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NOVEL HYBRID INORGANIC-ORGANIC ABRASION-RESISTANT COATINGS PREPARED BY A SOL-GEL PROCESS

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ABSTRACT

Novel abrasion-resistant coatings prepared by a sol–gel process have been developed and applied on the polymeric substrate Bisphenol A polycarbonate. In general, coatings utilize either 4,4′-diaminodiphenyl sulfone (DDS) or diethylenetriamine (DETA) that are then functionalized at their amine groups with 3-isocyanatopropyltriethoxysilane. Following functionalization, these coating materials are then spin coated onto bisphenol A polycarbonate sheet and cured. These reactants undergo a comparable sol-gel reaction similar to typical metal alkoxide chemistry, thereby producing an insoluble network material containing a good dispersion of the functionalized organic along with the hydrolyzed and condensed silicon alkoxide groups. The final coating is transparent and of a few microns in thickness. Following curing, an index of the abrasion resistance is assessed by an optical method, and the adhesion behavior of the coatings is investigated and quantified. It is demonstrated that these thin transparent coatings do provide considerable abrasion resistance over and above that of the uncoated polymeric substrate.

INTRODUCTION

It is well known that organic polymers generally show poor abrasion resistance relative to inorganic oxide ceramic materials. This has promoted the need for abrasion-resistant coatings for polymeric materials; in particular, cases exist where transparency of that coating is also very desirable. Certainly, some materials have been developed along this line including patents which indicate the use of metal oxides or organosiloxanes as coating materials to improve the abrasion resistance of organic polymers [1-4]. In addition, Schmidt et al. utilized silane coupling-agent-based materials (ORMOCERs) to develop coatings for such polymeric materials as polycarbonate and polyethylene terephthalate [5, 6].

More recently in our own laboratory, we synthesized and studied the structure-property behavior of novel organic/inorganic hybrid network materials which are prepared by a sol-gel method [7-12]. Some of these possess the advantages that they typically display a higher abrasion resistance and higher modulus at the same corresponding temperature relative to the pure organic-based polymer yet retain flexibility. The properties are, of course, dependent upon the relative composition of the metal alkoxide used and its content in the preparation of these materials relative to the nature of the functionalized organic. In our research we have also been able to generate high refractive index transparent film systems when titanium tetraisopropoxide is utilized as the metal alkoxide. We have, however, generated many systems where the type of metal alkoxide varies, including those based on silicon, aluminum, and zirconium in addition to the titanium materials [9-12]. Regarding the functionalized organic moieties, triethoxysilane-capped oligomers have been principally used to react with the metal alkoxide-based sols to form transparent hybrid networks, often in film form. These systems generally display some level of microphase separation as has been well documented based on small-angle x-ray scattering (SAXS) studies [7-12], and in one instance via transmission electron microscopy [10].

In the study described here, a series of novel hybrid network materials has been prepared by using titanium or zirconium metal aloxides as the inorganic component to react with triethoxysilane-capped organics. In order to increase the hardness of these coating materials, lower molecular weight organics have been chosen for the purpose of enhancing the composition of the inorganic phase and lowering the level of flexibility and softness often associated with the higher molecular weight oligomers or polymers that we have incorporated in our previous systems [7-12]. Two common commercial lower molecular weight organics, 4,4′-diamino diphenylsulfone (DDS) and diethylenetriamine (DETA), were chosen and endcapped with 3-isocyanatopropyltriethoxysilane and used as the functionalized organics for this study (see Fig. 1). As will be described below, we have utilized these systems as coatings for polymeric substrates and have then investigated the response of these thermally cured coatings for their abrasion resistance relative to the uncoated substrate materials. Some results of this work are reported here.

