

Reducing friction and miscibility studies of FEP dispersion/PDMS fluid blends

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Abstract. To develop new polymer blends having reduced friction force of fluorinated ethylene propylene (FEP) dispersion and improved adhesion of polydimethylsiloxane (PDMS) fluid, FEP dispersion was blended with PDMS fluids at different viscosities of 20 cSt and 100 cSt by using solution mixing method. The FEP/PDMS blends were coated on short hollow tubes and examined by penetrating the tubes into the rubber stoppers. It was found that the tubes coated with the blends showed reduced penetration and friction forces and improved adhesion. The tubes coated with the 100 cSt-PDMS blend in the ratio of 5:1.5 demonstrated the penetration and average friction forces as low as 3828 mN and 1524 mN, respectively. The formation of physical blends was characterized and confirmed by FTIR and DSC analyses.

1. Introduction

Fluorinated ethylene propylene (FEP) dispersion are commonly used as non-stick coating in many applications that require friction-reducing property, electrical insulation, biosafety, chemical resistance, and wear resistance [1]. An appropriate choice of the second polymer with specific properties can be blended for a variety of physical and chemical properties. Properties of the blend will depend largely on the degree of compatibility, miscibility of the polymers at the molecular level, and the characteristics of components and compositions [2]. Polydimethylsiloxane (PDMS) fluid is a hydrophobic material used for self-cleaning and lubricant coating in many applications [3]. PDMS fluid readily dissolves in solvent-born paints and, as a result, reduces the surface tension of the coating materials. PDMS fluid is, however, non-curable and able to be removed from the substrate [4]. Commonly, PDMS fluid is blended with organic coating materials such as alkyd, epoxy, and phenolic resins for reduced coefficient of friction of coating materials and improved adhesion and hardness, drying properties and durability of some exterior maintenance coating [5].

To combine the advantages of FEP dispersion and PDMS fluid, the aim of this study was to develop a polymer blend that could reduce friction force of FEP dispersion and improve adhesion of PDMS fluid. Blending of FEP dispersion and two different viscosities of PDMS fluids using a solution mixing technique was investigated. Miscibility of the FEP/PDMS blends was characterized and analyzed using Fourier transform infrared spectroscopy and differential scanning calorimetry.

2. Experimental

2.1. Materials

As-received FEP dispersion was mainly colloidal FEP particles, polyamine imide (PAI), chromium (III) oxide, and solvents of mainly methyl isobutyl ketone (MIBK), N-methyl-2-pyrrolidone (NMP),



ethanol, and aromatic hydrocarbon. FEP dispersion was purchased from DuPont[®]. Chemical structures of FEP, PAI, and PDMS were shown in figure 1. Viscosities of PDMS fluids were 20 cSt and 100 cSt. PDMS fluids were purchased from Dow Corning[®]. Prior to the blending process, the as-received FEP dispersion in the container was rolled at 30 rpm for 30 minutes using a roller mixer. Polymer agglomerates and other contaminants were strained using 100-mesh wire sieves.

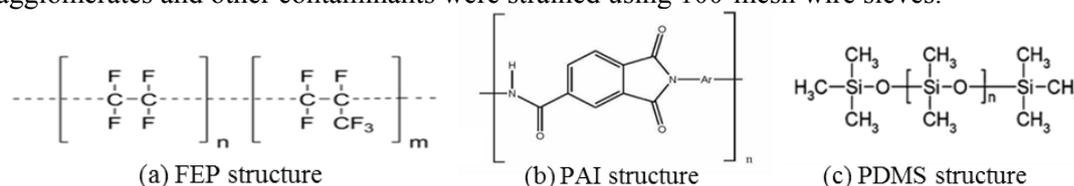


Figure 1. Chemical structure of polymers.

2.2. Coating preparation

Using a solution blending method, the as-receive PDMS fluid was added into the FEP dispersion. The same ratios were applied to the blending of FEP dispersion to PDMS fluids at viscosities of 20 cSt and 100 cSt were 5:1.0 and 5:1.5. The container of mixtures were rolled at 30 rpm for 5 minutes using a roller mixer at room temperature to ensure complete mixing. Pure FEP dispersion, pure PDMS fluid, and the blend solutions were coated on substrates, which were short and small hollow tubes made of 316 stainless steel. The tubes were 4 mm long and had 450 μm diameter. The distal end of the tubes had a bevel of 15 degrees. The substrates were cleaned to remove surface contaminations.

