix. The two types of PTFE helices have very smooth molecular profiles and can be considered as cylinders, as confirmed by building molecular models. These smooth profiles have been suggested as being responsible for the good low-friction properties of this polymer.[44] It is possible to produce fluorocarbon-like, low-surface-energy polymers by the addition of small amounts of selected fluorocarbon additives to nonfluorinated polymers.[45] With scraping or abrading, with time or the application of heat to speed the diffusion process, the additive concentrates at the air/solid interface produce a fluorocarbon-like surface.[46] The action of the fluoropolymer film is mainly that of reducing the surface energy at the air/solid interface.[47] In any event, the lower critical surface tension (γ_c) of the adhesion film, the better it will be as a release agent.[47] Estell[4] also reports that the PTFE incorporated in the polyacetals transfers to the opposite mating surface and extends wear life. Therefore, the Taber wear factor of POM/PTFE blends was dramatically decreased.

The "constitutive law of wettability" states that "in general, the wettability of organic surfaces is determined by the nature and packing of the surface atoms or exposed groups of atoms of the solid and is otherwise independent of the nature and arrangement of the underlying atoms and molecules."[48] The surface tension, polarity, and wettability (γ_c, critical surface tension) of fluoropolymers were increased by the surface treatment.[41–43] Therefore, the wettability of modified PTFE (WPTFE, LZ-PTFE, LZ-WPTFE, CPTFE) was greater than that of PTFE. For this reason, as the POM/modified-PTFE blends were scraped or abraded, the modified PTFE concentrated at the air/solid interface could not give a surface that possessed low surface energy. Hence, the wear resistance of POM/modified-PTFE blends was worse than that of POM/PTFE blends. The POM/CPTFE blends had the best wear resistance property of all POM/modified-PTFE(LZ-PTFE, WPTFE, LZ-WPTFE, CPTFE) blends. It is suggested that the NaF acted as a good coupling agent and offered a very strong bonding strength between the CPTFE and the POM as the structure (B). The result of wear resistance of blends are shown in Figure 3.
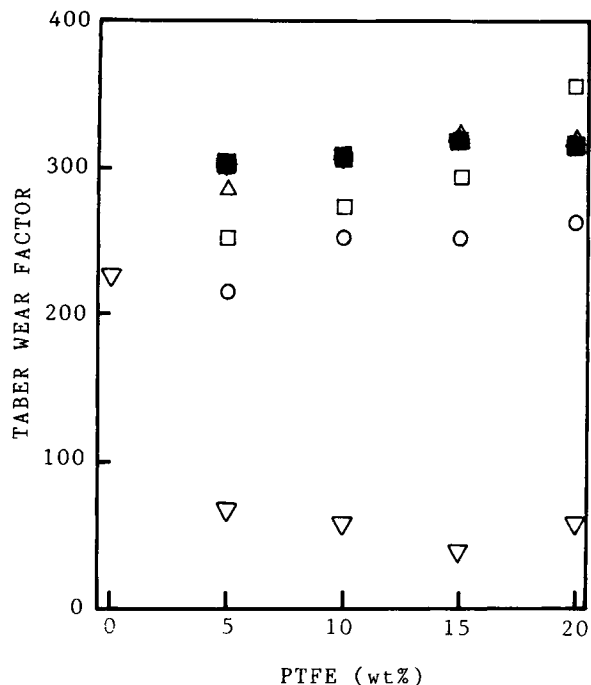
Figure 3 Variation of wear with polytetrafluoroethylene percentage by weight in POM for five kinds of blends: (∇) POM/PTFE; (■) POM/LZ-PTFE; (□) POM/LZ-WPTFE; (△) POM/WPTFE; (○) POM/CPTFE.

