



CHAPTER IV

TRIBOLOGICAL PROPERTIES OF PFMA-PMMA COPOLYMER THIN FILMS

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Perfluoroalkylethyl methacrylate and polymethyl methacrylate copolymers (FMA/MMA) were synthesized at various FMA mole ratios. 5wt% copolymer solutions were spun cast onto 1mm thick PMMA sheet substrates. The effects of monomer ratio on tribological properties were investigated from surface energy measurements and TE79 multi-axis tribology machine measurements. There was an optimum ratio of FMA to MMA, in the range of $(1-5) \times 10^{-3}$, for coatings to attain a minimum kinetic friction coefficient. The results obtained are discussed with reference to proposed friction and wear mechanisms.

Keywords: Poly(perfluoroalkylethyl methacrylate-methyl methacrylate) copolymer,
friction coefficient, Wear, Spin coating, Surface tension

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1. Introduction

There are two widely used methods for improving tribological properties of polymers: surface coating or fabricating polymer composites. For the surface coating, the main requirements for this approach are that the polymer must adhere well onto the substrate, and it must have good wear or scratch resistance properties. These two requirements are difficult to obtain simultaneously scratch and mar resistances of automotive coating [1] and friction and wear resistances of organic coating on steel [2] are some typical examples. It has been known that PTFE possesses a relatively small friction resistance, but it can be easily scratched [3]. One of the relatively high scratch resistance polymers is polymethyl methacrylate (PMMA)[3]. In addition, it has relatively high adhesion property, good mechanical properties, good chemical and weather resistances. It is transparent and colorless and can be easily colored. Even though PMMA has a relatively high scratch resistance amongst polymers, it is still lower than that of glass [4].

There have been several studies on the tribological properties of PMMA [5-13]. A study of tribological properties of fluoropolymer and epoxy has been carried out Brostow [14]. The fluorine containing monomer studied was perfluoroalkylethyl methacrylate monomer (FMA). Its structure is very similar to MMA monomer but it possesses an extremely low surface energy [15]. Some advantages of FMA are compatibility, ease in copolymerization, and a higher energy dissipation capability resulting in lower friction and wear. Atomic transfer radical polymerization (ATRP) was discovered as far back as 1995; this polymerization method has many advantages compared to the typical living free radical

polymerization method [16]. Via ATRP method, fluorinated methacrylic polymer was synthesized by statistical copolymerization in solution [17]. Tribological properties with a series of methyl methacrylate and n-butyl methacrylate copolymer were investigated in which macro and nano-tribological condition can be controlled by the composition of a random copolymer of methacrylate and n-butyl methacrylate [18]. However, to the best of our knowledge, there has been no systematical study in tribological properties of methyl methacrylate and perfluoroalkyl ethyl methacrylate copolymer.

In this study, we shall report some tribological properties of FMA/MMA copolymer surface coating on PMMA with focus on the effect of fluorine content.

2. Experimental Section

2.1 Materials

Perfluoroalkylethyl methacrylate (Aldrich, AR grade) was purified by distillation under vacuum. Methyl methacrylate (Acros, AR grade) and toluene (Labscan, AR grade), which were used as monomer and solvent respectively, were passed down into a basic alumina column immediately prior to use. Copper(I) bromide (Aldrich, AR grade) was dissolved in a boiling saturated aqueous NaBr solution over 30 min. Pure Copper(I) bromide was obtained by cooling and diluting the solution with water, followed by filtering and washing sequentially with distilled water, ethanol, ethyl acetate diethyl ether and pentane, then drying in a vacuum oven for 24 h [19]. 1mm thick polymethyl methacrylate sheet (Towapex, commercial

grade) was cleaned by ultrasonic cleaning. n-pentylamine (Aldrich, AR grade) N-pentyl-2-pyridinalmethanimine was synthesized following the Haddleton's method [20]. Pyridene-2-carboxaldehyde (Aldrich, AR grade), 4-amino benzoic acid (Fluka, AR grade), ethyl-2-bromoisobutyrate (Aldrich, AR grade), ethylene glycol (JT Baker, AR Grade), and diiodomethane (Acros, AR Grade) were used as received.