An in-house, dip-spin coating equipment was specifically designed for simultaneously spinning the substrate after withdrawing the substrate from a coating solution. The process parameters for this investigations were as follows. The dipping and withdrawal velocities of the substrate were 25 mm/s. The spinning speed of the substrate was 600 rpm. The immersion time in polymer solution was 10 s. Compressed air pressure for polymer solution inner the tube removal was set 400 kPa. The coating environment was at 25°C and 80% relative humidity. As PDMS fluid is non-curable, this study then set curing temperature and time for pure FEP dispersion and FEP/PDMS blend solutions at 205 \pm 10 °C and for 15 minutes, respectively, following FEP dispersion factsheet. As recommended in PDMS fluid factsheet, the drying temperature was at ambient temperature.

2.3. Method of analysis

2.3.1. Lubricity property testing. The penetration and friction forces of coatings were measured and controlled by using a texture analyzer (Shimadzu UH & AG-IS). Signals of both forces from the 50 N load cell penetration of texture analyzer were recorded using Trapezium software. The tube penetration depth was about 20 mm into the rubber stopper. The tube penetrations were made in a constant speed of 25 mm/s. The tests were conducted on a total of eight types of coatings on the tube samples including uncoated tube, pure FEP dispersion, pure 20 cSt-PDMS fluid, pure 100 cSt-PDMS fluid, FEP/20 cSt-PDMS blends with the ratio of 5:1.0 and 5:1.5, and FEP/100 cSt-PDMS blends with the ratio of 5:1.0 and 5:1.5.

2.3.2. Fourier transforms infrared spectroscopy (FTIR) analysis. In order to investigate the interaction between two polymers, FTIR analysis was carried out. FTIR spectra of functional groups in the polymers could be used to determine main chemical compositions of the samples. For solution characterization, FTIR spectra of the pure PDMS fluids were taken using Perkin Elmer Spectrum One FTIR Spectrometer. The light source was the middle range infrared in the range of 4000-600 cm^{-1} . The wavelength resolution was 4 cm^{-1} . For coating surface characterization, FTIR spectra of pure FEP dispersion and blends of FEP/PDMS with the ratio of 5:1.5 of the PDMS fluid having viscosities of 20 cSt and 100 cSt were taken using Perkin Elmer Spectrum Spotlight FTIR Imaging System. The samples were examined using Micro-ATR technique. The light source was the same range as the above and the wavelength resolution also the same.

2.3.3. Differential scanning calorimetry (DSC) analysis. DSC analysis was carried out in a Mettler Toledo DSC 1. In this study, the samples were the coating of pure FEP dispersion and FEP/PDMS blends with the ratio of 5:1.5 of the PDMS fluid having viscosities of 20 cSt and 100 cSt. The samples of 5.000 mg were scratched from the substrates, sealed in an aluminum pan, and heated from 25°C to 340°C at a heating rate of 10 °C/min to investigate the degree of crystallinity at first heating scan. The samples were cooled down from 340°C to 25°C at a cooling rate of 10°C/min to investigate the cold crystallization temperature (T_{cc}). The samples were then heated up the second time from 25°C to 340°C at a heating rate of 10°C/min. The degree of crystallinity is the percentage of crystallinity content in a semicrystalline substance. The percentage crystallinity of FEP crystalline in the blends were estimated according to the following equation $\%Crystallinity = (\Delta H_f / \Delta H_f^{\circ}) \times 100\%$, where ΔH_f and ΔH_f° are the enthalpy (J/g) of fusion of the blends and the enthalpy of 100% of FEP crystalline with a value of 24.3 J/g [6], respectively.

3. Results and discussion

3.1. Lubricity property testing

For lubricity property, a distal point of the tube was brought to touch the surface of the rubber stopper. The distal point stretched the rubber stopper, then cut into the surface, and began to penetrate into the rubber stopper. Uninterruptedly, the shaft of the tube passed through the original cut into the rubber stopper. The forces that the distal point cut the rubber stopper were termed the penetration force (measured at the maximum force) while the forces required to continue penetrating the shaft of the tube were termed friction force (measured at a stable force after penetration) [7]. The friction forces were measured at penetration depth after 8 mm to a total distance of 20 mm. The results of the penetration and friction forces of all types of coatings on the tube samples are shown in figure 2 and summarized in table 1. The average, minimum, and maximum friction forces were included. From the results, the blends reduced the penetration and the friction forces of pure FEP dispersion and could reduce both forces further with higher viscosity and increasing proportion of PDMS fluids. The FEP/100 cSt-PDMS fluid blends had the lowest penetration and friction forces. As expected, both forces measured from the uncoated tube sample were the highest.