Processability

The torque of blends during extruding vs. various compositions of five kinds of blends are shown in Figure 4 indicating that the POM/CPTFE blends had the highest torque of all blends. It is suggested that NaF acted as an effective coupling agent and offered strong adhesion interaction between the POM and the CPTFE [structure (B)]. Additionally, the free NaF (Figure 2) that dispersed in POM increases the interface friction in blending. For these reasons, the POM/CPTFE blends had the highest torque during blending. Figure 4 showed that the POM/WPTFE blends possessed lowest torque during extruding of all blends since the WPTFE content went up to 15 wt % because the WPTFE homogeneously dispersed in POM. The coupling agent could increase the adhesion interaction between POM and additives (PTFE and WPTFE). Therefore, the torque of the POM/LZ-PTFE and the POM/LZ-WPTFE blends in extruding were higher than that of POM/WPTFE blends in extruding. In the POM/PTFE blends, the fine PTFE powder had a strong tendency to agglomerate [Fig. (5A)]. Thus, it is very difficult to disperse fine PTFE powder into highly viscous polymer melt. Therefore, the interface area
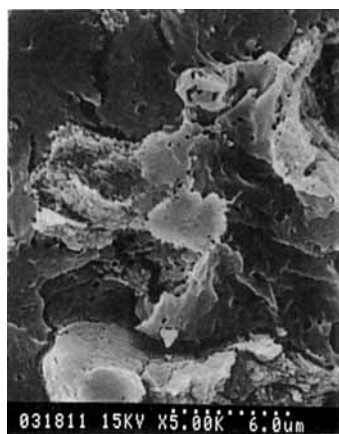
between the POM and the PTFE was lower than the interface area between the POM and the modified PTFE(LZ-PTFE, LZ-WPTFE, WPTFE). In this case, the lubricant efficiency of PTFE in POM was worse than those of modified PTFE(LZPTFE, LZ-WPTFE, WPTFE) in POM. Therefore, the torque of POM/PTFE blends in blending was higher than those of POM/modified-PTFE(LZ-PTFE, LZ-WPTFE, WPTFE) blends in blending as the PTFE content fell below 15 wt %. As the PTFE content rose to 20 wt %, the POM/PTFE blends possessed lowest torque during blending. It is because the interface area between the POM and the PTFE increased with increasing PTFE content. In this composition (POM/PTFE = 80/20), the lubricant efficiency of PTFE in POM would appear and decrease the torque of blends in blending. But, as the modified PTFE(LZ-PTFE, LZ-WPTFE, WPTFE) content went up to 20 wt %, the adhesion interaction between POM and modified PTFE(LZ-PTFE, LZ-WPTFE, WPTFE) increased the torque value of blends during blending.
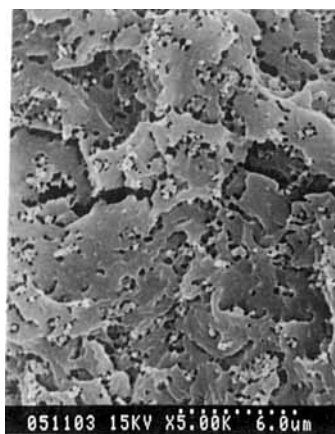
Morphology

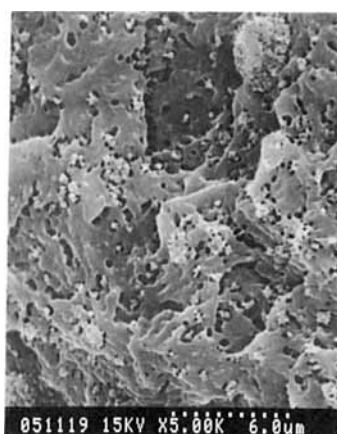In order to investigate the morphology for PTFE-filled, LZ–PTFE-filled, LZ–WPTFE-filled,
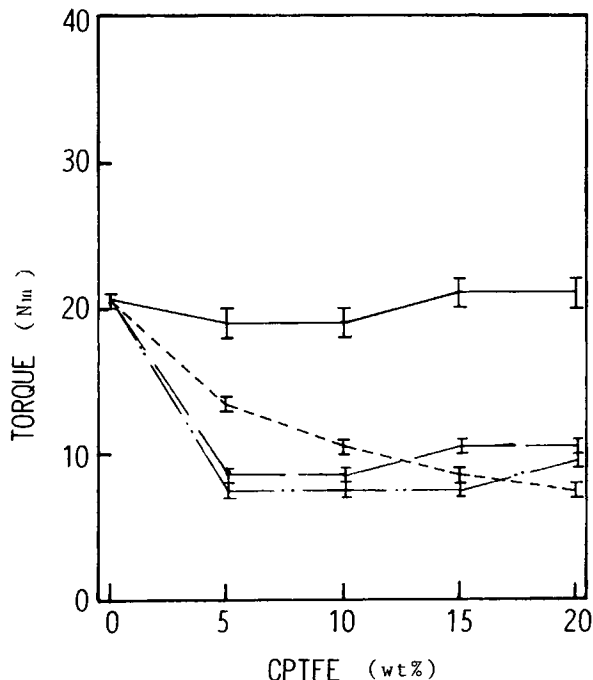
Figure 4 Variation of torque with polytetrafluoroethylene percentage by weight in POM for five kinds of blends: (---) POM/PTFE; (– – –) POM/LZ-PTFE, POM/LZ-WPTFE; (– · –) POM/WPTFE; (——) POM/CPTFE.
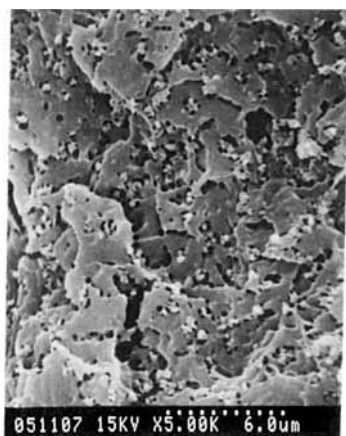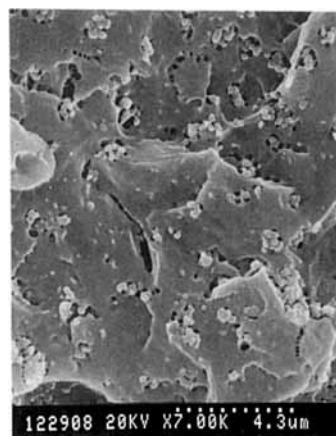
Figure 5   Scanning electron micrographs of five kinds of blends; (A) POM/PTFE(80/20); (B) POM/LZ-PTFE(85/15); (C) POM/LZ-WPTFE(85/15); (D) POM/WPTFE(85/15); (E) POM/CPTFE(85/15).

