Toughening of a High-Temperature Polymer by the Sol–Gel, *In Situ* Generation of a Rubbery Silica–Siloxane Phase

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ABSTRACT: A phenyl ether phenyl phosphate polymer, specifically poly(biphenyl ether triphenyl phosphate), was modified to increase its tractability and to improve its toughness. The first goal was achieved by increasing its solubility by sulfonation of the chain, and the second, by the *in situ* generation of a rubbery phase. This phase was generated by a modification of the usual sol–gel reaction (which usually generates a hard silicalike material by the hydrolysis of a tetrafunctional organosilicate). In this case, a difunctional silicate was included, thus introducing some softening organic groups into the dispersed phase. A bonding agent, *N,N*-diethylaminopropyltrimethoxysilane, was also included to improve the bonding between the two phases in this organic–inorganic composite. As expected, the glass transition temperatures generally increased slightly upon sulfonation, but decreased significantly upon introduction of the rubbery phase. Most important, the toughness of the polymer was successfully increased with, for example, only 8 wt % of the rubbery phase, quadrupling extensibility to 20 % and markedly increasing the toughness. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 79: 2326–2330, 2001

Key words: high-temperature polymers; poly(biphenyl ether triphenyl phosphate); sol–gel process; sulfonation; elongation; ultimate properties; toughening; *N,N*-diethyl-aminopropyltrimethoxysilane

INTRODUCTION

Poly(arylene ether)s exhibit exceptional thermal stability and mechanical properties, largely because of the aromatic groups in the chain backbone. As a result, both researchers and manufacturers have been showing increasing interest in this class of polymers.[1] They have already found a wide range of applications in industry, especially in the aerospace field, but few poly(arylene ether)s have reached wide commercial usage due to their poor solubility and processibility. In recent years, considerable efforts have been devoted to modifying this class of polymers to improve their processibility without unacceptable losses in their thermal stabilities and mechanical properties.

One way of improving the processibility of such polymers is to increase their solubility in acceptable solvents, for example, by chemically modifying their backbones by sulfonation. The now-standard method for toughening polymers, in general, is by the introduction of a dispersed rubbery phase, and various types of elastomers have now
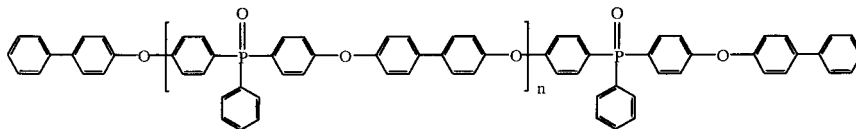
Scheme 1 PBETP.

been used in both thermoplastics and thermosets.[2–4] Diene polymers such as natural rubber and copolymers involving monomers such as butadiene are frequently used for this purpose. Their unsaturated structures can be an advantage with regard to reactions providing bonding between the dispersed phase and the host matrix, but can also cause losses in stability (particularly at higher temperatures). For this reason, there has been considerable interest in using totally saturated elastomers.[5,6] An important elastomer of this type is polydimethylsiloxane (PDMS) [—Si(CH$_3$)$_2$O—], which is the most important and by far the most widely used siloxane polymer. It has long been known to be a high-performance material because of its extremely low glass transition temperature and high thermal stability compared with those of other elastomers.

As has been done for many years, such phases can be dispersed into a polymer by mechanically blending,[7,8] but this process is time-consuming and energy-intensive. Moreover, it is very difficult to control the structure of the resulting composite material. There is frequently, for example, inhomogeneous dispersions of the phases, giving less than optimal improvements in the mechanical properties.

For these reasons, a novel technique was developed for precipitating ceramiclike materials into polymers, particularly elastomers such as PDMS.[7–10] The most important reaction for doing this is the acid- or base-catalyzed hydrolysis and condensation of tetraethoxysilane (TEOS) [Si(OC$_2$H$_5$)$_4$] or tetramethoxysilane (TMOS). This method, called the "sol–gel" process,[9,11,12] is illustrated by the following equation:

$$Si(OC_2H_5)_4 + 2H_2O \rightarrow SiO_2 + 4C_2H_5OH \quad (1)$$
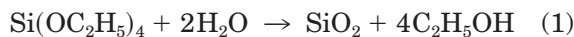
Obviously, the phase thus introduced is generally very hard, and its primary advantage with regard to the mechanical properties is increasing the modulus and ultimate strength. A somewhat softer dispersed phase should be more effective for increasing toughness (energy required for rupture). This can be accomplished in the sol–gel

approach by partially replacing the tetrafunctional organosilicate (TEOS or TMOS) by a difunctional one, such as dimethyldimethoxysilane (DMDMS). In this way, methyl groups should be incorporated into the otherwise rigid dispersed phase, giving it at least some rubbery character. The extent to which this would occur would obviously depend on the composition, specifically increasing with increase in the molar ratio [DMDMS]/[TEOS].

