Eur. Polym. J. Vol. 28, No. 6, pp. 583–590, 1992
Printed in Great Britain

0014-3057/92 $5.00 + 0.00
Pergamon Press Ltd

POLYACETAL/POLYTETRAFLUOROETHYLENE BLENDS—II. THE EFFECT OF CHEMICAL SURFACE TREATMENT OF POLYTETRAFLUOROETHYLENE*

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(Received 8 October 1991; in revised form 26 November 1991)

Abstract—The mechanical, physical, wear, dielectric, thermal and morphological properties of blends of polyacetal (POM) with surface-modified polytetrafluoroethylene (CPTFE) were examined and compared with those of POM/PTFE blends. The PTFE was added to POM to improve the wear properties; the tensile strength, Young's modulus and elongation of POM/PTFE blends decreased with increasing PTFE content but the tensile strength and the Young's modulus of POM/CPTFE blends were more than twice those of the POM/PTFE blends. The NaF salt which was adsorbed on the CPTFE acted as a coupling agent and provided very strong bonding between POM and CPTFE. The free NaF salt also seemed to form nuclei aiding POM crystallization; this effect was not found in POM/PTFE systems. For POM/PTFE, SEM showed that the size of PTFE particles was in the range 15–60 μm. In POM/CPTFE systems, the particle size of CPTFE was $< 1\ \mu$m. Increasing times of chemical surface treatment of CPTFE increased the tensile strength of POM/CPTFE blends.

INTRODUCTION

Polyacetals (POMs) are strong, hard, highly crystalline thermoplastics. They are used in applications where their frictional and wear characteristics are most important. These properties of polyacetals coupled with the wear resistance and low coefficient of friction imparted by polytetrafluoroethylene (PTFE) [1–7], carbon fibre [8–13], oil [14–17], aramide fibre [18, 19], mixer [20–22] and other additives [23–25], make the resin an excellent material for consideration in the production of functional parts of mechanical equipment. The PTFE incorporated in the POM transfers to the opposite surface and extends wear-life when items are properly designed and fabricated. Although POM/PTFE blends offer good wear resistance, the compatibility of POM and PTFE is poor. Therefore, the mechanical properties of their blends are poor. In this paper, chemical treatment of the surface of PTFE is used; various properties of blends of POM with the modified PTFE(CPTFE) are compared with those of POM/PTFE blends.

EXPERIMENTAL PROCEDURES

Materials

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

Chemical treatment

The detailed chemical surface treatment has already been described [26].

Melt blending

All blends were made by melt-mixing in a single screw laboratory extruder ($D = 0.7$ in., $L/D = 20$) and then pelletized. Prior to this step, powders of POM/PTFE or POM/CPTFE were combined at weight ratios of 100/0, 95/5, 90/10, 85/15 and 80/20 by a mechanical blender and dried in air for 3 hr at 82° to remove sorbed water. The various heating zones for extrusion were set at 120, 170, 170, 160°. The screw rpm was 15. The unblended POM was also processed under identical extrusion conditions to give a thermal history similar to that of the blend samples. Test pieces were prepared by compression moulding in a frame at 150 kg/cm^2 for 8 min, and then water-cooled.

Mechanical properties

Tensile properties were measured according to ASTM D638 using an Instron Universal Testing Machine Model 1130. The cross-head load was 500 kg, the speed was 5 cm/min, and the chart speed was 100 cm/min. The elastic moduli were determined from the slope of the initial part of the stress–strain curve in the linear section. The values were averaged over many measurements.

Dielectric properties

Dielectric constant (ϵ') and dissipation factor ($\tan\delta$) were tested by using a dielectric loss measuring set of Type TR-10C (Null detector: type BDA-9, Oscillator: type WBG-9) according to ASTM D150.

Taber wear factor

The Taber wear factor of each specimen was measured according to ASTM D1044 by Taber Machine model 5130. The wheels were H-17V Calibrase under a load of 4.9 N. The Taber wear factor was the loss of mass in milligram per one thousand cycles of abrasion.

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*Part I: W. Y. Chiang and C. Y. Huang. *Angew. Makromolek. Chem.* (in press).

