Polymer Bulletin 30, 39–45 (1993)

Polymer Bulletin

New ceramer high optical abrasion resistant transparent coating materials based on functionalized melamine and a tris(m-aminophenyl)phosphine oxide compound

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

Summary

The synthesis of new high optical abrasion resistance coating materials has been undertaken by functionalizing melamine and tris(m-aminophenyl)phosphine oxide with a triethoxysilane containing reagent. These highly functionalized compounds have been used for coating a bis-phenol-A polycarbonate substrate by the sol-gel method. Preliminary data shows the abrasion resistance of the polymer substrate is considerably improved when it is coated by these optically clear materials.

Introduction

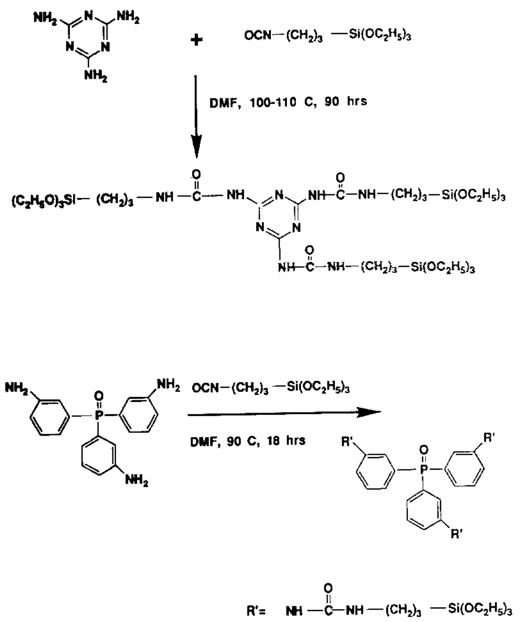
Compared to inorganic materials, transparent organic polymers generally have poor optical abrasion resistance. Therefore, there continues to be a need for developing abrasion resistant coatings for polymeric substrates. Several such materials have been developed based on the use of metal oxides or organosiloxanes to improve this property of organic polymers (1,2). In addition, Schmidt, et al. have utilized silane coupling agents based on materials called Ormocers to develop coatings for polymeric materials (3,4).

Recently, organic/inorganic hybrid network materials known as Ceramers, prepared by a sol-gel method, have been developed and studied in our laboratory. They combine some of the properties of inorganic materials with those of organic compounds (5-9). More recently ceramer hybrid materials based on low molecular weight organics have been prepared in our laboratory and successfully used as optically abrasion resistant coating materials for a polymeric substrate (polycarbonate, polyetherimide or poly-4-methyl-1-pentene) (10). These materials were obtained by incorporating metal alkoxides (e.g., silicon, titanium or zirconium) with triethoxysilane capped di or trifunctional aliphatic or aromatic amines, through a sol-gel process. The hybrid materials showed optical clarity and improved the abrasion resistance of the polymeric substrate; the best being the organic/inorganic hybrid system based on a triethoxysilane endcapped trifunctional aliphatic amine, namely diethylenetriamine (DETA), when used without incorporating any additional metal alkoxide.

In the study described here, two new hybrid ceramer transparent coating materials based on melamine and tris(m-aminophenyl) phosphine oxide have been prepared and their preliminary optical abrasion behavior studied. These trifunctional aromatic amines can be functionalized with the reagent 3-isocycanatopropyltriethoxysilane to produce coating materials with high alkoxy functionality processable by the sol-gel method (see Scheme 1). It is known that melamine has been extensively used in the coating industry for it generally improves adhesion, flame and heat resistance of the coatings. Also materials containing the phosphine oxide group are known to have potential flame resistancy (11,13).

---

*Corresponding author



Scheme 1. Functionalization reactions of melamine and tris(m-aminophenyl) phosphine oxide for preparation of ceramer coatings.

Experimental

Materials: Melamine (gold label), triphenylphosphine oxide and hydrazine hydrate were purchased from Aldrich Chemical Company and were used without further purification. 3-isocyanotopropyltriethoxysilane from Petrarch Systems was used for endcapping the aromatic amines. HPLC grade N,N-dimethylformamide (DMF), isopropanol and tetrahydrofurane (THF) were obtained from Aldrich and used as such. Bis-A-polycarbonate (1/16 inch sheet stock) Lexan grade made by General Electric Company was utilized as the polymeric substrate.

Procedure (i) Preparation of triethoxysilane capped melamine:

Melamine 6.3 g (0.05 mol) was added to dry DMF (50 ml) and the mixture was heated to (100-110° C) while being stirred under nitrogen for 1 hour, when some of it dissolved (Scheme 1). To this mixture, 3-isocyanotopropyltriethoxysilane 39.60 g (0.16 mol) was added and heating continued for 90 hours over which time the remaining solid went into solution as the reaction proceeded. The functionalization reaction was monitored during the reaction by FTIR spectroscopy. The final clear, almost colorless solution was then used for preparation of ceramer coatings.