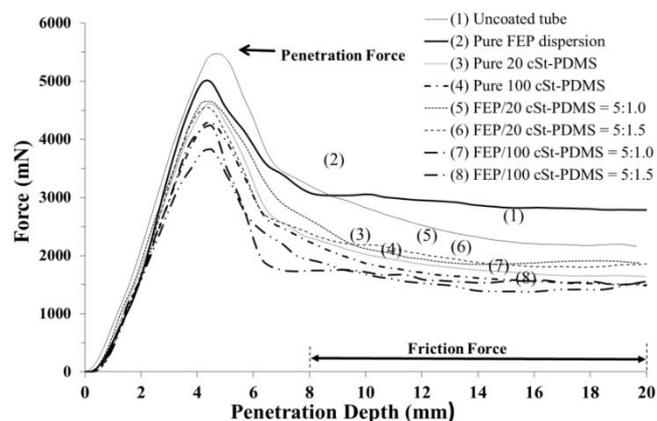


Figure 2. Forces of coating on the tube samples.

Coatings of the pure PDMS fluids on the tube samples were partially detached from the tube shafts during penetrating the rubber stoppers. Possible cause of poor adhesion of coating on the tube shafts was due to the fact that the PDMS fluid was non-curable and did not contain any functional groups that would allow the fluid to attach solidly on the substrate [3]. As a consequence, PDMS could be easily removed from the substrate [5]. Due to some partial detachment, both forces obtained from the

pure PDMS fluids might not represent correct values of the PDMS coatings. On the other hand, the coatings of pure FEP dispersion and the blends remained attached with the tube shafts during penetrating the rubber stoppers. Good adhesion of coatings might be contributed to the dissolution of PDMS fluid in the nonpolar FEP dispersion solvent [8]. PDMS fluid could then be blended well in FEP dispersion. At curing temperature, the solvents in the FEP/PDMS blends evaporate, colloid FEP particles deform, and PAI solution forms crosslink in the film [9]. It might be inferred that PDMS remained dispersed between FEP particles and PAI film. As a result, FEP/PDMS blended coatings possessed reduced penetration and friction forces and improved adhesion. Characterization using FTIR and DSC for understanding the interaction of two polymers were pursued.

Table 1. Penetration force and friction force.

Sample	Penetration force (mN)	Friction Force (mN)	
		Average	Min - Max
1)	5472	2196	1785-3178
2)	5009	2899	2786-3075
3)	4606	1829	1639-2329
4)	4290	1677	1479-2213
5)	4652	2002	1849-2684
6)	4550	1968	1801-2383
7)	4234	1599	1492-1758
8)	3828	1524	1377-1929

3.2. FTIR analysis

Figure 3 showed FTIR spectra indicating the peaks of pure PDMS fluid, pure FEP dispersion, and FEP/PDMS blends. FTIR spectra of pure PDMS fluid showed at 710, 810, 1025, 1096, 1264, and 2964 cm^{-1} . FTIR spectra of pure FEP dispersion showed at 646, 1164, 1222, 1384, 1517, 1725, 2964, and 3339 cm^{-1} . When PDMS was blended into FEP dispersion, FTIR spectra showed at 646, 710, 810, 1025, 1097, 1164, 1222, 1264, 1384, 1517, 1725, 2964, and 3339 cm^{-1} . The FTIR spectra of FEP/PDMS blends did not indicate the existence of other interaction between the component of polymers. Peaks of FEP in FEP/PDMS blend spectra remained at the original positions and had no sign of intensity change. Whereas those of PDMS in the blends showed decreases in transmittance, however, no shift of any peak. The decreases in transmittance of PDMS were in accordance with the ratio of FEP:PDMS, which was on the less side of 5:1.5. The results indicated the formation of physical blends.