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Table 1. Description of the composition of blends

Sample	Time (min)[a]	(POM[b]/CPTFE[c])[d]
90000	0	100/00
90005	0	95/05
90010	0	90/10
90015	0	85/15
90020	0	80/20
90305	3	95/05
90310	3	90/10
90315	3	85/15
90320	3	80/20
90505	5	95/05
90510	5	90/10
90515	5	85/15
90520	5	80/20
91005	10	95/05
91010	10	90/10
91015	10	85/15
91020	10	80/20

[a] Chemical surface treatment time.
[b] Polyacetal.
[c] Chemical surface treated polytetrafluoroethylene.
[d] Weight ratio.

X-ray measurements

The wide-angle X-ray diffractograms (WAXD) were recorded at room temperature on Rigaku D/MAX-IIIA X-ray diffractometer with CuKα radiation generated at 40 kV and 20 mA. The scan rate for the WAXD profiles was 1°/min.

Thermal properties

A DuPont 1090B Analyser equipped with a 951 Thermogravimetric Analyser (TGA) was used under N_2 at a heating rate of 20°/min to study the thermal degradation of blends.

SEM micrographs

For examining phase morphology, compression-moulded Izod bars were immersed in liquid N_2 and fractured. The fractured surfaces were coated with gold and viewed end-on by a Hitachi S-520 scanning electron microscope.

RESULTS AND DISCUSSION

Mechanical properties

In this study, the POM/PTFE and the POM/CPTFE blends contained up to 20 wt% (Table 1) of PTFE or CPTFE. The stress–strain properties of blends depended on composition. Tensile strength (Fig. 1), modulus (Fig. 2) and elongation (Fig. 3) vs blend composition all decreased with increasing PTFE content. The reason was described previously [5].

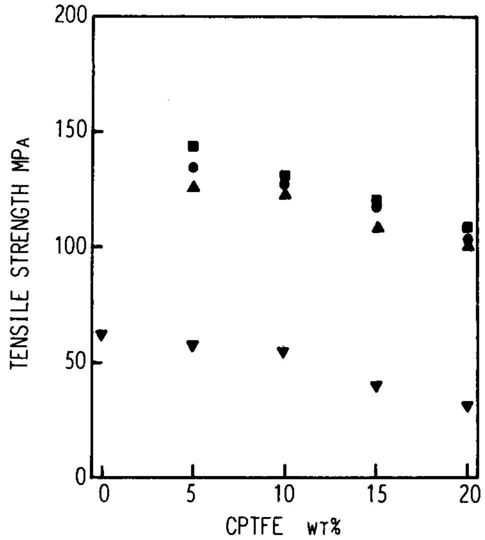
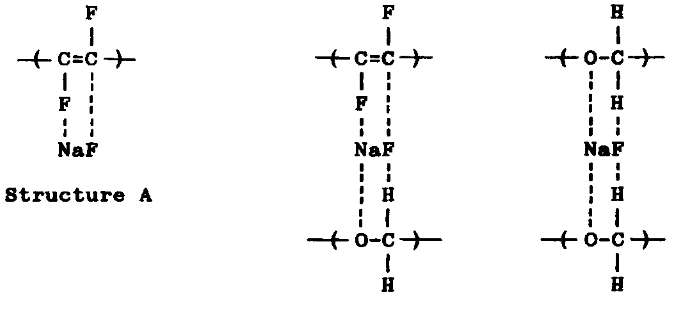


Fig. 1. Variation of tensile strength with CPTFE proportion (by weight) in POM(M90) for various chemical surface treatment times: ▼, PTFE; ▲, 3 min; ●, 5 min; ■, 10 min.

Figures 1 and 2 show that the stress at break and the Young's modulus of POM/CPTFE blends greatly increased as CPTFE was added to POM. The effects arise because the surface tension, polarity, wettability and bondability of PTFE were markedly increased by the surface treatment. The powder aggregation was improved. On the other hand, the dispersion force and interaction between CPTFE and matrix were also increased. The NaF salt that was produced during the etching would adsorb on the surface of treated-PTFE because of polarity and formed the structure **A**. As CPTFE was added to POM, the molecular structure of the POM/CPTFE blends would be that of structure **B**. In this case, NaF acted as a coupling agent and offered very strong adhesion between POM and CPTFE. The free NaF salt formed nuclei aiding crystallization of POM (Fig. 4) and the microstructure would correspond to structure **C**. In addition, the NaF salt produced in the sodium etching process was more rigid than POM. The NaF salt was also effective in increasing tensile strength and Young's modulus of POM/CPTFE blends, in addition to the chemical surface treatment of PTFE. Hence, the tensile strength and the Young's modulus of POM/CPTFE blends were more than twice those of POM/PTFE blends. Figure 1 shows that the tensile