(ii) Preparation of tris(m-aminophenyl)phosphine oxide (TAPO) (12,13)

Trisphenylphosphine oxide, 100g, was added very slowly to a cold stirred mixture (10° C) of 200 g fuming HNO_3 and 500 g concentrated H_2SO_4 while monitoring the temperature. The viscous dark red solution was then poured into ice cold water and the precipitate filtered and washed repeatedly with water and then with hot ethanol. It was dissolved in boiling glacial acetic acid and then 900 ml of methanol were added and the solution was cooled to ambient temperature. The yellow crystals which formed were then filtered and dried. The yield of the trinitro compound was 123g (82%) and it possessed a melting point of 243-245° C which matched well with the literature value of 242-244° C (12).

To a suspension of the trinitro product compound 57.82 g (0.14 mol) in 450 ml ethanol, 2.88 g of palladium on activated carbon (10%), were added. The mixture was warmed and while being mechanically stirred, hydrazine hydrate 53.2 ml in ethanol (40 ml) was added dropwise over a 1.5 hr. period while maintaining the temperature at about 50° C. The reaction mixture was then refluxed for 1.5 hours and filtered while hot. On cooling, the filtrate gave white crystals of TAPO which were vacuum dried. The yield was 38.9 gm (86%); the measured mp of 260-262° C compared well to the literature value of 258-263° C (13).

(iii) Preparation of triethoxysilane capped tris(m-aminophenylphosphine oxide): The reaction of TAPO with 3-isocyanatopropyltriethoxysilane was done in DMF as in the case of melamine - see Scheme 1. TAPO was completely soluble in DMF and the reaction temperature and time were 90° C and 18 hours, respectively. The final clear solution was used for preparation of ceramer coatings.

Preparation of Ceramer Coatings: A typical ceramer coating recipe consisted of adding 0.3 ml of 1N HCl to 6 gm of trifunctional melamine under brisk stirring. The mixture was allowed to stir for approximately 1-2 minutes before being spun coated onto a polycarbonate substrate. The substrate consisted of a Lexan grade polycarbonate with a thickness of 1/16" cut into squares of 4"x4". Before being spuncoated, the polycarbonate was cleaned with isopropanol. The wet spuncoated substrate was then transferred to a 60° C air circulating oven where the coating was allowed to dry until it felt nontacky to the touch. It was then placed between stainless steel panels and allowed to cure in a 148° C air circulating oven for 12 hours. The samples can also be cured at 130-135° C without the stainless steel panels. The stainless steel panels were necessary at the 148° C cure temperature to prevent warping of the polycarbonate. The sandwich was removed and allowed to cool to room temperature. The coating thickness from SEM (scanning electron microscopy) measurements was found to be between 1-3μm.

Optical Abrasion testing: The coated substrate was then subjected to a Taber abrasion test. Standard CS-10 abrader wheels composed of aluminum oxide particles in a rubber matrix were utilized, with a load of 250 gm on each wheel. The sample was allowed to be abraded cumulatively to 200 cycles of the Taber abrader. A wear track was created by the rotating wheels. The wear track scattered more light than the surrounding unabraded regions. The scattering was measured indirectly by measuring the absorbance of the wear track and calculating the transmittance as described elsewhere (10). Transmittance decreased with increased surface roughening. At intervals of 10, 50, 100, 150 and 200 cycles light absorbance through the wear track was measured on a Shimadzu 9000 flyscan spectrometer, by scanning with a 420 nm wavelength light over 1 cm^2 of the wear track. For comparison an uncoated bis-A-polycarbonate sheet with no coating served as the control. It is realized that this optical technique does not provide an index of wear rate or level of adhesion of the coating but it distinctly provides a practical index of optical clarity as influenced by uneven disruption of the coating layer (or control substrate).

Results and Discussion

Synthesis: The reaction between melamine or tris(m-aminophenyl)phosphine oxide (TAPO) with the isocyanatopropyltriethoxysilane reagent was monitored by FTIR spectroscopy. The characteristic absorption band due to the isocyanato group at 2270 cm^{-1} disappeared when the reaction was complete. As expected the reaction time and temperature for endcapping TAPO was less than in the case of melamine due to higher reactivity of the amino groups toward the isocyanate.

Due to instability of the ethoxysilane functionalities through hydrolysis and condensation reactions, the functionalized compounds were not isolated from their DMF solutions and were directly used for preparation of ceramer coating materials. However, under dry and neutral conditions the solutions could be kept unchanged for several months.

