

Fluoropolymer addition to an epoxy: phase inversion and tribological properties

Witold Brostow^{a,*}, Patrick E. Cassidy^b, Haley E. Hagg^a,
Magdalena Jaklewicz^a, Pablo E. Montemartini^{a,c}

^aDepartment of Materials Science and Chemistry, Laboratory of Polymers and Composites (LAPOM), University of North Texas, P.O. Box 305310, Denton, TX 76203-5310, USA

^bDepartment of Chemistry, Southwest Texas State University, San Marcos, TX 78666, USA

^cInstitute of Materials Science and Technology (INTEMA), National Research Council (CONICET), J.B. Justo 4302, 7600 Mar del Plata, Argentina

Received 16 November 2000; received in revised form 3 April 2001; accepted 6 April 2001

Abstract

Morphology, elastic modulus, static and dynamic friction of a commercial epoxy resin + fluorinated poly(aryl ether ketone) (12F-PEK) system have been studied. The system was cured at 24 and 70°C. We have obtained significant friction lowering, namely 30% less than the value for the plain epoxy at the 12F-PEK concentration of only 10 wt% after curing at 24°C. By contrast, after curing at 70°C, increases in both static and dynamic friction are observed. At 24°C, the SEM analysis shows that a phase separation starts at 10% 12F-PEK; completely phase-inverted morphology was found above 30% of the fluoropolymer. The system cured at 70°C has more compact structure and the phase separation process is shifted towards higher fluoropolymer concentrations. We explain the phase inversion at low fluoropolymer concentrations by the low free surface energy of 12F-PEK; as a consequence, we observe its accumulation on the surfaces of the samples. The samples with high 12F-PEK concentrations exhibit elevated elastic moduli and are highly ductile. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Fluoropolymers; Epoxy resins; Friction

1. Introduction

While automotive, aviation and other industries are gradually switching from metallic parts to polymeric ones, our understanding of friction involving polymer surfaces is hardly sufficient. This situation is in contrast to tribology of metals and alloys which is well developed [1]. Another confirmation of the status of polymer tribology comes from the book edited by Rohatgi [2] on friction and wear in composites. The book deals primarily with metal matrix composites; an exceptional chapter on carbon–fiber reinforced polymers proves that the presence of fibers lowers the wear resistance of the neat polymers.

Among key classes of polymeric materials, we focus on those based on epoxy resins. Their use is well established in a number of industries, including marine, pipe, can and drum coatings and also as adhesives, electric laminates, printed circuit boards (PCBs) and more. Coatings should be designed to impart favorable mechanical properties —

including low friction, resistance to scratch and abrasion, as well as specific chemical, electrical, magnetic and optical properties on various substrates. Scratch resistance as high as possible is needed to avoid damages that ruin not only the appearance but above all the function of a coating. Thus, tribology should play a primordial role in coatings design. Reducing friction is not only a goal by itself but also a way to improve scratch resistance [3].

Chemical modification of epoxy resins is a possible approach in order to fulfill particular application requirements. One of us has proposed the use of oligomers containing peroxy groups as epoxy modifiers in order to improve adhesion [4–6]. Blending is another alternative. Systems of the type epoxy + high performance thermoplastics, for instance, polyetherimides, polysulfones and poly(methyl methacrylate), have been reported in the literature [7–11] — largely created to achieve toughening. Fluorinated polymers are known as low friction materials; this property is explained by their low surface energies. The problem is not quite so simple, polytetrafluoroethylene (PTFE) has received much attention because of its low friction behavior; however, its wear rate is high, limiting its application range. Moreover, we would like to continue to use epoxies

* Corresponding author. Tel.: +1-940-565-4358; fax: +1-940-565-4824.

E-mail addresses: brostow@unt.edu (W. Brostow), pc03@swt.edu (P.E. Cassidy), pem0005@unt.edu (P.E. Montemartini).

by modifying them rather than replacing them by vastly different polymers. This situation behooves us to find other options for creating low friction epoxy-based materials.