Poly(biphenyl ether triphenyl phosphate) (PBETP) is a type of poly(arylene ether), which is one of the classes of high-temperature polymers of interest to the U.S. Air Force. Its structure is shown in Scheme 1. Compared with other poly(arylene ether)s, it has much improved nonflammability and oxygen plasma resistance due to the presence of the phosphate moieties in its backbone.[13] In the present study, PBETP was toughened by a rubbery phase *in situ* precipitated as described above. This is an extension of previous work on high-temperature polymers of Air Force interest, in which either silica-type phases were introduced to improve mechanical properties such as moduli and ultimate strengths[14–17] or rubbery
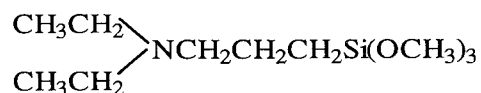
DAPMS
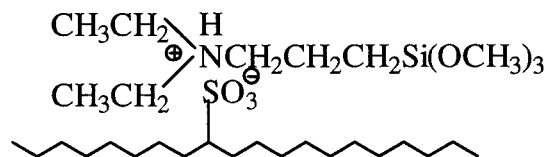
Scheme 2 Expected interaction of the sulfonated PBETP with the bonding agent DAPMS.
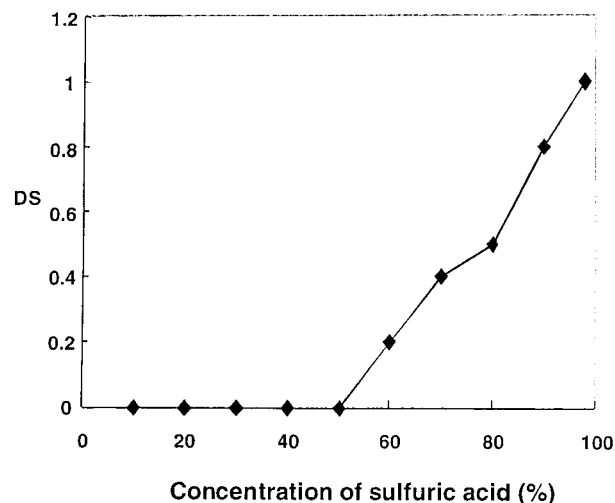
Figure 1 Effect of concentration of sulfuric acid on the degree of sulfonation of the PBETP.

phases were introduced to increase toughness.[1,18] In the present case, PBETP first had to be made more tractable by sulfonation of some of its phenyl groups.[19] In addition, the interactions between the rubbery phase and PBETP were enhanced by also including a coupling agent, *N,N*-diethylaminopropyltrimethoxysilane (DAPMS).[14] The amino groups at one end of this molecule should have strong ionic interactions with the sulfonic groups on PBETP, whereas the triethoxysilane ends will participate with the alkoxy groups on TMOS and DMDMS in the sol–gel process generating the dispersed phase. Scheme 2 shows the structure of DAPMS and its expected interaction with the sulfonated PBETP. This should provide good bonding between the two phases, thus optimizing improvements in the toughness of the resulting composites.

EXPERIMENTAL

Materials

PBETP was synthesized at the Polymer Branch of the Wright-Patterson Air Force Base.[10] TMOS,

DMDMS, and DAPMS were purchased from the Fluka Co., and methanol and diethylamine, from Fisher Inc.

Sulfonation of the PBETP

PBETP, 2.0 g, and 10 mL 9% sulfuric acid were placed into a three-neck flask fitted with a thermometer and a condenser. The mixture was stirred at 60°C until the polymer had completely dissolved. The resulting clear, yellowish solution was slowly poured into an excess of water. The precipitate was washed with water, giving a yellowish sulfonated polymer.

Preparation of the PBETP/Rubbery Phase Composites

The sulfonated polymer was dissolved in methanol. After a clear solution was obtained, the desired amounts of TMOS, DMDMS, and DAPMS were added and the mixture was stirred at room temperature until a clear solution was again obtained. The molar ratio [DMDMS]/[TMS] was 1.0, and the amount of DAPMS was 10 mol % of the sulfonic groups in sulfonated PBETP. A stoichiometric amount of distilled water was then added, and the mixture was further stirred for 24 h at room temperature. After the desired hydrolysis and condensation of the sol–gel reactions, the resulting solution was slowly dried in air. The resulting composite films were further dried under a vacuum at 60°C for 48 h.