Abrasion Resistance Studies - Preliminary Results: Figure 1 shows that for the polycarbonate control, the decrease in transmittance is faster than that of the melamine coated sample. The flattening of the transmittance curve at the higher abrasion cycles is attributed to a decrease in sensitivity with increasing number of scratches. The functionalized melamine and the phosphine oxide coated substrates exhibit a higher transmittance than the uncoated polycarbonate, which shows a higher optical abrasion resistance for the uncoated material. Evidence of the higher resistance can be seen in Figures 2 and 3 which show the SEMs of the wear tracks of the uncoated polycarbonate and the melamine coated sample as a function of the abrader cycles. After only ten cycles the polycarbonate shows distinct wear tracks while the melamine sample is relatively scratch free. The polycarbonate is abraded by an "etching" process where the surface gets abraded by closely placed scratches as indicated by the arrows, while the melamine is abraded by a tearing mechanism whereby the abrasive action of the wheels tears the coating (see arrow) but leaves the surface of the coating intact between the tears. It should be noted that the SEM micrographs have been centered on the wear tracks with a view towards delineating the features of the wear track. These wear tracks are few and dispersed, the coating between the tracks is relatively scratch free. A similar progression was seen for the phosphine oxide coating. The application of a pressure sensitive #610 3M tape was unsuccessful in peeling off (180° peel) any fragment of either the coating from the substrate, thus denoting good adhesion to the substrate.

Conclusion

Melamine and tris(m-aminophenyl)phosphine oxide (TAPO) can be functionalized by an isocyanato reagent containing triethoxysilane functionality. The functionalized compounds can then successfully be used through a sol-gel process for preparation of ceramer coating materials. Light transmittance and SEM micrographs which show good adhesion to the polycarbonate substrate show evidence of increased resistance of these coatings to abrasion.

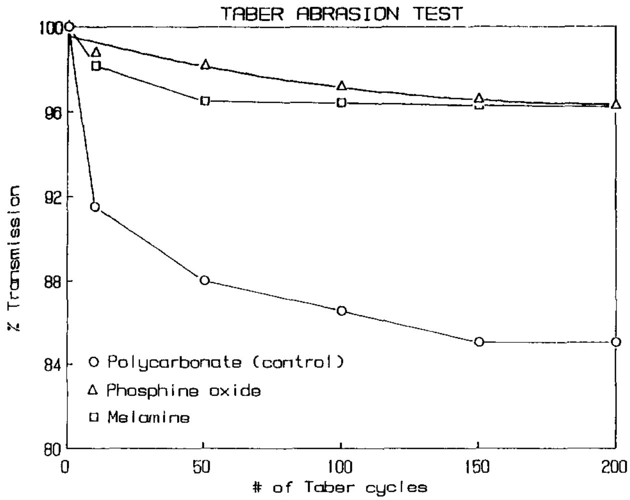


Figure 1. Percent transmission of melamine and phosphine oxide coated polycarbonate as a function of number of cycles of the Taber abrader.

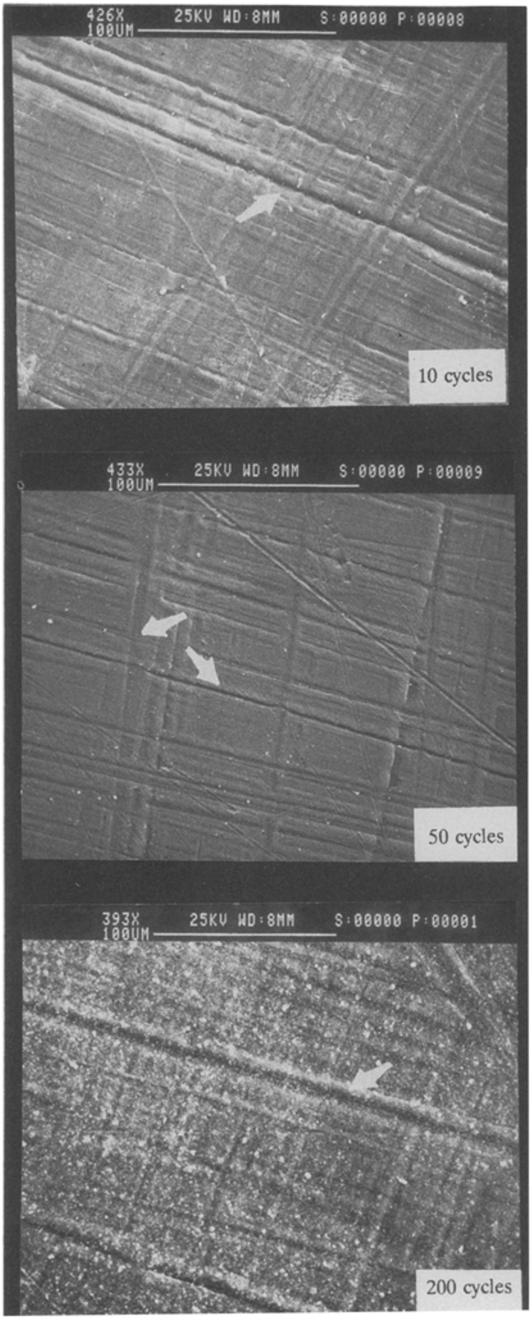


Figure 2. SEM micrographs of the uncoated polycarbonate as a function of abrader cycles.