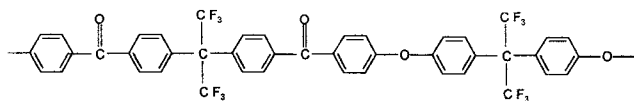
One of us [12] has modified poly(aryl ether ketones) (PEKs) by adding hexafluoroisopropylidene (HFIP) groups into the main chain. Attaching fluorinated units as HFIP, one can obtain highly ordered surface structures with low surface energies [13]. Moreover, HFIP groups also increase solubility of PEK with desirable electrical properties, and improve thermal stability [14]. This is important since un-fluorinated PEK exhibits low solubility — what affects its applications.

In this paper, we combine a commercial epoxy with a fully fluorinated PEK (12F-PEK), cure the epoxy, and investigate the morphology and frictional properties of the resulting materials. Since the epoxy is the inexpensive component of material, we start from the pure epoxy side and gradually add 12F-PEK. Needless to say, the objective is the development of low friction epoxies by the fluoropolymer addition.

2. Experimental

2.1. Materials

12F-PEK was synthesized in the Department of Chemistry at Southwest Texas State University. Its chemical formula is:



It is soluble in most common solvents; its dielectric constant at 10 GHz is 2.4 [12]; its thermophysical characteristics are reported below. The epoxy used was a diglycidyl ether of bisphenol A resin (Shell Chemicals, EPON™ 828) cured with an aliphatic amine (triethylenetetramine (TETA), Shell Chemicals — EPI-CURE™ 3234).

In order to obtain a blend at the molecular level, a common solvent was used to mix the epoxy resin with 12F-PEK. The fluoropolymer was dissolved in acetone (20 ml acetone/1 g 12F-PEK) and then the epoxy resin was added. The mixture was completely miscible. Samples containing from 5 to 50% 12F-PEK by weight in the final system, epoxy + 12F-PEK + curing agent, were studied. The curing agent was then added (13 g curing agent/100 g epoxy). According to the producer specifications, one half of the mixture was cured at 70°C during 3 h while the other half was cured at 24°C in order to simulate room temperature curing applications. The samples were stored at 24°C. All tests were performed at least 7 days after preparing the samples.

2.2. Differential scanning calorimetry

DSC measurements were performed using a Perkin–Elmer DSC-7 calorimeter. The temperature range investigated was from 20 to 200°C at the heating rate of 10 K/min in the presence of nitrogen (20 ml/min flow). After the first run, samples were cooled to the room temperature and a second scan used to determine the glass transition temperature T_g and if possible the melting point.

2.3. Scanning electron microscopy

SEM was used to study the morphology of the samples. Natural fracture surfaces were examined after coating with gold by vapor deposition using vacuum sputtering. The specimens were investigated in a JEOL JSM-T300 scanning microscope.

2.4. Mechanical testing

The modulus of elasticity was evaluated by three-point bending tests. The Systems Integration Technology (SINTECH) machine and the Perkin–Elmer DMA-7 were used. Samples with nominal dimensions of 18 mm × 9 mm × 0.7 mm were tested with a 15 mm support span at the rate of 0.1 mm/min. Flexural modulus was calculated from initial linear parts of the stress versus strain curves. All tests were conducted at 24°C.

2.5. Friction testing

The SINTECH machine was used to perform the friction tests. A 4.5 kg load cell and a sled with the nominal weight of 700 g were used. The testing speed was 150 mm/min. A polished stainless steel surface was used. Resistances to the initial and then continuous movement were measured to determine, respectively, static and dynamic friction (often called friction coefficients). The results reported here are the averages each of five tests conducted at 24°C.