Characterization Techniques

Differential scanning calorimetry (DSC) was performed using a Perkin–Elmer DSC system at a heating rate of 10°C/min under a nitrogen atmosphere. These measurements were used to estimate the values of the glass transition temperature, T_g.

Moduli, ultimate strengths, and maximum extensibilities were measured using an Instron mechanical tester (Model 1122) at room temperature. The samples had dimensions of approxi-

Table I   Effects of DS on the Glass Transition Temperatures of PBETP

Parameter	DS				
	0	0.5	0.7	0.8	1.0
T_g (°C)	235	245	248	250	248

Table II   Mechanical Properties of the Composites

DS	Rubbery Phase (wt %)	Modulus[a] (MPa)	Ultimate Strength (MPa)	Extensibility (%)	Toughness (MPa)
0.0	0.0	5560.	44.5	0.80	0.20
1.0	0.0	1160.	40.2	4.2	0.80
	5.0	651.	34.5	5.3	1.1
	8.0	868.	30.7	18.2	4.2
	10.0	723.	28.7	20.0	4.9
	15.0	579.	24.8	24.1	5.2

[a] Low-deformation limits.

mately $40 \times 5 \times 0.2$ mm^3, and the length between clamps was 20 mm. The extensions were carried out at a crosshead speed of approximately 5 mm/min.

RESULTS AND DISCUSSION

Effects of the Sulfonation of PBETP

The sulfonation greatly improved the solubility of the polymer, which now showed some solubility in common polar solvents such as methanol. This greatly facilitated the preparations of the inorganic–inorganic composites via the sol–gel process.

It is difficult to definitively identify the sites of the sulfonation on the polymer. Every phenyl group, either on the backbone or side groups, can be sulfonated but with different likelihoods due to their different reactivities. Although interesting, this information is not crucial with regard to the improvements in processability thus obtained. In this study, the degree of sulfonation (DS) is taken to be the number of sulfonic groups per repeat unit of the polymer. This number obviously depends on the temperature, reaction time, and concentration of sulfuric acid. For example, Figure 1 shows the effect of sulfuric acid concentration on the DS. It demonstrates that the minimal concentration for sulfonation is 50% and that increasing it to 98% can give a sulfonation degree of 1.0 (an average of one sulfonic group per polymer repeat unit).

In spite of the cited significant changes in solubility, there was relatively little change in the glass transition temperature. As shown in Table I, the T_g of the polymer generally increased only slightly with increase in the degree of sulfonation, presumably because of the increased polarity. With regard to mechanical properties, there were slight decreases in the initial modulus and ulti-

mate strength (as gauged by the stress at rupture), but increases in extensibility and toughness. These results are shown in Table II.

Effects of the Rubbery Phase on the Composite Properties

As shown in Table III, addition of the rubbery phase does decrease the glass transition temperature, which is consistent with the desired softening effect. Also, it is seen that at least some of samples are transparent, but this seems to be unpredictable at this stage in the work.

Figure 2 shows stress–strain curves of composites with 0–15 wt % of the rubbery phase. Values of the initial modulus and ultimate properties obtained from these curves are given in Table II. Increases in the amount of the rubbery phase are seen to decrease the initial modulus and ultimate strength, but generally to give large increases in extensibility and toughness. Most important, relatively small amounts of the phase give large increases in toughness. For example, only 8 wt % of the rubbery phase quadrupled the extensibility of the polymer to 20% and increased its toughness approximately fivefold! These successful modifications could certainly add to the suitability of this polymer in a variety of applications.

Table III   Effects of Rubbery Phase Content on T_g

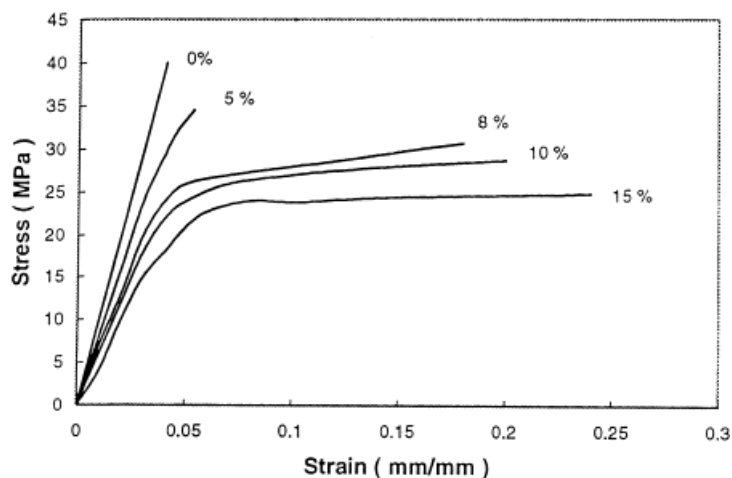| Parameter	Content of Silica–Siloxane (%)				
	0	0.5	0.8	10	15
T_g (°C)	248	239	237	223	210
Transparency	O[a]	T[b]	O	T	T

