Polymer Bulletin 30, 393–399 (1993)

Polymer Bulletin

Synthesis and application of abrasion resistant coating materials based on functionalized bis and tris maleimides

B. Tamami, C. Betrabet, and G. L. Wilkes*

Department of Chemical Engineering and Polymer Materials and Interfaces Laboratory, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061-0211, USA

ABSTRACT

Trialkoxysilane functionalized bis and trismaleimide based systems have been synthesized and used for coating a bisphenol-A polycarbonate substrate by the sol-gel method. The abrasion resistance of the substrate is improved by the optically clear materials following thermal curing of the coating.

INTRODUCTION

Organic/inorganic hybrid network materials prepared by the sol-gel method have been investigated over the last few years in our laboratory (1-4). These hybrid materials combine some of the properties of inorganic materials with those of organic compounds. Recently, several novel materials based on low molecular weight organics have been prepared and successfully used as abrasion resistant coating materials for a polymeric substrate (5-7). These coating materials were based on aliphatic and aromatic di- and tri-functional amines. In this study, a series of new coating materials based on bis and tris maleimides have been prepared and their ability to promote abrasion resistance has been studied. It is generally known that maleimide containing systems often provide advantages or improvement in adhesion and thermal stability and often display solvent resistance (8,9). Hence, these materials may serve as useful reagents for more thermally stable optical abrasion resistant coatings.

Because of the electron deficient nature of the double bond within the maleimide function, it can readily undergo bimolecular reactions such as the Michael type addition reaction at a relatively low temperature (9-12). With this in mind, we have synthesized the bis and tris maleimide compounds I-V shown in Scheme 1. Bismaleimide compounds I-IV have the same structures except that the linkages between the phenyl groups are methylene, meta-sulfone, para-sulfone, and ether, respectively. In the trismaleimide compound V, the linkage is the phosphine oxide group. Differences in the nature and polarities of these linkages may have effects on the flexibility, hardness, heat resistancy and adhesion behavior of the final coatings. Following their preparation, these same products were functionalized via a Michael type addition reaction using an amino reagent containing the necessary trialkoxysilane groups to give compounds VI-X. These compounds were then used to prepare coatings by a sol-gel method for the polymeric substrate bisphenol-A polycarbonate.

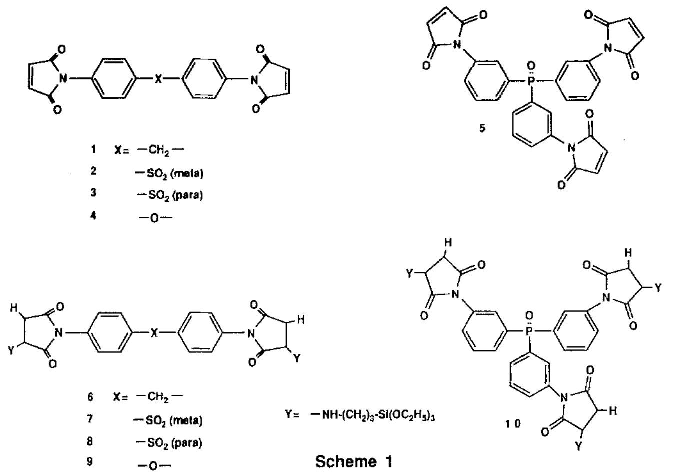
EXPERIMENTAL

Chemicals Utilized

High purity 4,4'-diaminodiphenylmethane, 3,3'-diaminodiphenyl sulfone, 4,4'-diaminodiphenylsulfone, 4,4-diaminodiphenyl ether and triphenylphosphine oxide were purchased from Aldrich and used without further purification. Tris (m-aminophenyl)phosphine oxide was prepared from triphenylphosphine oxide by nitration with HN0 /H S0 and subsequent reduction with 10%Pd/C and hydrazine

---

*Corresponding author



Scheme 1. Functionalized compounds used in this abrasion study.

as has been described by Varma, et al. (13,14). 3-Aminopropyltriethoxysilane was purchased from Aldrich and used without further purification. Maleic anhydride was dried by refluxing and then distilled from fused sodium acetate. Solvents such as acetone and tetrahydrofuran (THF) were dried prior to use.