EXPERIMENTAL

Materials

Titanium isopropoxide ($Ti(OiPr)_4$) and zirconium *n*-propoxide ($Zr(OPr)_4$) from the Akzo Corporation as well as 4,4′-diaminodiphenyl sulfone (DDS) and diethylenetriamine (DETA) from the Aldrich Chemical Company were used without further purification. 3-Isocyanatopropyltriethoxysilane from Petrarch Systems was

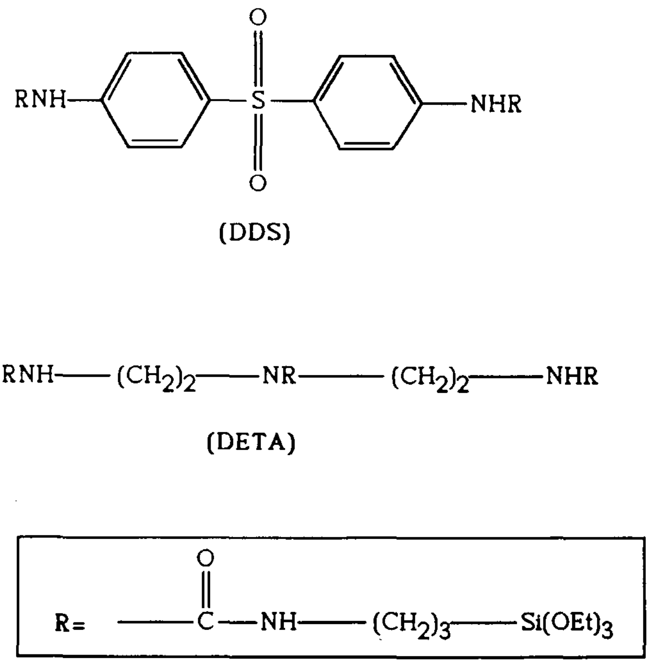

FIG. 1. The structures of triethoxysilane-capped diethylenetriamine (DETA) and 4,4′-diaminodiphenyl sulfone (DDS).

used to endcap and therefore functionalize the organics DDS and DETA. HPLC grade *N,N*-dimethylformanide (DMF), isopropanol (IPA), and tetrahydrofuran (THF) were purchased from the Aldrich Chemical Co. and used without further purification. Bisphenol A polycarbonate (1/16 inch Lexan), sheets were obtained from the General Electric Plastics Company and utilized as the polymeric substrate. In some cases the polycarbonate substrate was exposed to an oxygen plasma treatment. The conditions under which this process took place initially cleaned the surface of the polycarbonate substrate with ethanol and dried it. The sample was then placed in the plasma chamber and pumping was commenced to reach a vacuum of less than 2 torr. The gas line was first flushed with oxygen for 5 minutes, after which the plasma gas (oxygen) was utilized to treat the substrate for a period of 5 minutes at a power of 100 W. It was found that shorter times could be utilized as well, but for all data presented in this report the oxygen plasma exposure time was 5 minutes. After removal from the plasma chamber, substrates were spin coated with abrasion-resistant coating as will be described shortly.

Procedure

Preparation of Triethoxysilane-Capped DDS

First, 17.78 g (0.073 mol) DDS was dissolved into 40.5 g DMF. Next, 42 g (0.17 mol) 3-isocyanatopropyltriethoxysilane was slowly added to this solution and stirred for 3 hours. Infrared spectroscopy was then utilized to confirm the loss of the isocyanate functionality as endcapping takes place through the formation of urea linkages—data not included. The solution was kept under nitrogen before using.

Preparation of Triethoxysilane-Capped DETA

In the preparation of the functionalized DETA, 5 g (0.048 mol) DETA was mixed with 20 g IPA. Then 41 g (0.166 mol) 3-isocyanatopropyltriethyoxysilane was slowly added to this solution and stirred for 3 hours. Infrared spectroscopy was also utilized to survey the extent of this endcapping reaction (the formation of urea linkages). This solution was stored under nitrogen before using.