2.2 Polymerization

The polymerization procedure was based on the Haddleton's method [17]. $[M]/[I]/[Cu]/[L]=100/1/1/2$. Cu(I)Br(0.67 g, 4.68×10^{-4} moles), benzoic acid (2.34×10^{-4} mole) and a magnetic follower were placed in a clean dry three-necked round bottom flask which was connected with a nitrogen gas line and a condenser (sealed at the top). The flask was cycled between the nitrogen and nitrogen gas for five times. The solution containing Toluene (5 ml.), N-pentyl-2-pyridinalmethanimine (0.173ml, 9.36×10^{-4} moles), Ethyl-2-bromoisobutyrate (0.069ml, 4.68×10^{-4} moles) and monomer (4.68×10^{-4} moles) were deoxygenated by nitrogen purging for 15 min prior to adding into the reaction flask. The reaction flask was then placed in a preheated oil bath at 90 °C. (t=0). After the 300 min, the reaction was stopped by shocking in iced bath. Polymer solution were passed down into a basic alumina column and precipitated into n-pentane. Nine molar fractions of copolymers were prepared with the following [FMA]/[MMA] ratios: 0/100, 0.05/99.95, 0.1/99.9, 0.2/99.8, 0.5/99.5, 0.7/99.3, 1/99, 10/90, and 20/80.

2.3 Characterization Instrumentation

The spectra of those polymers FTIR spectra of copolymers were obtained by using a BIORAD spectrometer (FTS-45A). 2 mg of polymer powder was mixed with 60 mg KBr salt into pellets and the spectra were recorded.

^1H , NMR spectrometer (Bruker, Advance DPX 400) operated at 300 MHz was used to determine molar fractions of copolymer. The polymer solutions were prepared by dissolving ~ 50 mg of polymer in 3 ml of deuterated chloroform (CDCl_3).

Energy Dispersive X-ray Spectroscopy to determine molar fraction of copolymer. It was operated under accelerating voltage 25.0 kV and live time of 100 sec.

The weight-average molecular weight, MW and polydispersity index, PDI of copolymer at FMA mole ratio < 50% were determined by gel permeation chromatography (Waters 150-C plus) with standard polystyrene calibrations. THF was used as an eluent and the flow rate used was 1.0 ml/min.

2.4 Contact Angles and Surface Tension Measurements

Water, diiodomethane and ethylene glycol were used for contact angles and surface tension measurements. The specimens were prepared by spin coating technique (2000 rpm, 120 seconds) at polymer concentration 5% by weight in toluene. The coated PMMA sheets were dried in a vacuum oven for 3 days at the ambient temperature. They were then clamped to a flat surface and water (20 μl) was dispensed from a syringe which was suspended from above. The surface was raised and so that the blunt ended needle remained in the drop. The drop was advanced by dispensing a further 10 μl of liquid. A snap shot profile of the advanced drop was

immediately captured by a digital camera (Nikon, Coolpix 990) connected to a PC. The angle was then receded by withdrawing 10 μl . of water from the drop and another snapshot was captured. This process were repeated five times, the profiles were analyzed using Adobe Photoshop and the series of advancing and receding angles measured on the both sides of the drop were averaged. Diiodomethane and ethylene glycol were also used as solvents following the same procedure to obtain various contact angles and for the calculation of surface tension values following the van Oss-Good method [21].

2.4 Mechanical and Tribological Properties

The coated samples, which were also prepared under the same condition as for contact angle measurement, were used in this part. The dynamic friction coefficient was also measured by a TE 79 Multi –axis tribometer. A stainless steel ball (diameter 12.7 mm) made of ball bearing steel was drawn over the surface with the normal load at 800 g. A constant rotational speed of 10 rpm and the rotational radius of 20 mm were used in all experiments. All experiments were performed at room temperature (22-25 °C). During the experiments, the friction force was continuously recorded during each test. In each test, both single and multipass experiments were performed.

2.6 Surface Characterization

The scratched samples were thoroughly investigated by optical microscopy (Leica, DMRXP). The magnification was 6.4: 4 magnifications for the objective lens and 1.6 magnifications for eyes lens.