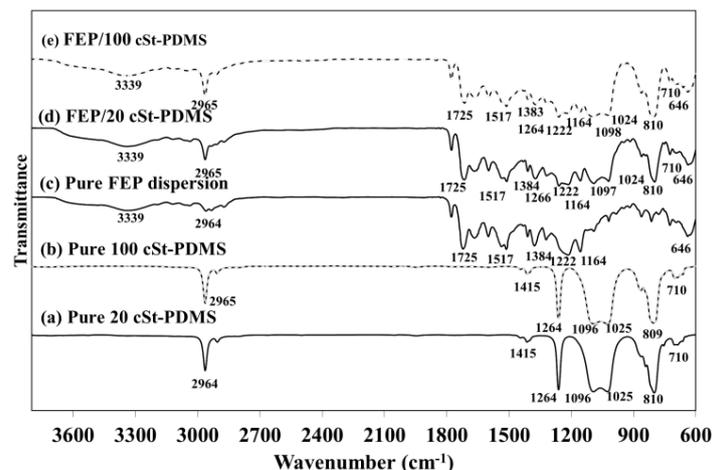


Figure 3. FTIR spectra of pure PDMS fluid, pure FEP dispersion, and FEP/PDMS (5:1.5) blends.

3.3. DSC analysis

Enthalpy of fusion and %crystallinity of FEP crystal of all samples were shown in figure 4. The crystallization temperatures of FEP and FEP/PDMS blends were about 237°C. The %crystallinities were estimated by using the equation on the peaks obtained from the first scans. The %crystallinities were decreased when the PDMS fluids were blended into the FEP dispersion. PDMS molecular chains might entangle with FEP. From the PDMS factsheet, the polymer chains of 100 cSt-PDMS fluid were longer than those of 20 cSt-PDMS fluid [4]. It was implied that the shorter chains of 20 cSt-PDMS fluid could disturb FEP in molecular level and result in a lesser amount of crystallization. In addition, the much smaller peaks observed on the second heating scans of the blends might be affected by insufficient crystallization during cooling from the first scans. Equivalent to annealing the samples, the curing at 205 ± 10 °C for 15 minutes, as mentioned in section 2.2, that was 30 degrees lower than the crystallization temperatures also allowed the FEP crystals to grow and could result in higher amount of crystallinity. Higher %crystallinity could enhance hardness and adhesion of the coatings [10]. With DSC results, it could be indicated that the PDMS fluid had no interaction with the pure FEP dispersion.

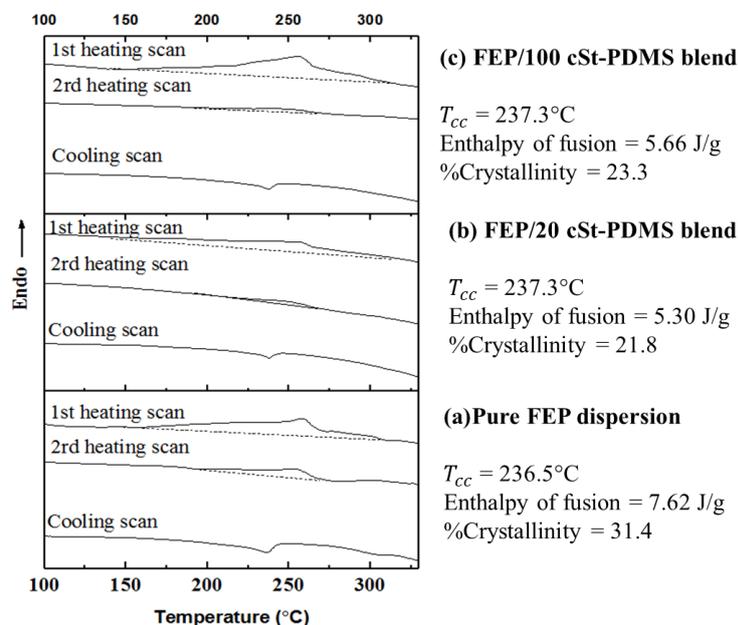


Figure 4. DSC results of pure FEP dispersion and FEP/PDMS (5:1.5) blends.

4. Conclusion

This study was to develop new FEP/PDMS blends. Several types of FEP/PDMS blends were coated on short hollow tubes and examined by penetrating the tubes into the rubber stoppers. Their lubricity properties, as a result, were compared with the tubes coated with pure FEP dispersion and pure PDMS fluid. The blends reduced penetration and friction forces and demonstrated improved adhesion. The samples coated with the blend at PDMS viscosity of 100 cSt in the ratio of 5:1.5 possessed the lowest penetration and friction forces, which were less than those of pure FEP dispersion. Miscibility of FEP/PDMS blend was observed with the formation of physical blends characterized and confirmed by FTIR and DSC analyses. This study was limited to lubricity properties testing. Other properties testing are of interested for coating application. Future work may include different the viscosity of PDMS and different ratio of blends.

Acknowledgements

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