Preparation of Coatings

Typical example: Five grams of IPA was first mixed with 0.1 mL HCl (10 N) and 0.3 mL H_2O, then to this solution was slowly added 5 g $Ti(OiPr)_4$ with fast stirring, leading to a clear titania sol. In order to avoid local inhomogeneity, it was crucial to maintain a slow addition rate of the alkoxide and to utilize a fast stirring rate. This procedure developed a clear titania sol (pH 2.2). Then the chosen amount of functionalized organic was mixed with the titania sol and stirred for 27 hours to obtain a viscous homogeneous system for spin coating on the polycarbonate sheet. These coated samples were further heat treated (cured) to at least 60°C before testing. In order to avoid deformation of the coating substrate, the curing temperature was never higher than the glass transition temperature of the polymeric substrate.

As is well known, the titanium-containing system is quite reactive for both the hydrolysis and condensation reactions. Therefore, to avoid undesirable precipitation of titanium dioxide particulates, only a low water content (as stated above) was needed to promote the hydrolysis and condensation reactions. For the even more reactive zirconium-containing systems, all the preparation procedures were similar to the titanium-based systems except that no H_2O was directly added to the systems since the water from the HCl solution and surrounding air was sufficient for hydrolysis and condensation.

For the analysis results presented in this paper, the sample designation will be denoted as MX-DETA, where M is either titanium isopropoxide (Ti) or zirconium *n*-propoxide (Zr), and X indicates the weight percent of the titanium or zirconium alkoxide used relative to the weight of the functionalized organic. For example, 30 wt% of zirconium *n*-propoxide to 70 wt% of functionalized DETA is denoted as Zr30-DETA.

Characterization

To provide a qualitative index of adhesion of the thermally cured coating on the substrate, ASTM D3359 procedure was used [13]. First, a coated sample was precleaned with ethanol. Next, a sharp razor or Exacto knife was used to prepare a raster of cuts in the sample. For coatings having a dry film thickness up to and including 50 μm, the cuts were spaced 1 mm apart, and 11 such cuts were made in both orthogonal directions. After making the required cuts, the film was lightly brushed with soft tissue to remove any detached flakes. A pressure-sensitive adhesive tape (3M #610) was then uniformly applied to the clean surface. To ensure good contact with the surface, pressure was firmly applied to the tape. After 1 minute of application, the tape was removed by seizing the free end and rapidly pulling it off at as close to an angle of 180° as possible. Following peel, the grid area was inspected for removal of the coating from the substrate. The level of adhesion was semiquantatively scaled from 0B to 5B, based on the amount of cross-cut area removed. Level 5B indicates no coating was removed while 0B meant more than 65% of the sample was removed. Levels 1B through 4B were assigned to intermediate degrees of removed as discussed elsewhere [13].

A peel adhesion tape test was also used in a more quantitative test to judge the level of adhesion behavior. In this case the same pressure-sensitive adhesive was applied to the coating surface. In order to ensure good contact with the coating, the adhesive tape was again firmly pressed to the coated substrate surface. One end of the tape was held by a piece of hard paper as a backing material. The tape was peeled away (180°) from the substrate as shown in Fig. 2. The force required to peel the tape from the substrate was measured by an Instron Model 1122 using a 1 cm/min peeling rate and 180° peeling angle. The peel strength was calculated by $W = P(1 - \cos \Theta)$, where P is the peeling force per unit of width and Θ is the peeling angle as has been described by Hato et al. [14]. Following this test, the failure surface was observed by scanning electron microscopy (SEM) or optical microscopy (OM). If the network coating was well adhered to the polymeric substrate, the failure surface occurred between the adhesive tape and the coating, whereas if the coating failed, the tape adhesive layer contained remnants of the coating. It is clearly recognized that there may well be different adhesion behaviors with the adhesive tape itself for different specimen compositions. Therefore, the reader should note that the adhesion values from this method are principally only suitable when comparing the relative adhesion behavior of a given composition by varying processing history, etc.