3. Results and Discussion

3.1 Polymerization

Figure 1 shows FTIR spectra for the PMMA and PFMA-PMMA copolymer at various ratios. The absorbance peak of C-F stretching, which is originated from FMA part, can be observed at 1100-1200 cm^{-1} . Its intensity increases as FMA ratio increases. Consistent with $^1\text{H-NMR}$ result, the increase in intensity of distinguished peaks belonging to methylene protons ($-\text{COOCH}_2-$) at 4.23 and 2.45 ppm originating from PFMA can be observed with increasing FMA ratio. The molar ratio of FMA monomer in copolymer was obtained from the integral ratio of methyl protons ($-\text{COOCH}_3$) to methylene protons ($-\text{COOCH}_2-$) as originating from PMMA and PFMA, respectively. The $^1\text{H-NMR}$ molar ratios are close to the expected values than those obtained by EDS technique; data from both techniques are tabulated in Table 1. The table also lists M_w , M_n , polydispersity and weight average of degree of polymerization, \bar{X}_w of PMMA-PFMA synthesized. M_w values fall between 10800 and 12800 g/mol as FMA mole ratio was varied between 0 and 20%, whereas polydispersity values are close to 1.1. We note that N should be close to 100 but it decreases as %FMA content increases. This finding may be attributed to the effect of the interaction between perfluoroalkyl groups because of the poor solubility in THF which is used as the eluent, a reduced hydrodynamic radius can be expected [22, 23].

3.2 Surface Energy

Figure 3 shows a plot of the total surface energy, $\gamma_{\text{total}} = \gamma_{\text{AB}} + \gamma_{\text{LW}}$, versus % FMA mole ratio, where γ_{AB} and γ_{LW} are the acid-base and The Lifshitz van der Waals surface energies, respectively [21]. The total surface energy γ_{total} decreases monotonically with % FMA mole ratio and its main contribution comes from γ_{LW} the dispersive surface energy. Our data are consistent with the data of Park and his co-worker [24] in which they showed that the random copolymer of PFMA-PMMA reach the optimum surface energy at 1%wt(~0.2%mole).

3.3 Friction Properties

Figure 4 shows the kinetic friction coefficient, μ_k , versus %FMA mole ratio. There are three regimes which can be identified. For % FMA mole ratio between 0 and 0.1%, μ_k decreases slightly from 0.46 to 0.40. In the second regime, % FMA mole ratio varies between 0.1 and 0.5%, μ_k remains nearly constant at 0.40. Increasing % FMA mole ratio above 0.5%, μ_k increases toward its asymptotic value of 0.46, a value which is identical to that of 0% FMA film. There are possibly at least two factors that can account for the behaviors observed in Figure 4. The initial decrease in μ_k with increasing % FMA mole ratio comes mainly from the decrease in the surface energy [15], as evidenced by the data of Figure 3. The plateau and the subsequent increase in μ_k with % FMA mole ratio are probably the results of the reductions in the copolymer hardness factor and T_g , resulting in higher contact area, higher energy dissipation and hence higher friction [3].

3.4 Wear Characteristic

Figure 5 shows micrographs of films of various %FMA after being tested by the tribometer 1 time and ten times. The samples, with respect to their wear characteristics, can be grouped into 3 categories: (i) 0-0.05%FMA there are the least wears observed on the track after the first pass, but after 10 passes a lot of hard brittle debris can be observed, (ii) 0.1-0.5% mole FMA, there is special pattern of wear track similar to a stick-slip motion, (iii) 0.7-20%FMA the dislocation is lesser and the film looks softer as the %FMA increase.

At very low FMA contents (0-0.05%), the delamination of the film is very low in the first run because of the higher in film/substrate adhesion force and the film hardness. After many cycles, the dislocation and crack formation of thin film occurred easily because of the poor energy dissipation and the brittleness of the film. At intermediate FMA contents (0.1-0.5%), the optimum ratios of ball/film adhesion force, film/substrate adhesion force and film deformation force in this regime may have combined to produce the lowest total friction coefficient (Figure 4). As can be seen in Figures 5c, d, e, there is a small amount of debris; mostly smooth scars can be observed. At higher FMA contents (0.7-20%) the adhesion force was lower and the delamination occurred more easily and the film dislocation was less severe. Hardness may have played an important role in this regime because the total friction component was higher. At 20% FMA, there was an interesting phenomenon. Rolled ribbon debris was observed, which may have played the role of slightly decreasing the friction coefficient relative to the lower FMA content samples. The wear mechanism in this regime can be identified as the grain-sliding wear [25]. In summary, the general wear mechanism can be proposed for the FMA/MMA films investigated. First, the transmittance of stress energy at contact area played the role,

which increased the plastic deformation after many cycles of testing were performed. Subsequently, crack nucleation of coating film (cohesion failure of film) and adhesion failure of film to substrate simultaneously occurred and propagated. Finally, they were followed by the delamination of wear particles [1, 26].