3. Glass transition temperatures

The glass transition temperatures T_g determined by DSC for the plain epoxy and pure 12F-PEK are 92 and 186°C, respectively. The T_g values for the epoxy + 12F-PEK blends cured at 24°C are shown in Fig. 1. Up to 20% 12F-PEK, the samples show a single T_g . Above that concentration, a second T_g appears at a higher temperature. While X-ray diffraction shows semicrystallinity of 12F-PEK [14], the melting point was not observed in DSC.

We know that the occurrence of two glass transition temperatures indicates the presence of at least two phases within the samples. The lower T_g corresponds to the transition of the epoxy-rich phase. The increase in T_g up to 20% is related to the presence of 12F-PEK *dissolved* in an epoxy-rich phase. At 30%, the second T_g shows the presence of a second phase — rich in 12F-PEK. While two phases may

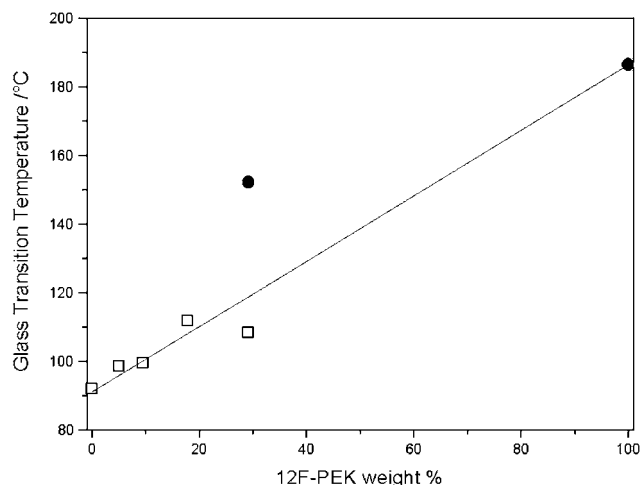


Fig. 1. Glass transition temperatures for the blends as a function of 12F-PEK concentration.

exist also below 30% 12F-PEK (see Section 4 below), this is not detectable using the DSC.

4. Morphology

The images from the SEM in Figs. 2 and 3 show the morphology of the samples cured at 24 and 70°C, respectively. The structure of the plain epoxy which appears in Fig. 2a serves as the reference for comparison with the other samples.

The 5% 12F-PEK sample (cured at 24°C) is homogeneous throughout the bulk of the material (Fig. 2b). Increased magnification shows a high concentration of 12F-PEK at the surface — as better seen in Fig. 2c. This tendency of 12F-PEK to occupy the free surface can also be seen in Fig. 3b. The 12F-PEK component seeks the free surface due to the low surface energy of the fluoropolymer. Because of the low surface energy, as the 12F-PEK content increases, phase separation between 12F-PEK and epoxy is evident and *phase inversion* begins in small domains, so that the fluoropolymer-rich phase becomes the matrix. Typically, the phase inversion occurs between 40 and 60% of the added component, as noted, for instance, by Földes et al. [15]. In our case, we observe an inversion of the phase structure in small domains even at concentrations as low as 10% 12F-PEK. This phase inversion is clear in the 12F-PEK-rich region of Fig. 2d. Above 10% 12F-PEK, the domains of phase inversion become wider spread (Fig. 2d). Once 30% 12F-PEK is reached, the entire sample is composed of the phase-inverted structure (Fig. 2e). Similar morphologies have been reported by Hedrick [8] and others [9,11] in epoxy + reactively terminated poly(ether sulfone) blends. A paper from McGrath and co-workers [16] on polyether polyurethanes modified with polydimethylsiloxane (PDMS) reports migration of PDMS to the air–polymer surface and formation of a predominantly PDMS-rich

surface. The migration occurs already around 15% of PDMS and is explained by the low surface energy of the added component. While our system is different, there is a similarity in the early phase inversion. We also note the conclusion of Ho et al. [17] on the basis of their studies of polyether or ester-based polyurethanes that mechanical and other properties are strongly dependent on the phase-separated structures.