[a] Opaque.
[b] Transparent.

Figure 2 Stress–strain curves for the PBETP/silica–siloxane composites. The molar ratio of [DMDMS]/[TMOS] was 5, and the rubbery phase contents were 0, 5, 8, 10, and 15%.

CONCLUSIONS

The aromatic polymer PBETP was successfully modified by sulfonation to make it more soluble in common solvent and thus more easily processible. The sulfonated polymer could then be markedly toughened by the *in situ* sol–gel generation of relatively small amounts of a silica–siloxane rubbery phase.

REFERENCES

1. Kumudinie, C.; Premachandra, J. K.; Mark, J. E.; Dang, T. D.; Unroe M. R.; Arnold, F. E. Polymer, in press.
2. Multicomponent Polymer Materials; Paul, D. R.; Sperling, L. H., Eds.; American Chemical Society: Washington, DC, 1986; Vol. 211.
3. Rubber-Toughened Plastics; Riew, C. K., Ed.; American Chemical Society: Washington, DC, 1989; Vol. 222.
4. Rubber Toughened Engineering Plastics; Collyer, A. A., Ed.; Chapman & Hall: New York, 1994.
5. Taylor, R. E.; Register, R. A. J Appl Polym Sci 1995, 57, 105.
6. Rosch, J.; Mulhaupt, R. J Appl Polym Sci 1995, 56, 1599.
7. Mark, J. E.; Allcock, H. R.; West, R. Inorganic Polymers; Prentice-Hall: Englewood Cliffs, NJ, 1992.
8. Mark J. E. J Appl Polym Sci Appl Polym Symp 1992, 50, 273.
9. Judeinstein, P.; Sanchez, C. J Mater Chem 1996, 6, 511.
10. Kumudinie, C.; Premachandra, J. K.; Mark, J. E.; Unroe M. R.; Arnold F. E. Polym Prepr 1998, 39, 571.
11. Hench L. L.; West, J. K. Chem Rev 1990, 90, 33.
12. Novak, B. M. Adv Mater 1993, 6, 422.
13. Ding, Y.; Hay, A. S. J Polym Sci Part A Polym Chem 1998, 36, 519.
14. Premachandra, J. K.; Kumudinie, C.; Zhao, W.; Mark, J. E. J Sol–Gel Sci Tech 1996, 7, 163.
15. Chen, J. P.; Ahmad, Z.; Wang, S.; Mark, J. E.; Arnold, F. E. In Hybrid Organic–Inorganic Composites; Mark, J. E.; Lee, C. Y.-C.; Bianconi, P. A., Eds.; American Chemical Society: Washington, DC, 1995.
16. Mark, J. E.; Premachandra, J. K.; Kumudinie, C.; Zhao, W.; Dang, T. D.; Chen, J. P.; Arnold, F. E. In MRS Proceedings Volume, Better Ceramics Through Chemistry VII. Organic/Inorganic Hybrid Materials; Coltrain, B. K.; Sanchez, C.; Schaefer, D. W.; Wilkes, G. L., Eds.; Materials Research Society: Pittsburgh, 1966; p 93.
17. Premachandra, J. K.; Kumudinie, C.; Mark, J. E.; Dang, T. D.; Arnold, F. E. J Macromol Sci-Pure Appl Sci A 1999, 36, 73.
18. Kumudinie, C.; Premachandra, J. K.; Mark, J. E.; Dang, T. D.; Unroe, M. R.; Arnold, F. E. In MRS Proceedings Volume, Organic/Inorganic Hybrid Materials; Laine, R. M.; Sanchez, C.; Brinker, C. J.; Giannelis, E., Eds.; Materials Research Society: Warrendale, PA, 1998; p 315.
19. Kopitzke, R. W.; Linkous, C. A.; Nelson, G. L. J Polym Sci Part A Polym Chem 1998, 36, 1197.