4. Conclusion

Well defined and predetermined molecular mass PFMA-PMMA copolymers were synthesized by the atom transfer radical polymerization (ATRP) technique. 5% of copolymer solutions were cast onto the 1 mm thick PMMA sheet substrates. The effects of monomers ratios on tribological properties were investigated. The major conclusions are:

- 1 The total surface energy γ_{total} decreases monotonically with % FMA mole ratio and the main contribution comes from γ_{LW} the dispersive surface energy.
- 2 With increasing FMA content from 0.0-0.5% FMA, the friction coefficient decreases slightly and then abruptly decreases; this is due to the decrease in surface tension. Between 0.5-20% FMA, the friction coefficient increases. This behavior is probably the result of a lowering in hardness, which overcomes the effect of the surface tension.
- 3 The delamination wear mechanisms proposed can be explained by the relationships between stress energy dissipation, plastic deformation, cohesion failure, and adhesion failure.

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Captions of Figures

- Figure 1 FTIR spectra of PFMA-PMMA copolymers (a) FMA_0 (b) FMA_01 (c) FMA_1 (d) FMA_10 (e) FMA_20.
- Figure 2 ^1H NMR spectra of PFMA-PMMA copolymers (a) FMA_0 (b) FMA_01 (c) FMA_1 (d) FMA_10 (e) FMA_20.
- Figure 3 Variation of surface tension components and total value using van Oss-Good Method for the surface of PFMA-PMMA copolymers thin film cast on 1 mm thick PMMA sheet, as a function of %mole FMA.
- Figure 4 The effect of [FMA]/[MMA] mole ratio on dynamic of the scratch friction by using TE-79 Multi-axis Tribometer.
- Figure 5 Photograph of scratch tracks as observe after one(left) and ten(right) scratches by using TE-79 Multi-axis Tribology Machine (a)FMA_0, (b) FMA_005, (c) FMA_01, (d) FMA_02, (e) FMA_05, (f) FMA_07, (g) FMA_1, (h) FMA_10, and (i) FMA_20.

Table 1 Molecular Characteristics of PFMA-co-PMMA Copolymers Used in This Study

Sample Name	FMA/MMA mole fractions	% mole FMA			\bar{M}_n	\bar{M}_w	PI	$\bar{X}_w(\text{FMA})$	$\bar{X}_w(\text{MMA})$	\bar{X}_w
		Expected values*	$^1\text{HNMR}$	EDS						
FMA_0	0/100	0.00	0.00	0.00			1.16			
FMA_01	0.01/99.99	0.11	**	0.18	9373	10827	1.16	0	108.1	108.1
FMA_1	0.1/99.9	1.06	1.29	1.50	8657	10054	1.16	0.1	99.8	99.9
FMA_10	1/99	10.45	10.19	10.30	9007	10443	1.16	1.1	98.7	99.7
FMA_20	20/80	20.80	20.42	20.20	9639	11570	1.2+	8.3	71.2	79.5
					10712	12800	0	14.0	53.2	67.2
							1.20			

*Calculated from the actual weights.