The samples cured at 70°C show similar morphology — but *shifted to higher 12F-PEK contents*. The phase separation process competes here with the chemical crosslinking reaction between the epoxy and the curing agent. Due to the temperature increase, at 70°C, the crosslinking reaction is favored and occurs faster. This causes phase separation of the 12F-PEK and epoxy-rich phases to occur only at higher 12F-PEK contents than at 24°C. No signals of either phase inversion or higher fluoropolymer concentrations are found close to the surface in the samples with up to 10% 12F-PEK (Fig. 3a). At 20% 12F-PEK, differences are found between the free surface and the bulk (Fig. 3b). This is another demonstration of the low surface energy of 12F-PEK. The phase inverted domains of the samples containing higher 12F-PEK percentage show a different structure in comparison with the samples cured at 24°C. This difference is also due to the increased rate of the curing reaction. The faster the chemical reaction, the shorter the time available for the phase separation process to occur. Despite the fact that the final network structures are necessarily similar, the phase inversion does appear in the samples. At the same time, from the structure shown in Fig. 3c, it is evident that 12F-PEK is not separated completely from the epoxy-rich domains.

5. Flexural modulus

Fig. 4 shows the flexural modulae of the samples as measured by three-point bending in the DMA and the SINTECH machine. Results from the two sets of equipment can be considered together since identical samples produced the same results in both machines. Consider the concentration dependence of the modulae for the samples cured at 24°C; a minimum occurs below 10% 12F-PEK. Adding 12F-PEK in small amounts *disrupts the epoxy network*, thereby decreasing the stiffness. After the second phase is formed, that disruption of the matrix phase is largely eliminated; therefore, the added component goes into ‘its own’ phase and the epoxy phase becomes more similar to the pure epoxy. This is reflected at concentrations between 12% 12F-PEK or so until 30%. The modulus stays constant and close to that for the pure epoxy. Above 30% 12F-PEK, the phase inversion is complete and the increasing concentration of the fluoropolymer manifests itself in a modulus increase.

The samples cured as 70°C show qualitatively similar behavior. Again, there is a constant modulus from approximately 12% of the fluoropolymer up to 30% or so. However,