Proton nuclear magnetic resonance ^1H NMR spectra were recorded on a Bruker WP 270 MH_z spectrometer using $CDCl_3$ as solvent and TMS as an internal standard. Infrared (IR) spectra were recorded on a Nicolet FTIR spectrophotometer.

Procedures

i) Synthesis of Bismaleimides and a trismaleimide.

Bis or trismaleimides I-V (Fig. 1) were synthesized by the reaction of maleic anhydride and the corresponding di or triamine in acetone. The intermediate maleamic acids were then cyclodehydrated in-situ with acetic anhydride/sodium acetate in boiling actone (10). The acetone solutions were then poured in an ice-water mixture and the precipitate was filtered, washed, dried and where necessary purified by column chromatography. The typical experimental procedure is given below for the preparation of tris(m-maleimidophenyl)phosphine oxide (V) by the above method. In a three neck flask equipped with a condenser, mechanical stirrer and a dropping funnel, maleic anhydride 6.53g(0.066 mol) in 40 ml of dry acetone was added to tris(m-aminophenyl)phosphine oxide 6.52g(0.02 mol) in 100 ml of acetone. Vigorous stirring was carried out for over ten minutes while maintaining the temperature at 20° C. Soon a precipitate started to form and stirring was continued for 1.5 hour. To this suspension, fused sodium acetate (2gm) and acetic anhydride (30 ml) were added and allowed to reflux for 7 hours, as the solids slowly went into solution. The brown solution was poured into ice-water. The cream colored precipitate was filtered, washed repeatedly with cold water, dried and crystallized from chloroform/petroleum ether with a yield of 10.1 gm (90%).

ii) Synthesis of triethoxysilane functionalized bis and tris-maleimides.

Triethoxysilane functionalized compounds VI-X, shown in Scheme 1, were synthesized by the Michael type addition reaction of 3-aminopropyltriethoxysilane with the corresponding bis or tris-maleimides in dry tetrahydrofuran at room temperature under nitrogen. Completion of each reaction was determined by NMR spectroscopy. The clear light red solutions containing each respective product was then used directly for the sol-gel process. A typical experimental procedure is given below for preparation of functionalized tris(m-maleimidophenyl)phosphine oxide (X).

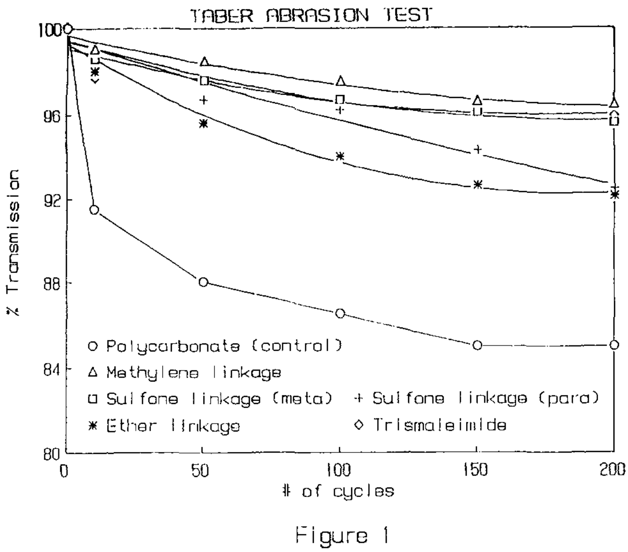


Figure 1. Percent transmission of bismaleimide and trismaleimide coated polycarbonate as a function of the number of cycles on the Taber abrader.

Tris(m-maleimidophenyl)phosphine oxide (V), 2.82g (0.005 mol) were dissolved in dry THF (15 ml). To this solution while stirring under nitrogen, 3-aminopropyltriethoxysilane 3.32g (0.015 mol) was added. The color changed to light red and stirring continued for 24 hours. The solvent was evaporated and the ^{1}HNMR spectrum of the residue showed no olefinic protons at 6.95 ppm indicating the reaction had gone to completion.