**It cannot be detected by $^1\text{HNMR}$

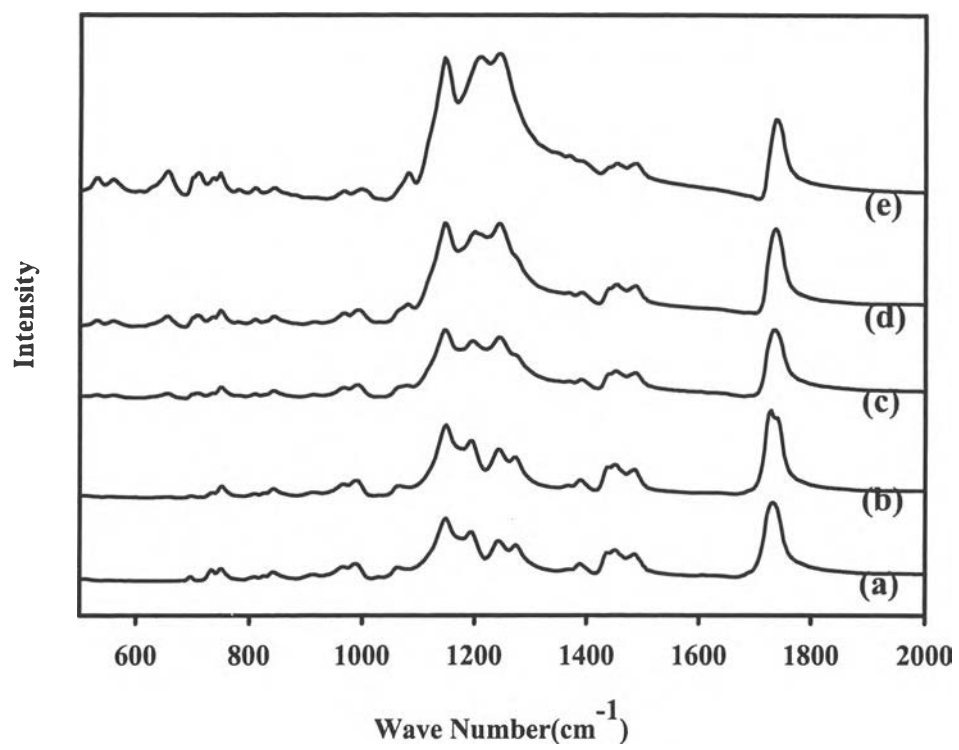


Figure 1

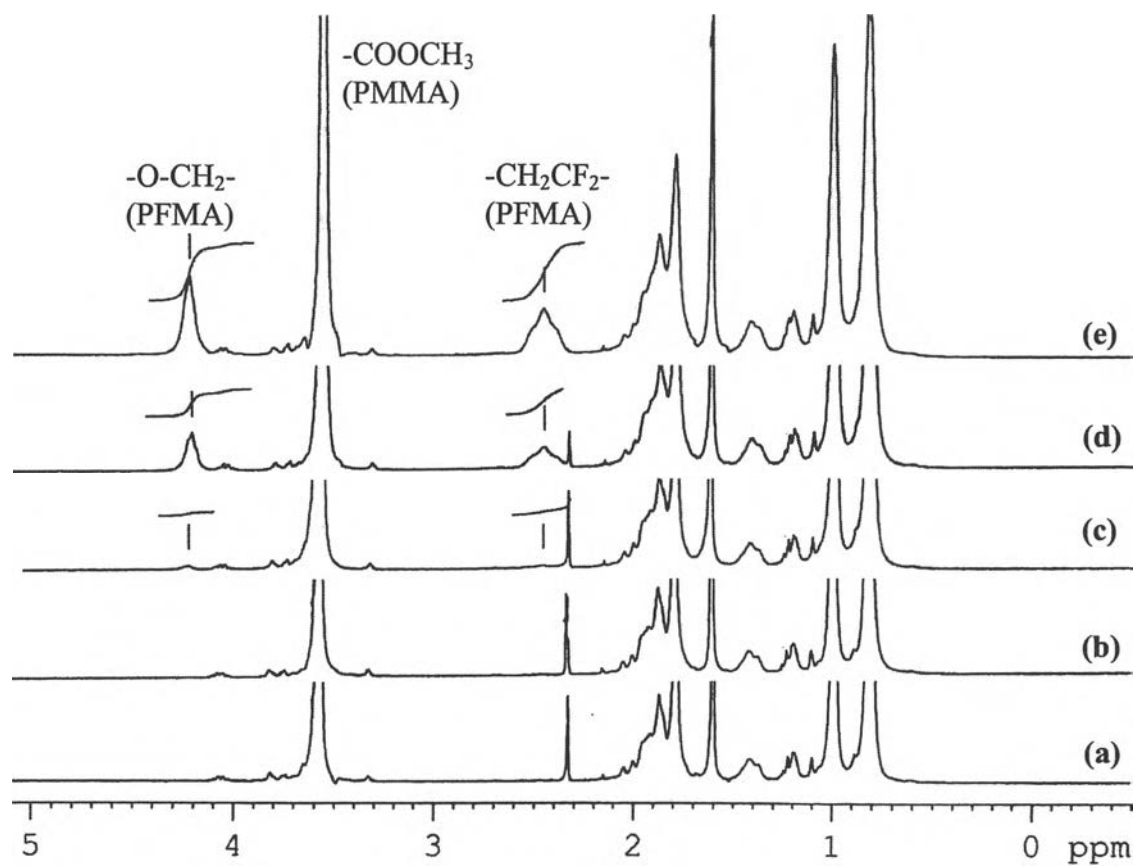