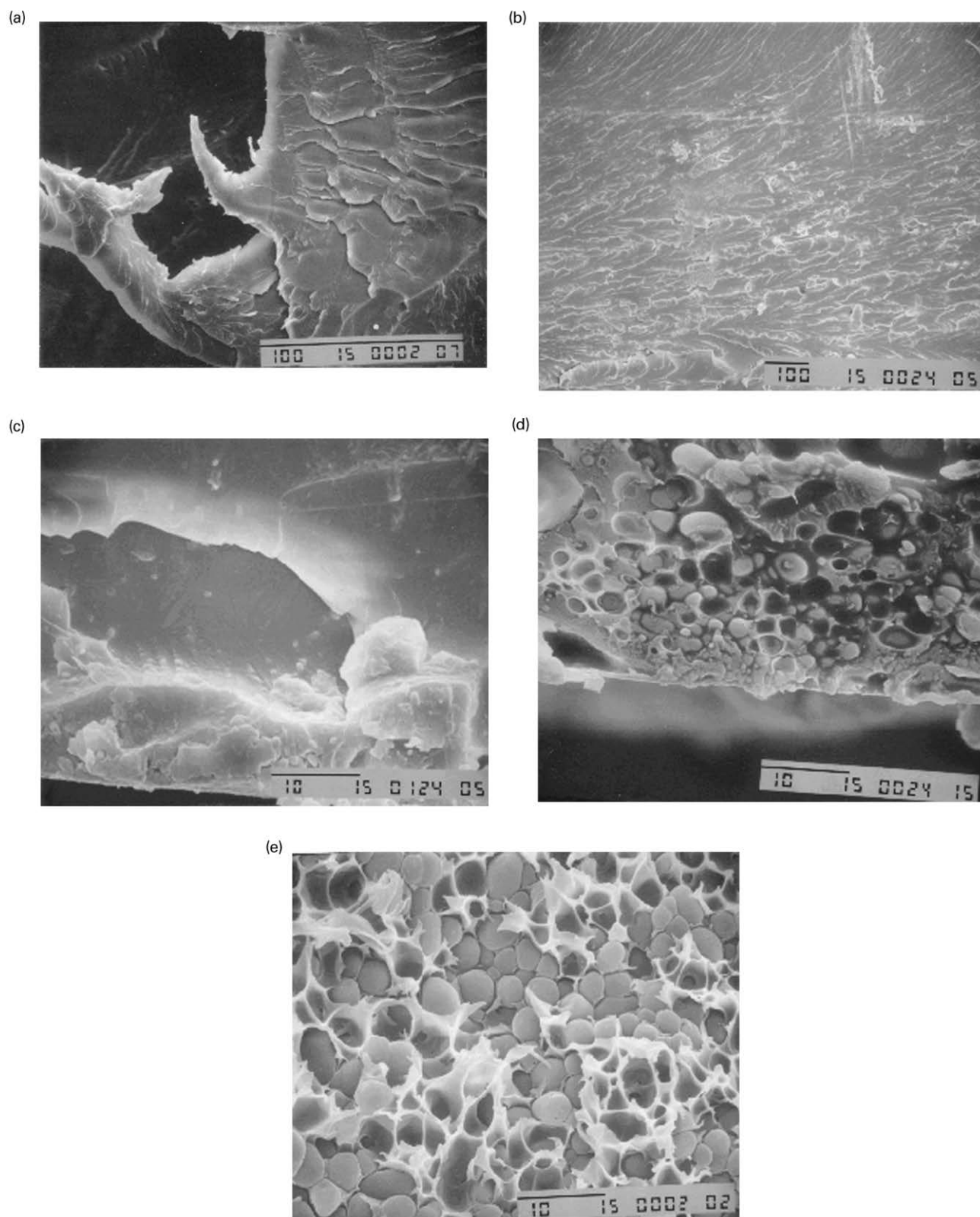


Fig. 2. Scanning electron micrographs of blends cured at 24°C with different 12F-PEK contents: (a) 0%; (b) 5%; (c) 5%; (d) 15%; (e) 30%.