Structure A **Structure B** **Structure C**

Structures A–C

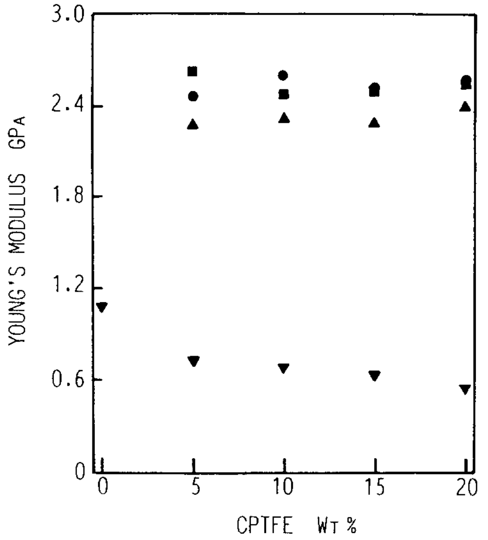


Fig. 2. Variation of Young's modulus with CPTFE proportion (by weight) in POM(M90) for various chemical surface treatment times: ▼, PTFE; ▲, 3 min; ●, 5 min; ■, 10 min.

strength of blends increased with increasing chemical surface treatment time of CPTFE. It is suggested that the surface tension, polarity, wettability and bondability of CPTFE were increased with prolonged treatment. Young's modulus (Fig. 2) and elongation (Fig. 3) of POM/CPTFE blends were independent of the duration of chemical treatment. Figure 3 shows that the elongation of POM/CPTFE blends was smaller than that of POM/PTFE blends. It shows that the adhesion interaction between POM and CPTFE was better than that between POM and PTFE.

Dielectric properties

When a polar polymer is placed in an electric field, the polar groups tend to be oriented in the field. Thus, in an alternating electric field, the polar groups in a polymer will orient and give high dielectric constants. Ideally, PTFE is a non-polar polymer. Consequently, the dielectric constant of POM/PTFE blends decreased with increasing PTFE content (see Fig. 5). The dissipation factor is the ratio of conductance to susceptibility of a plastic dielectric and is a measure of the conversion of reactive power to real power, showing up as heat [27]. Since PTFE is a nominally non-polar polymer, ϵ'' is small. Hence, the dissipation factor of POM/PTFE decreases with increasing PTFE content. These results are shown in Fig. 6. Nevertheless, in POM/CPTFE blends, the dielectric constant and dissipation factor increased with increasing CPTFE content (Figs 5 and 6), because the polarity of CPTFE was markedly increased by the surface treatment and the NaF salt content. In addition, polar polymer and NaF salt which could

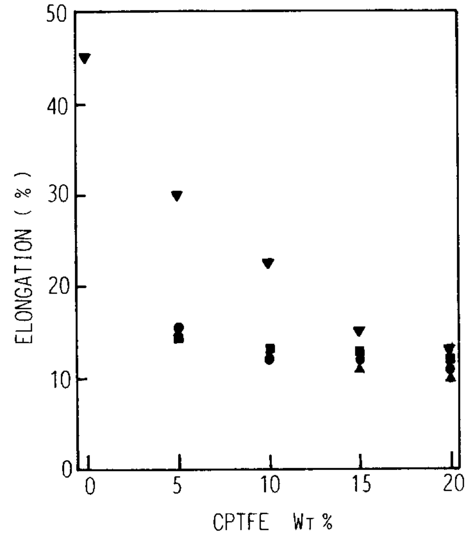


Fig. 3. Variation of elongation with CPTFE proportion (by weight) in POM(M90) for various chemical surface treatment times: ▼, PTFE; ▲, 3 min; ●, 5 min; ■, 10 min.

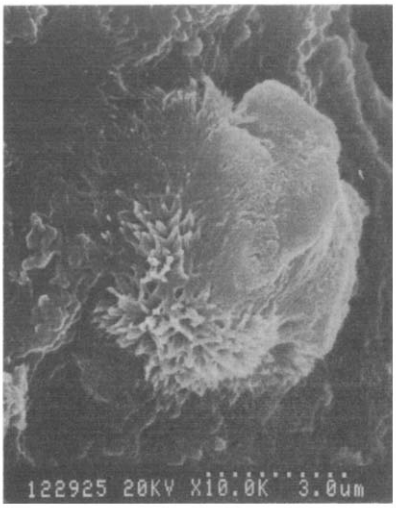


Fig. 4. Scanning electron micrograph of NaF salt in POM.