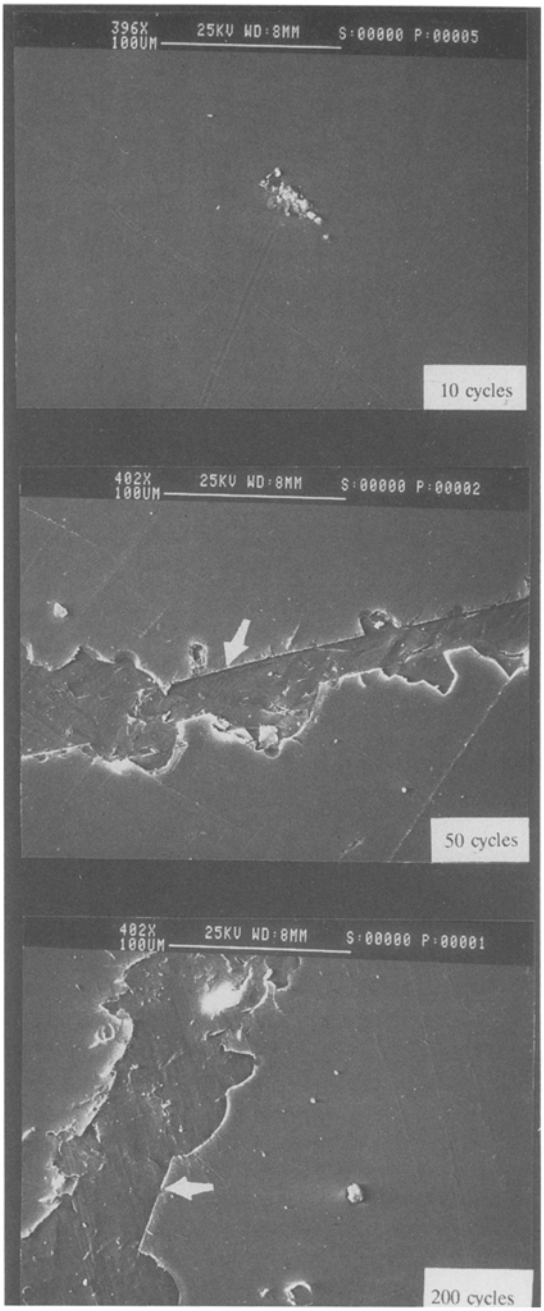


Figure 3. SEM micrographs of the melamine coated sample as a function of abrader cycles.

Acknowledgement

The authors acknowledge the financial support of AKZO Inc. and the Office of Naval Research (Sponsor # N00014-88-K-0007 A00003).

References

1. J. Kasi, JPn. Kokai Tokkyo Koho, JP6335, 633 (88,35,633).
2. M. Ishigaki, M. Inagaki, M., T. Sakakibara, JPn. Kokai Tokkyo Koho, JP6348, 364 (88, 48, 364).
3. R. Nass, E. Appac, W. Glaubitt, H. Schmidt, J. Non-Cryst. Solids, 121, 370 (1990).
4. H. Schmidt, H. Walter, J. No-Cryst. Solids, 121, 428 (1990).
5. H. Huang, B. Orler, G.L. Wilkes, Macromolecules, 20, 1322 (1987).
6. H. Huang, R.H. Glaser, G.L. Wilkes, ACS Symp. Series, 360, 354 (1987).
7. H. Huang, G.L. Wilkes, Polym. Bull., 18, 455 (1987).
8. B. Wang, H. Huang, G.L. Wilkes, S.Liptak, J.E. McGrath, Polym. Mat. Sci. Eng., 63, 892 (1990).
9. J.L.W. Noell, G.L. Wilkes, D.K. Mohanty, J.E. McGrath, J. Appl. Polym. Sci., 40, 1177 (1990).
10. B. Wang, G.L. Wilkes, ACS Polym. Prepr., Fall 1991.
11. M. Lewin, S.M. Atlas, E.M. Pearce, Flame-Resistant Polymeric Materials, Plenum, New York, 1975.
12. F. Challenger, J.F. Wilkinson, J. Chem. Soc., 1924, 125, 2675.
13. I.K. Varma, G.M. Fohlen, J.A. Parker, U.S. Patent 4,395,557.

Accepted October 28, 1992 K