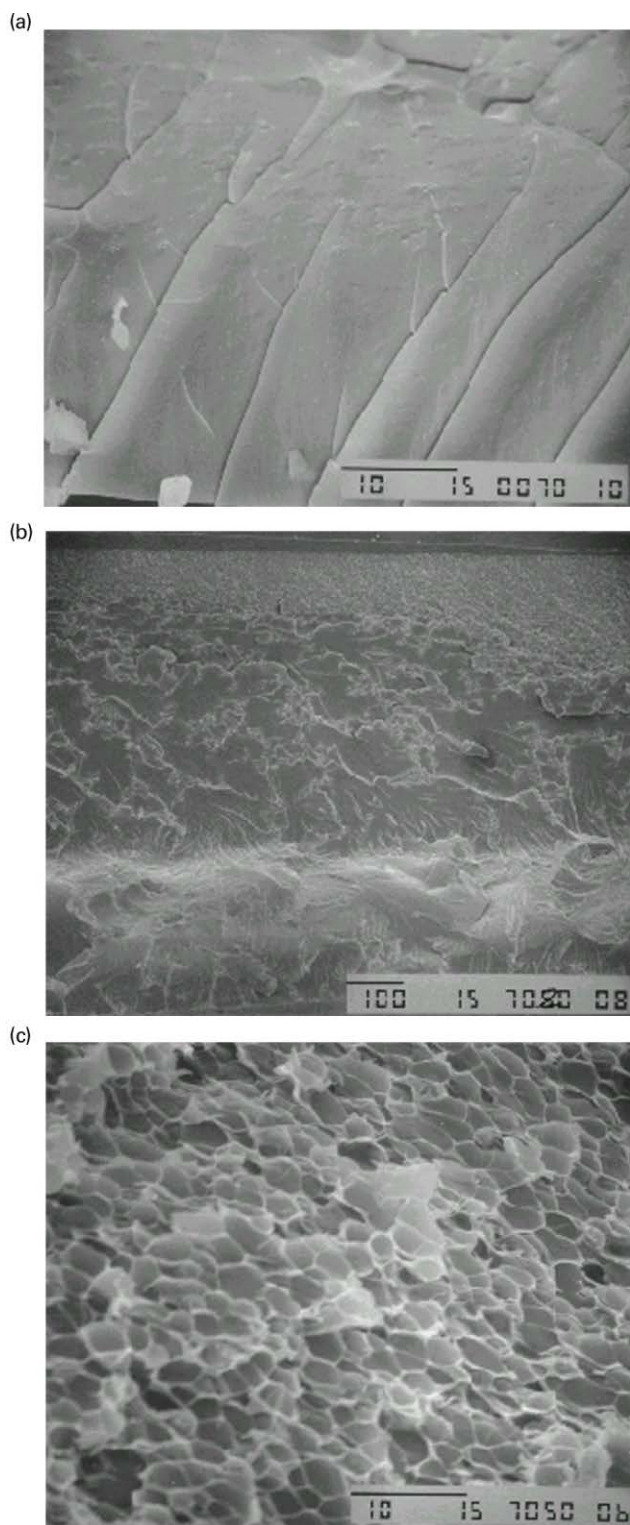


Fig. 3. Scanning electron micrographs of blends cured at 70°C with different 12F-PEK contents: (a) 10%; (b) 20%; (c) 30%.

flexural moduli are 20% higher in comparison with those of the samples cured at 24°C. The modulus increase is explained by the sample morphology. The compactness of the samples cured at 70°C increases the stiffness of those

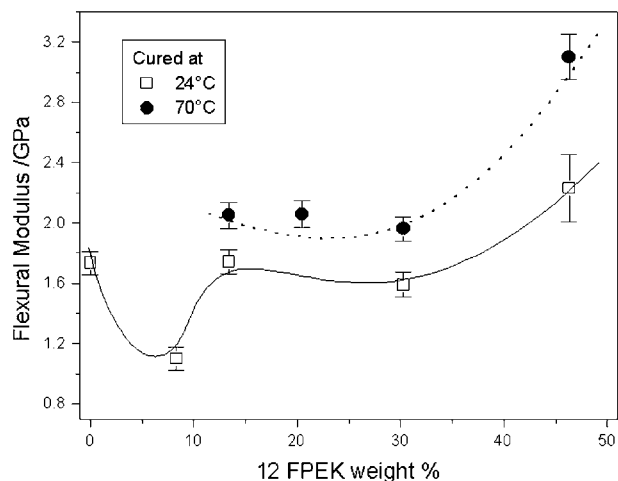


Fig. 4. Flexural modulus for the blends as a function of 12F-PEK concentration.

blends. Thus, we have in these systems the important capability to vary the mechanical performance by changing the curing temperature.

6. Friction properties

Consider here also the property variation with concentration. The static friction of the samples cured at 24°C decreases by adding as little as 5% 12F-PEK and remains practically constant above 10% 12F-PEK (Fig. 5). While flexural modulus was explained by considering the bulk structure of the samples, friction behavior depends on the surface morphology. As Fig. 2 shows, in the samples cured at 24°C, the free surface contains a higher than average 12F-PEK content. Adding 5% 12F-PEK reduces static friction because of the high concentration of the low friction component present at the surface. Further addition of 12F-PEK modifies the bulk structure, but not the surface. Therefore, static friction stays constant beyond 10% 12F-PEK. The