iii) Preparation of Coatings

The functionalized bismaleimide compounds were obtained in weight concentrations ranging from 38-42% in tetrahydrofuran. A typical coating recipe consisted of adding 0.3 ml of 1N HCl to the bismaleimide solution under brisk stirring. The acid was added to promote the sol-gel reaction at the triethoxysilane groups. This concentration of the acid was chosen such that the resulting viscosity of the mixture did not change appreciably over the short period of the coating application. The mixture was allowed to stir for approximately 1-2 minutes before being spuncoated onto a bisphenol-A polycarbonate substrate. The polycarbonate, Lexan grade, substrate was 4X4" square, 1/16" thick and was wiped with isopropanol before being spuncoated. The coated substrate was transferred to a 60° C air circulating oven and allowed to dry until it felt nontacky to the touch. It was then placed between stainless steel panels and cured at 148±4° C for 12 hours, after which the sandwich was removed and allowed to cool to room temperature. The samples can also be cured between 130 to 145° C without the stainless steel panels. The Taber abrader was used to abrade the samples. The abrader wheels were Calibrase, CS-10, wheels composed of aluminum oxide abrasive particles in a rubber matrix. The load on each wheel was 250 gm. The abrasive action of the wheels created a wear track, which scattered more light than the unabraded regions. The scattering was measured indirectly by measuring the absorbance of the wear track on a Shimadzu-9000 flyscan spectrometer. The average absorbance was calculated by measuring the absorbance over 1 cm^2 of the wear track using a 420 nm (blue)

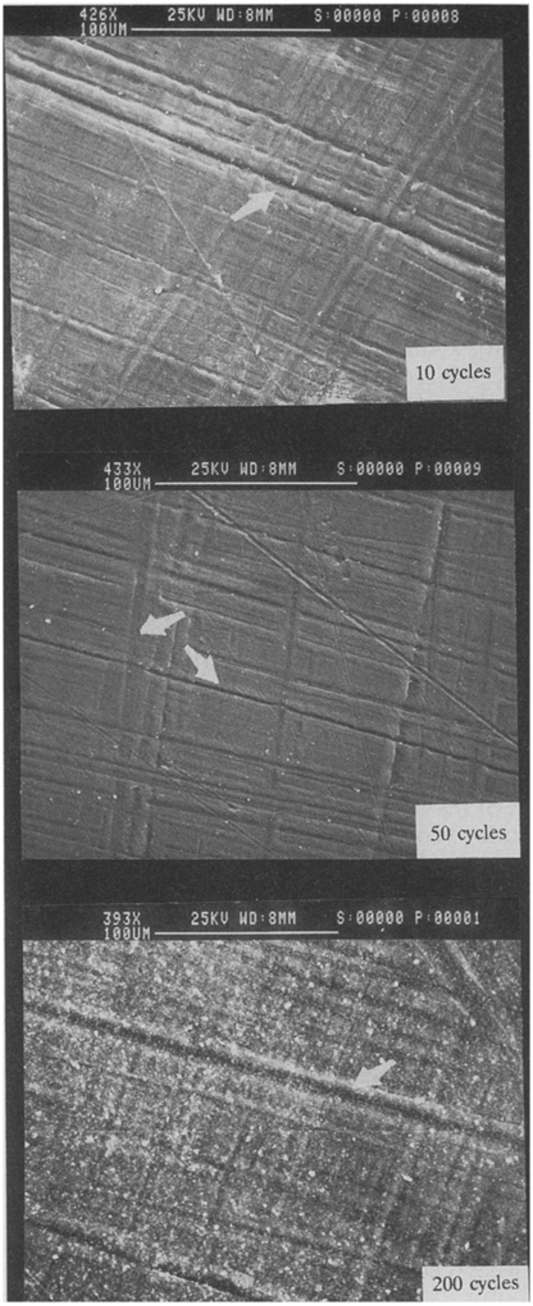


Figure 2. SEM micrographs of the uncoated polycarbonate samples after 10, 50 and 200 cycles on the Taber abrader.