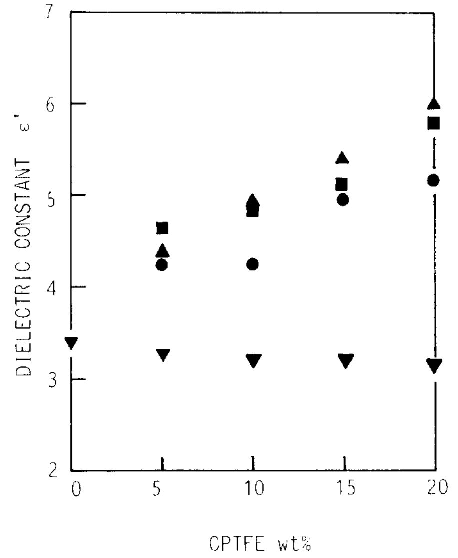


Fig. 5. Variation of dielectric constant with CPTFE proportion (by weight) in POM(M90) for various chemical surface treatment times: ▼, PTFE; ▲, 3 min; ●, 5 min; ■, 10 min.

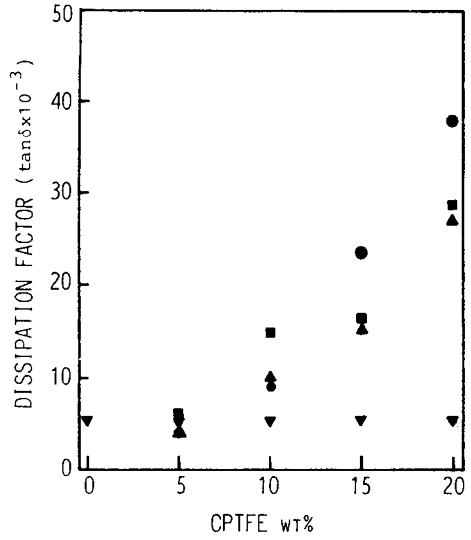


Fig. 6. Variation of dissipation factor with CPTFE proportion (by weight) in POM(M90) for various chemical surface treatment times: ▼, PTFE; ▲, 3 min; ●, 5 min; ■, 10 min.

absorb moisture were plasticized by this moisture and similarly exhibit higher dielectric constant and dissipation factor.

X-ray diffraction measurements

The X-ray diffraction scans of polymer blends, with various weight fractions of PTFE or CPTFE, as a function of the Bragg angle, are shown in Figs 7 and 8. Figure 7 (POM/PTFE) shows that, as the content of PTFE increased, the crystalline diffraction peak ($2\theta = 22$–$24°$) becomes weaker. Figure 8 shows that the crystalline diffraction peak ($2\theta = 22$–$24°$) of a blend POM/CPTFE containing 15 wt% CPTFE was stronger than that of a blend which contains 10 wt% CPTFE. This result differs from that for POM/PTFE [5] and POM (M270)/CPTFE [26] blends. According to Price [28], the transformation of a supercooled polymer melt into a solid crystalline phase involves two distinct steps viz. the birth of crystallites (termed primary nucleation) and the propagation of individual crystallites (called growth). As CPTFE (with the salt) was added to POM, it provided nuclei to aid crystallization of POM and also hindered the crystallites from propagating. The aiding effect of POM in crystallizing was higher than that of the hindering of the crystallites from propagating as the CPTFE content went up to 15 wt%. Therefore, the diffraction peak of $2\theta = 22$–$24°$ for 15 wt% CPTFE was stronger than that for the blends which contained 10 wt% CPTFE. Additionally, the position of the peak was independent of the composition, as expected. It is obvious that the unit cell dimensions of POM remain unchanged [29]. This result was the same as that for POM/PU [30, 31] blends.