Abrasion Resistance Studies

A Taber abrader utilizing a silicone carbide CS-10 wheel with a 250-g load was used for the abrasion resistance studies. Polycarbonate substrates with, as well as without, coatings were tested by the Taber abrader for 10, 50, and 200 cycles.

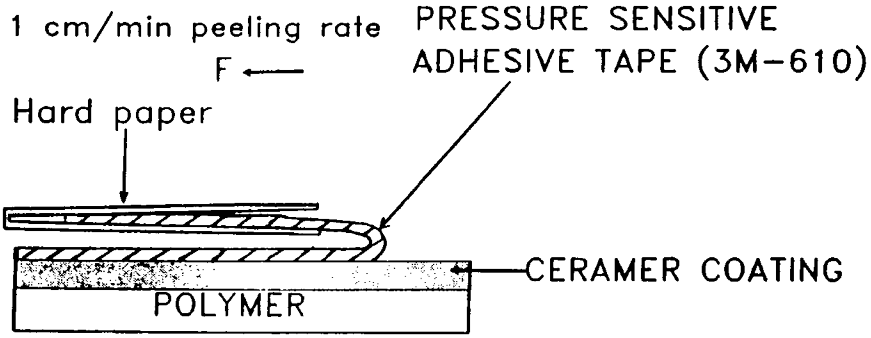

FIG. 2. Schematic design of the peel adhesion tape test.

Following the Taber test, a light transmittance test (wavelength 420 nm) using a beam size of 20 × 4 mm was used to measure the percent of transmittance change in the wear track area relative to the unabraded materials. A Shimadzu CS-99000 UV-VIS spectrometer was used for this study. The results were plotted as percent of transmission versus number of wear cycles. An abrasion-resistant sample will show a high percent of transmission relative to a poorly abrasion resistant sample. While it is realized that this method does not provide all features of abrasion wear rate and adhesion response, it does provide a practical and quantitative index of the uneven surface disruption which influences surface reflectivity (and thus transmittance) due to wear.

RESULTS AND DISCUSSION

Homogeneity of Coatings

All the final coatings displayed optical transparency, which indicated that the metal alkoxides were well incorporated with the triethoxysilane-capped organics, thereby giving no macrophase separation. By use of small-angle x-ray scattering procedures discussed elsewhere, we have shown that some level of microphase separation can occur in these hybrid materials [12, 15]. In applying this method to these coating materials, only a small degree of heterogeneity was noted and therefore these data have not been included. Indeed, the preparation methods of these coating systems are quite similar to those used in our early studies [7–12].

As has been pointed out elsewhere, the extent of hybrid network formation is dependent on reaction temperature and time, molar ratio of water to metal alkoxide, and acid level [7–9]. In order to promote some level of reaction to gain a suitable viscosity for the coating, the solution of the functionalized organics and metal alkoxide sols was stirred for 27 hours before the coating was applied. Indeed, if these solutions were used without sustained mixing, they sometimes displayed some formation of inhomogeneous particles. These particles are believed to be due to self-condensation of the highly reactive zirconium or titanium alkoxide. That is, the presence of moisture can catalyze hydrolysis and condensation of zirconium or titanium alkoxide, thereby leading to particle formation. Based on the formulations and viscosities used for these coatings, the general range of thickness was 2 to 4 μm for the wear studies. A typical example is shown in Fig. 3 which provides a SEM photomicrograph of one such coating.