Figure 2

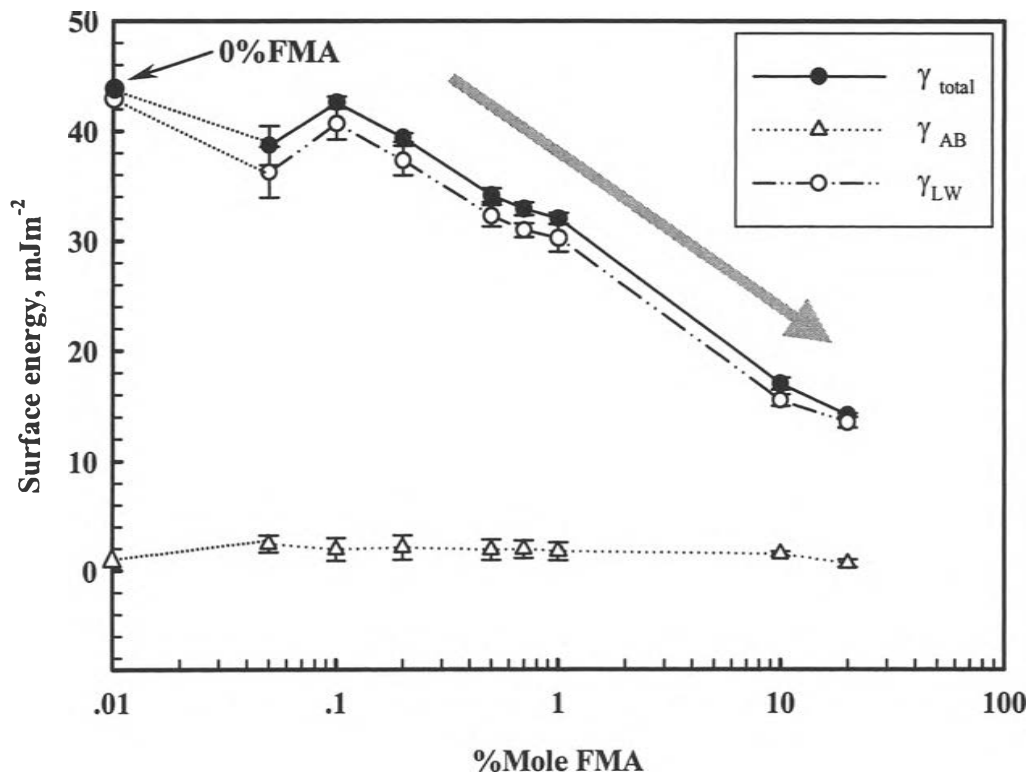


Figure 3

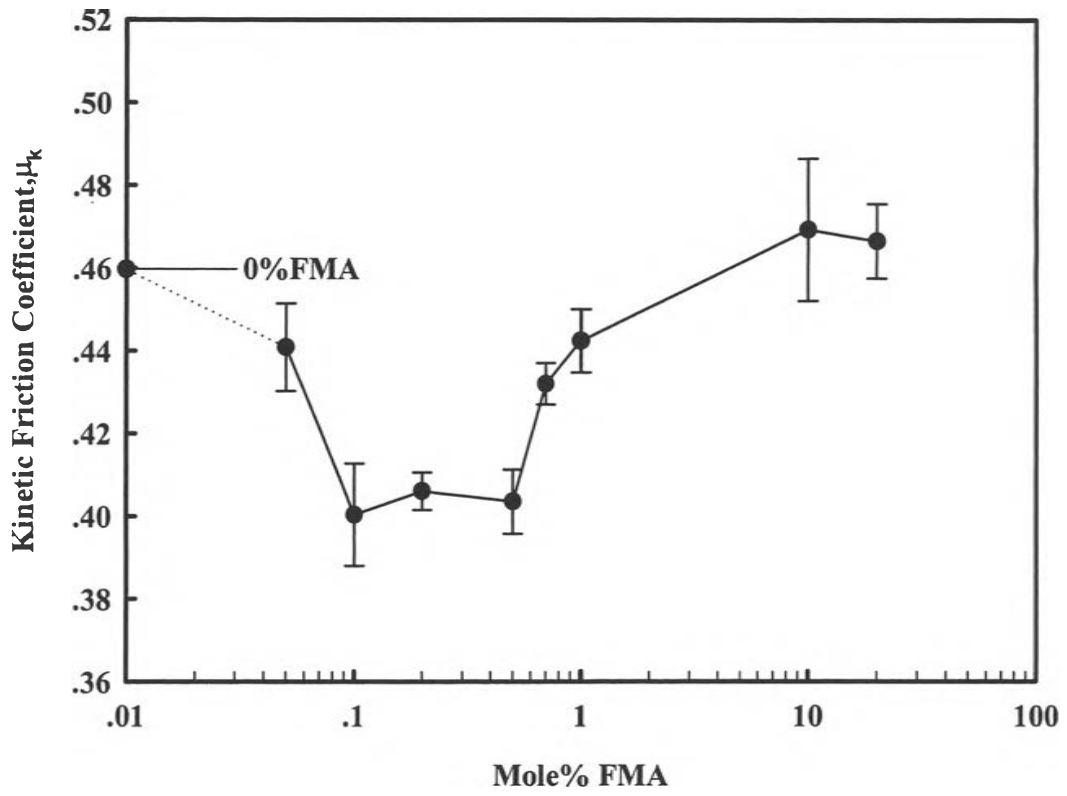
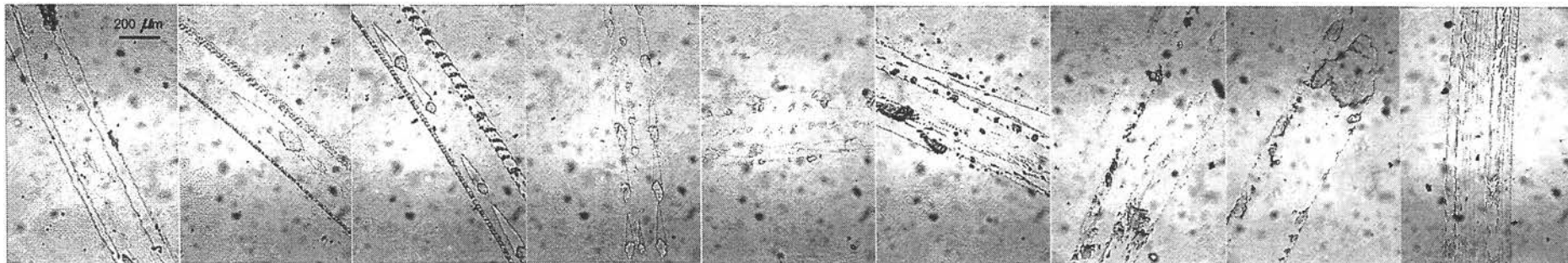