Taber wear factor

It is known that below 19° PTFE molecules are in the form of a 13/6 helix; at higher temperatures, they untwist slightly into a 15/7 helix. The two types of PTFE helices have very smooth molecular profiles and can be considered as cylindrical, as confirmed by molecular models. This smooth profile has been suggested as responsible for the good low-friction properties of this polymer [32]. As a result, blends containing PTFE have low friction coefficient. Therefore, the Taber wear factor of POM/PTFE blends was dramatically decreased. However, the adhesion between POM and PTFE was poor; thus, the defects in the interface increased with increasing PTFE content. For these two reasons, the lowest Taber wear factor of POM/PTFE blends was found for 15 wt% PTFE content. As the PTFE surface was etched, the smooth surface of PTFE was destroyed. Consequently, the lubricity of PTFE decreased with increasing time of chemical surface treatment. Therefore, the wear resistance of POM/CPTFE blends decreased with increasing time of chemical treatment of PTFE. These results are shown in Fig. 9.

Process-ability

The torque of blends during blending vs CPTFE weight fraction are shown in Fig. 10. The torque of POM/CPTFE blends in blending was lower than that of POM when CPTFE content was < 10 wt%. But, the torque of blends in blending slightly increased when the CPTFE content exceeded 10 wt%. It is suggested that the rough surface of CPTFE and NaF salts increase the interface friction. It is also the reason why the torque of POM/CPTFE blends in blending is higher than that of POM/PTFE blends.

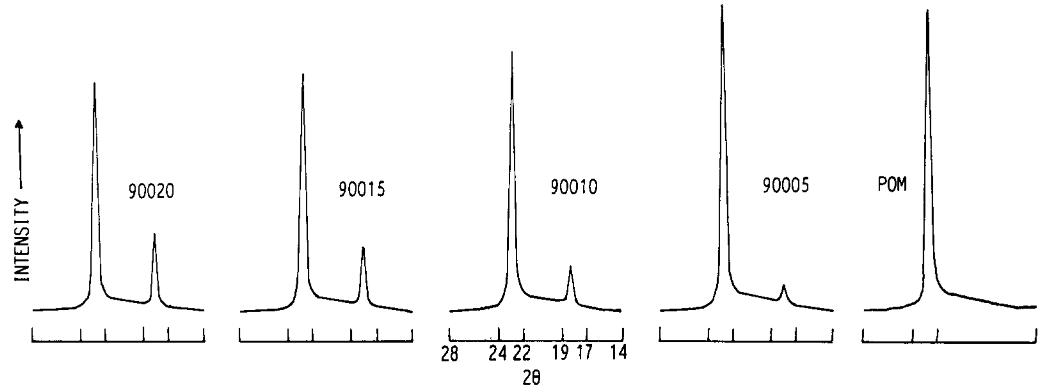


Fig. 7. The intensity distribution of X-ray diffraction scans of POM(M90)/PTFE blends.

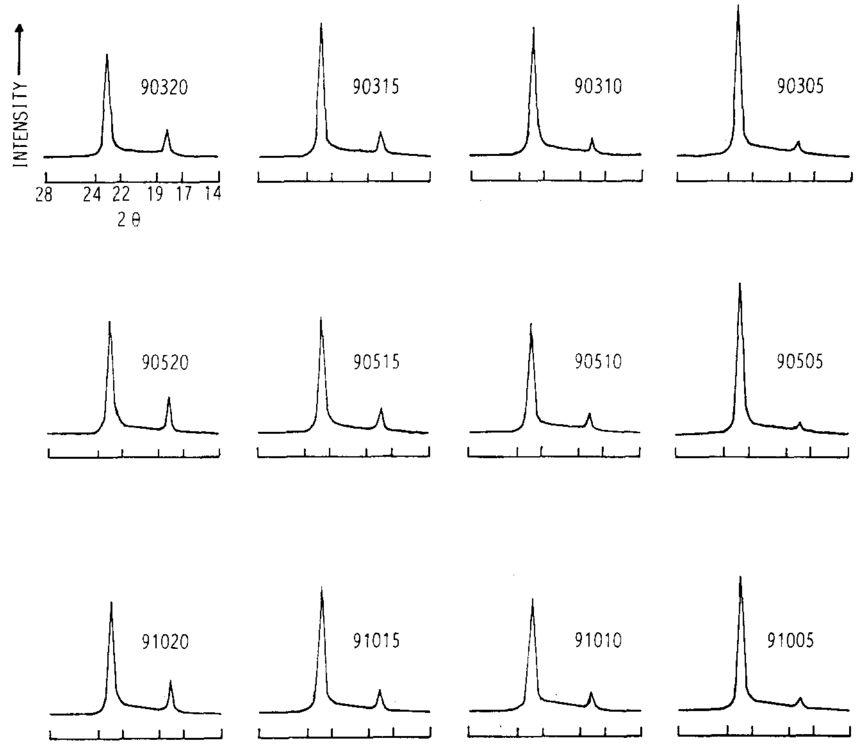


Fig. 8. The intensity distribution of X-ray diffraction scans of POM(M90)/CPTFE blends.