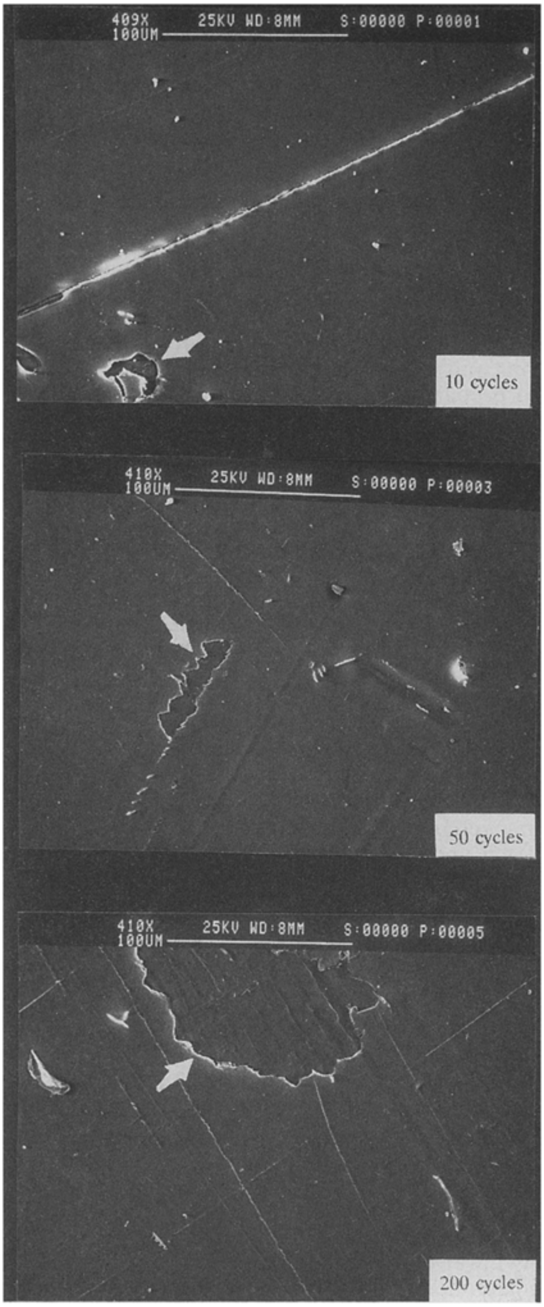


Figure 3. SEM micrographs of the bismaleimide (sulfone-meta) coated polycarbonate sample after 10, 50, and 200 abrader cycles.

wavelength. The samples were abraded cumulatively to 200 cycles. At intervals of 10, 50, 100, 150 and 200 cycles the average absorbance was measured and the transmittance calculated. The loss of transmittance was taken as a measure of the abrasion and surface roughening as we have described elsewhere (5).

RESULTS AND DISCUSSION

i) Characterization of the bis and trismaleimide products

Bismaleimides I-IV were prepared in high yields (7, 90%) by using a modification of the procedure developed by Searle (15,16) and were characterized by ^{1}H-NMR, IR spectroscopy, and, by comparison of their melting points with literature values. Characteristic absorption bands due to imide rings were observed at 1710-1745 cm^{-1} and 1770-1785 cm^{-1}. Other prominent absorption bands arising from either the phenyl group 1600 cm^{-1}, C-N (1370-1390 cm^{-1}) or SO_2 (1155 and 1330 cm^{-1}) absorbants were also observed. In the proton NMR spectra, multiplets due to aromatic protons and the singlet at 6.85 ppm due to olefinic protons were observed. Attempts to prepare the trismaleimide (V) by the reported reactions of the corresponding trisamine and maleic anhydride were not satisfactory (14). However, applying the above modified method using acetone as solvent and in-situ cyclization of the intermediate amic acid gave compound (V) in high yield and purity. It was also characterized by its ^{1}H-NMR and IR spectra.

Trialkoxysilane functionalization of bis and tris-maleimides I-V were done in dry THF using 3-aminopropyltriethoxysilane as the reagent. Other solvents such as ethanol or acetone could also be used, but THF was the most satisfactory. Special care was taken to use as dry a solvent as possible to prevent side reactions (11). The completion of reactions were determined by ^{1}H-NMR spectroscopy on solvent free crude reaction products. The signal at 6.85 ppm due to the olefinic hydrogens of the maleimide systems disappeared on completion of the reaction and new signals at about 1.25 and 3.8 ppm due to ethoxy protons, and 0.70, 1.60, 2.25 ppm, due to different methylene groups, appeared. In addition, signals due to methylene and methine protons of the imide rings were observed at ca. 2.2 - 3.1 and 4.0 ppm respectively. The functionalized compounds were also characterized by IR spectroscopy. The carbonyl regions of the IR spectra showed bonds at ca. 1785(w) cm^{-1} and 1720(s) cm^{-1}, characteristic of the imide $c=0$ stretching absorptions. Bands due to NH stretch and deformation of secondary amine groups were also observed at ca. 3480 cm^{-1} and 1630 cm^{-1} respectively.