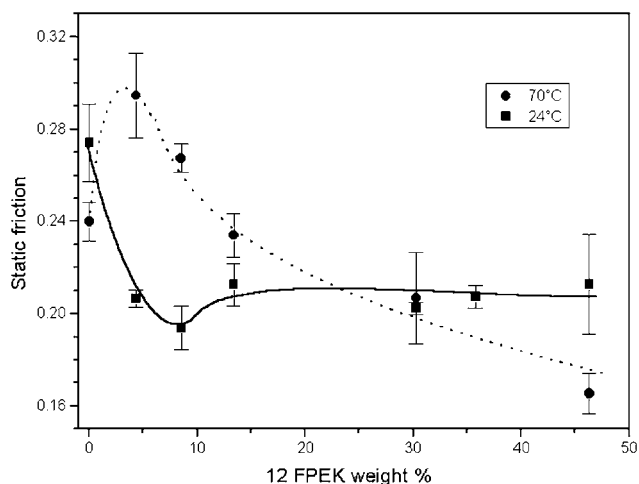


Fig. 5. Static friction for the blends as a function of 12F-PEK concentration.

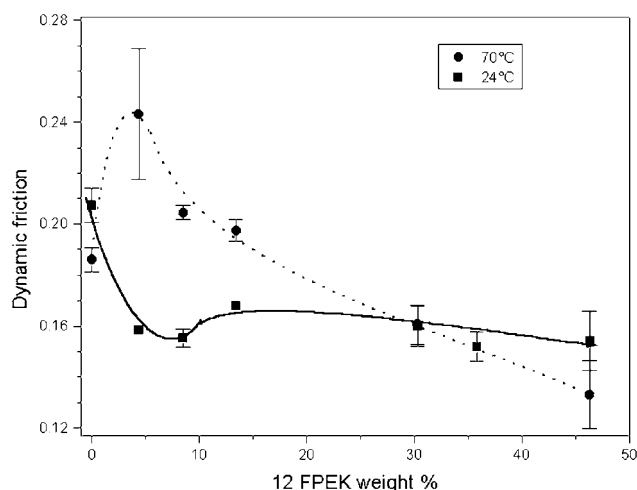


Fig. 6. Dynamic friction for the blends as a function of 12F-PEK concentration.

static friction was reduced as much as 30% from that of the plain epoxy. Rao [18] has reported similar results adding 20% polytetrafluoroethylene into polyoxymethylene and polyamide 66.

As discussed before, the samples with up to 15% 12F-PEK and cured at 70°C do not contain 12F-PEK concentrated at the surface. Small amounts of 12F-PEK present at the surface represent only a disruption to the pure epoxy surface. Therefore, the friction first goes up for 5 and 10% of the fluoropolymer. We recall the discussion in Section 5 about lowering of the modulus by 10% 12F-PEK. Similarly here, 5 or 10% of the fluoropolymer are sufficient for a significant effect — this time on friction. In the samples with 20% or greater 12F-PEK, even though the fluoropolymer is not preferentially going towards the surface, an increase in its overall concentration manifests itself and a reduction in static friction is observed.

For the blends cured at both 24 and 70°C, the dynamic friction is higher than the static. Both static and dynamic friction follow the trends explained above (Fig. 6).

7. Concluding remarks

The microstructures of epoxy + 12F-PEK blends have been characterized and explained. At low concentrations, we have obtained homogeneous systems. Above 10% 12F-PEK, phase separation was detected. The second phase shows epoxy-rich inclusions surrounded by the fluoropolymer-rich phase. The second phase growth reaches a complete phase inverted morphology at 30% 12F-PEK. The low free surface energy of 12F-PEK is responsible for the phase inversion in the samples; phase separation is reflected in the appearance of two glass transition temperatures. An increase in the curing temperatures produces a more compact structure but at low 12F-PEK

concentrations no differences are found between the surface and the bulk.