The PTFE possessed good frictional property; therefore, the torque of POM/PTFE blends decreased with increasing PTFE content.

Thermogravimetry analysis

The TGA analysis of POM/CPTFE blends is shown in Fig. 11. It shows that the thermal stability was in the order PTFE > 20 wt% CPTFE > 15 wt% CPTFE > 10 wt% CPTFE > 5 wt% CPTFE > POM. This order is found because the heat resistance of PTFE or CPTFE is better than that of POM.

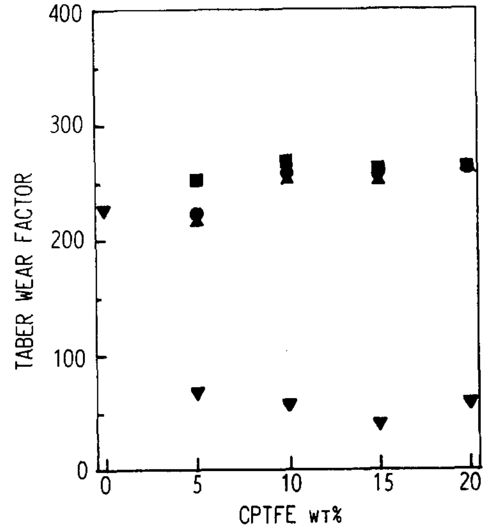


Fig. 9. Variation of wear with CPTFE proportion (by weight) in POM(M90) for various chemical surface treatment times: ▼, PTFE; ▲, 3 min; ●, 5 min; ■, 10 min.

Morphology

In order to investigate the morphology for filled-PTFE, filled-CPTFE and PTFE-free polyacetals, the morphology of the cryofractured surfaces of polymer specimens were examined by scanning electron microscopy. Figure 12 (POM/PTFE) shows a micrograph of the cryofractured surfaces of the specimens. The sizes of PTFE agglomerates increased from 15 to

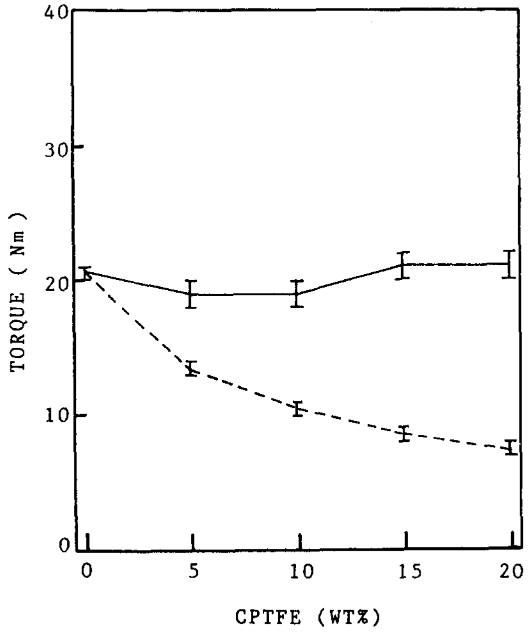


Fig. 10. The torque of blends in blending: ---, POM(M90)/PTFE; ——, POM(M90)/CPTFE.

60 μm with increasing PTFE content. Figure 13 shows micrographs of POM/CPTFE blends. It shows that CPTFE is homogeneously dispersed in POM. On the other hand, the particle size of agglomerates of CPTFE was less than that for PTFE. It is suggested that the surface tension, polarity, wettability and bondability of PTFE were markedly increased by surface treatment. Hence, the dispersion forces and interaction between CPTFE and matrix were increased and CPTFE dispersed homogenously in POM.