Due to the sensitivity of the ethoxysilane functionalities to hydrolysis and condensation reactions, the functionalized compounds were used directly as synthesized in THF for use in the sol-gel coating process.

ii) Abrasion Resistance Studies:

Figure 1 shows percent transmission as a function of the Taber abrader cycles. The decrease in transmittance of the polycarbonate control is faster than the bismaleimide and trismaleimide coated samples. Changing the functional group between the phenyl groups does not significantly affect the abrasion resistance, although the ether linkage seems to exhibit a slightly lower resistance, possibly due to its flexibility. Also, the abrasion resistance is unaffected by the change in control. The flattening of the curves at the higher abrader cycles is due to the decreased sensitivity in the transmittance due to multiple scattering. Hence, it is the first 200 abrasion cycles that we have found, that provides a good base comparison for abrasion resistance. The polycarbonate control exhibits a sharp, distinct wear track, as seen by the relatively lower transmittivity (85%) of this region as compared to the bismaleimide and trismaleimide coated samples whose transmittances range from 92 to 96%. Additional evidence for the effectiveness of the coating can be seen from the SEM micrographs in Figures 2 and 3. The micrographs show the progression of the surface texture as a function of abrader cycles. The polycarbonate is abraded through a mechanism wherein the surface is gradually "etched" out by scratches (grooves) as indicated by the arrows spaced close together. On the other hand the bismaleimide coating is abraded by a tearing mechanism wherein the coating is torn away from the surface. The SEM micrographs are focused on the wear track. These wear tracks are few and dispersed, the coating in between them being relatively scratch free. This may not be immediately apparent from the SEM micrographs which have been centered on a 'tear' to provide detail about the wear track. The adhesion of the coating to the substrate was measured by a 180° peel test using 3M, #610 adhesive tape (6). The tape was unable to peel any coating from the substrate, thus denoting good adhesion.

CONCLUSIONS

Clear transparent coatings of functionalized bismaleimides and a trismaleimide with good adhesion were obtained on polycarbonate which were subsequently cured using the sol gel process. These coatings exhibit higher abrasion resistance than the uncoated polycarbonate as can be perceived from the higher transmittance of the abraded samples and by SEM observations.

ACKNOWLEDGEMENT

The financial support of AKZO Inc. and the Office of Naval Research is acknowledged.

REFERENCES

1. Huang, H., Orler, B., and Wilkes, G.L., Macromolecules, 1987, 20, 1322.
2. Huang, H., Glaser, R.H., and Wilkes, G.L., ACS Symposium Series, 1987, 360, 354.
3. Huang, H., and Wilkes, G.L., Polym. Bull., 1987, 18, 455.
4. Wang, B., Huang, H., Wilkes, G.L., Liptak, S., and McGrath, J.E., Polym. Mat. Sci. Eng., 1990, 63, 892.
5. Wang, B. and Wilkes, G.L., Polym. Preprint, 1991, in press.
6. Wang, B., and Wilkes, G.L., submitted to Chemistry of Materials.
7. Tamami, B. Betrabet, C., and Wilkes, G.L., in preparation.
8. Wilson, D., Stenzenberger, H.D., and Hergenrother, P.M., Polyimides, Chapman and Hall, NY, 1990.
9. Grave, J.R. and Bufkin, B.G., J. Coat. Tech., 1981, 53, 45.
10. Mustafa, A., Asker, W., Khaltah, S., and Zayed, S., J. Org. Chem., 1961, 26, 787.
11. Sheremeteva, T.V., Larina, G.N., Zhenevskaya, M.G., and Gusinskaya, V.A., J. Polym. Sci., (C), 1967, 16, 1631.
12. Varma, I.K., Tomar, A.K., and Anand, R.C., Polym. Mater. Sci. Eng., 1987, 57, 92.
13. Challenger, F., and Wilkinson, J.F., Chem. Soc., 1924, 125, 2675.
14. Varma, I.K., Fohlen, G.M., and Parker, J.A., U.S. Patent 4,395,557.
15. Kumar, D., Chem. Ind., 1981, 21, 189.
16. Searle, N.E., U.S. Patent 2,444,536.

Accepted February 22, 1993 K