Even at fluoropolymer concentrations as low as 10% 12F-PEK, its content increases at the free surface producing a friction reduction of 30% in samples cure at 24°C. Thus, we have achieved our main objective defined in Section 1. Afterwards, with further addition of 12F-PEK, friction properties remain practically constant. This is especially pertinent for coating applications where the adhesion properties of the epoxy in contact with the substrate are important — while 12F-PEK concentrates on the top polymer–air free surface. Thus, each constituent performs a different key function and at a different location.

Since the samples cured at 70°C show first a friction increase upon addition of 12F-PEK, the curing temperature is of the paramount importance. This provides us indeed with a capability to manipulate the properties.

Another issue raised in Section 1 is that of wear. In a subsequent paper [19], we shall report a study of scratch resistance of the same materials as investigated here — determined under either constant or progressive loads, at the time of the passage of the indenter as well as after subsequent healing or scratch recovery. The present work is a part of a larger program aimed at creating surfaces with improved tribological properties by methods *other than* using external lubricants [20].

Acknowledgements

Support for this research has been provided by the State of Texas Advanced Research Program, Austin (Project #003594-0075-1999). One of us (P.E.M.) has also received support from the Consejo Nacional de Investigaciones Cientificas y Tecnicas (CONICET), Buenos Aires. Discussions with Dr Anatoly Y. Goldman, Alcoa CSI, Crawfordsville, IN, are appreciated.

References

- [1] Rabinowicz E. Friction and wear of materials. 2nd ed. New York: Wiley, 1995.
- [2] Rohatgi PK, editor. Friction and wear technology for advanced composite materials Materials Parks, OH: ASM International, 1994.
- [3] Bles MH, Winkelman GB, Balkenede AB, den Toonder JMJ. Thin Solid Films 2000;359:1.
- [4] Bazylak L, Bratychak M, Brostow W. Mater Res Innovat 1999;3:132.
- [5] Bratychak M, Brostow W. Polym Engng Sci 1999;39:1541.
- [6] Bazylak L, Bratychak M, Brostow W. Mater Res Innovat 2000;3:218.
- [7] Oyanguren PA, Riccardi CC, Williams RJJ, Mondragon IJ. Polym Sci Phys 1998;36:1349.
- [8] Hedrick JL, Yilgor I, Jurek M, Hedrick JC, Wilkes GL, McGrath JE. Polymer 1991;32(11):2020.
- [9] Woo EM, Bravenec LD, Seferis JC. Polym Engng Sci 1994;34:1664.
- [10] Woo EM, Wu MN. Polymer 1996;37:2485.
- [11] Kinloch AJ, Yuen ML, Denkins SD. J Mater Sci 1994;29:3781.

- [12] Cassidy PE, Aminabhavi TM, Farley JM. *J Macromol Sci, Rev Chem Phys* 1989;C29:365.
- [13] Hopken J, Moller M. *Macromolecules* 1992;25:1461.
- [14] Tullos GL, Cassidy PE, Clair AK. *Macromolecules* 1991;24:6059.
- [15] Földes E, Fekete E, Karasz FE, Pukanszky B. *Polymer* 2000;41:975.
- [16] Wang LF, Ji Q, Glass TE, Ward TC, McGrath JE, Muggli M, Burns G, Sorathia U. *Polymer* 2000;41:5083.
- [17] Ho T, Wynne KJ, Nissan RA. *Macromolecules* 1993;26:7029.
- [18] Rao M, Hooke CJ, Kukureka SN, Liao P, Chen YK. *Polym Engng Sci* 1998;38:1946.
- [19] Brostow W, Bujard B, Cassidy PE, Hagg HE, Montemartini PE. *Mater Res Innovat* 2001, to be published.
- [20] Brostow W, Castaño VM, Huanosta A, de Icaza A, Nicho ME, Saniger JM. *Mater Res Innovat* 1999;3:85.