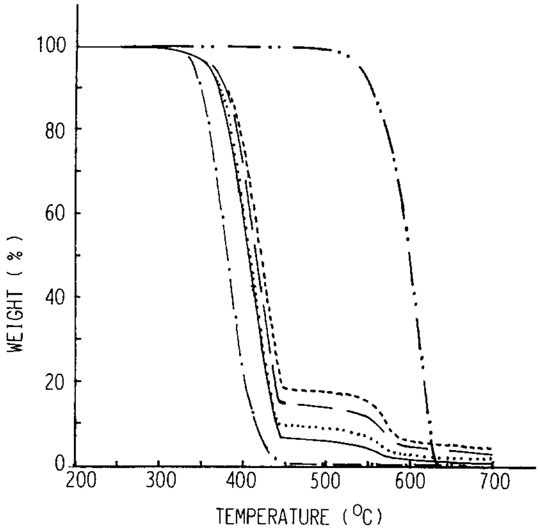


Fig. 11. Thermal decomposition of POM/CPTFE blends; CPTFE surface treatment time: 3 min: —·—, POM(M90); ——, 90305; · · ·, 90310; — — —, 90315; - - -, 90320; —··—, PTFE.

CONCLUSIONS

POM/PTFE blends have very good wear resistant property but the mechanical properties are poor. Using the chemical surface treatment method to etch PTFE causes homogeneous dispersion of CPTFE in POM. The NaF salt provides strong bonding between POM and CPTFE and furnishes nuclei to aid POM in crystallizing. As a result, the mechanical strengths of POM/CPTFE blends are higher than those of