WPTFE-filled, and CPTFE-filled polyacetals, the morphology of the cryofractured surfaces of polymer specimens were examined by scanning electron microscopy. Figure 5 showed micrographs of the cryofractured surfaces of these five materials. It was found that the PTFE powder had a strong tendency to agglomerate [Fig. 5(A)]. However, the modified PTFE (LZ-PTFE, LZ-WPTFE, WPTFE, CPTFE) dispersed in POM homogeneously [Fig. 5(B–E)]. On the other hand, the particle size of agglomerative-modified PTFE was smaller than that of agglomerative PTFE. It is because the surface tension, polarity, wettability, and bondability of PTFE were markedly increased by surface treatment.[41-43] Hence, the dispersion force and interaction between modified PTFE(LZ-PTFE, LZ-WPTFE, WPTFE, CPTFE) and matrix were increased. In Figure 5(B–E), it shows that the morphology of POM/CPTFE [Fig. 5(E)] differs from that of POM/LZ-PTFE [Fig. 5(B)], POM/LZ-WPTFE [Fig. 5(C)], and POM/WPTFE [Fig. 5(D)] blends. From SEM micrographs, it was observed that the void between the POM and the CPTFE of the POM/CPTFE blend was smaller and less than the void between the POM and the modified PTFE of POM/LZ-PTFE, POM/LZ-WPTFE, and POM/WPTFE blends. It is because the NaF acted as an interface agent and offer a very strong bonding force between the POM and the CPTFE. This was one of the reasons the POM/CPTFE blends had highest mechanical strength of all blends.

CONCLUSIONS

The POM/PTFE blends show a very good wear resistance, but the mechanical strength of the POM/PTFE blends all decreased with increasing PTFE content. Using the chemical surface-treatment method to etch PTFE could cause CPTFE to homogeneously disperse in POM. The NaF salt that adsorbed on the surface of etched PTFE offered a strong bonding force between the POM and the etched PTFE. These results caused the mechanical strength of POM/CPTFE blends to be more than twice as high as that of POM/PTFE blends. The modified PTFE (LZ-PTFE, LZ-WPTFE, WPTFE) homogeneously dispersed in POM. On the other hand, the surface tension, polarity, wettability, and bondability of PTFE was increased by the surface modification. Therefore, the mechanical strength of POM/modified PTFE (LZ-PTFE, LZ-WPTFE, WPTFE) were better than those of POM/PTFE blends. As the POM/modified-PTFE blends were scraped or abraded, the modified PTFE concentrated at the air/solid interface could not produce a surface that possessed low surface energy. Therefore, the wear resistance of POM/modified-PTFE blends were worse than that of POM/PTFE blends.

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