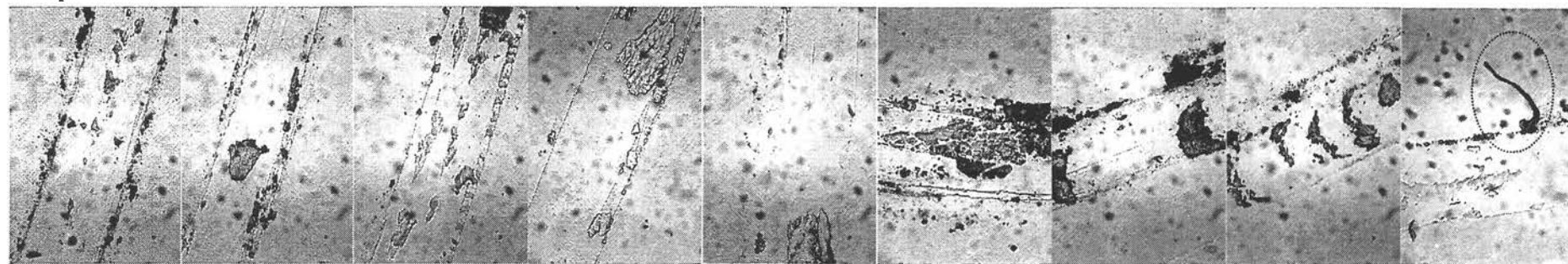


Figure 4

1st pass



10th passes



(a)

(b)

(c)

(d)

(e)

(f)

(g)

(h)

(i)

Figure 5