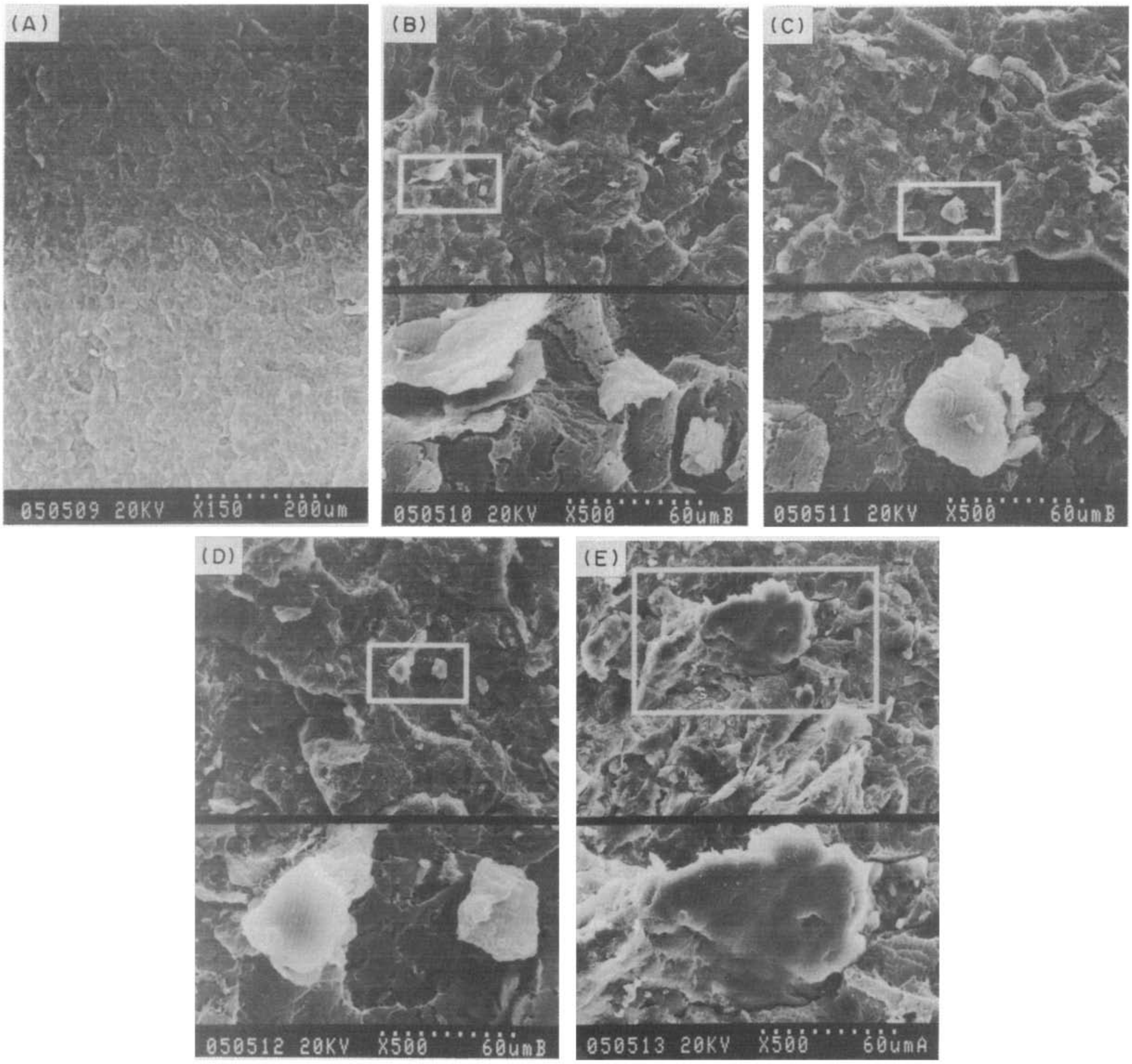
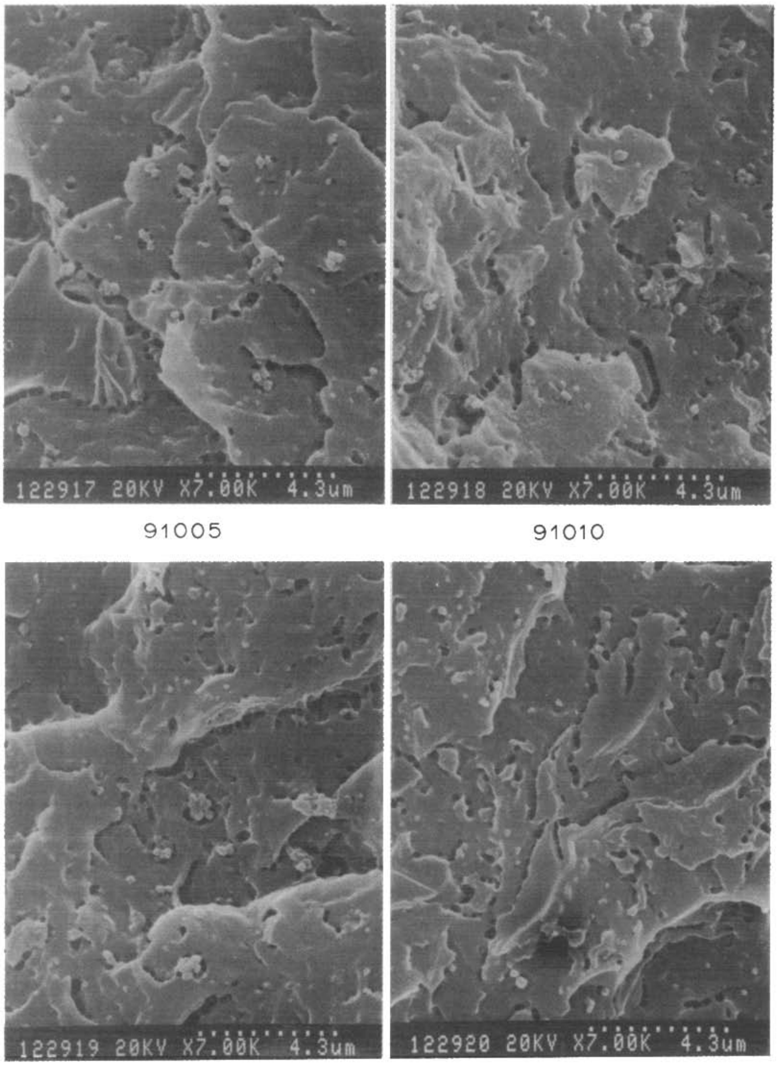


Fig. 12. Scanning electron micrographs of POM(M90)/PTFE blends: (A) M90; (B) 90005; (C) 90010; (D) 90015; (E) 90020.



91005 91010

91015 91020

Fig. 13. Scanning electron micrographs of POM(M90)/PTFE blends: surface treatment time: 10 min.

POM/PTFE blends. For the same reason, the processability of POM/PTFE blends is better than that of POM/CPTFE blends.

Acknowledgements—The authors express their sincere appreciation to Dr T. S. Lin, President of Tatung Institute of Technology, for his encouragement and support. Thanks are due to the National Science Council for financial support under contract number NSC79-0405-E036-03.

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