Adhesion

Utilizing the ASTM D3309 test method, the level of adhesion between the coatings and polymeric substrates was determined as shown in Table 1. The adhesion values of all the coatings on the polycarbonate substrate were clearly dependent on the curing temperature. In general, a higher curing temperature provided a higher adhesion value. In order to further understand the correlation of adhesion strength with curing temperature, the adhesion tape peel test was used to evaluate this dependence with the results shown in Table 2. For the coating system Zr30-DETA, the adhesion value increased from 31 to 114 to 122 N/m when the curing temperature increased from 60 to 125 to 145°C, respectively. The peel strength

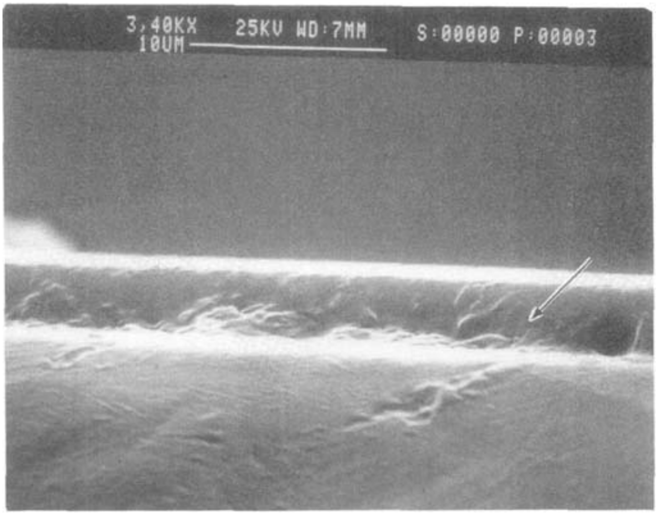

FIG. 3. SEM of Ti30-DDS coated polycarbonate. The sample was heat treated to 150°C prior to fracture and inspection. The arrow denotes the coating layer.

values were further indirectly supported by the SEM microscopy studies. As shown in Fig. 4(a), the 60°C cured coating was nearly completely transferred to the tape, as can be noted from the flake-like regions, i.e., adhesion failure occurred. However, for the cure temperature of 145°C, no transfer of the coating occurred. In fact, to reveal that this coating was still well adhered to the polycarbonate substrate, a pointed indentor was passed with pressure over the coated substrate and then the surface was investigated by SEM. Figure 4(b) shows the "scratched" area, and it is clear that the coating layer can be seen, which indicates that it is well adhered on the substrate. This increase in durability of the coating that extends from the higher cure temperatures is speculated to be due to the following two reasons: 1) A higher

TABLE 1. Adhesion Results Obtained on Selected Hybrid Coatings Spin-Coated on Polycarbonate as Determined by ASTM Test D3359 (see text for details)

	Curing temperature, °C	Adhesion (0B-5B)
Zr30-DETA	60	0 B
	125	2-3 B
	145	4-5 B
Zr50-DETA	60	0 B
	145	4-5 B
Ti50-DDS	60	0 B
	125	2-3 B
	150	5 B

TABLE 2. Results of the 180° Peel Adhesion Tape Test of Hybrid Coatings on Polycarbonate

Sample	Curing temperature, °C	Adhesion, N/m
Zr30-DETA	60	31
	125	114
	145	122
	145[a]	131
Zr50-DETA	145	133
Ti50-DETA	145	116

[a] PC surface pretreated with oxygen plasma at 100 W for 5 minutes.

curing temperature increases the cohesive strength of the coating by promoting a higher extent of reaction, and 2) when the curing temperature is close to the T_g of the polymeric substrate, the now more compliant substrate may lead to less shrinkage stresses as curing of the coating occurs.

Oxygen plasma pretreatment of the polycarbonate surfaces was also found to have a slight beneficial effect on the adhesion of the coatings. It is well known that an oxygen plasma is able to generate —COOH groups on polymeric surfaces [16]. The failure surfaces of these plasma-treated substrate systems were also observed via OM or SEM. As observed with the untreated polycarbonate surfaces described above, most of the coating appeared on the adhesive tape after the peel test with a 60°C cured sample, while most of the coating remained on the polycarbonate surface with the 145°C cured sample. However, results of the 180° peel adhesion tape test performed on two Zr30-DETA samples cured at 145°C distinctly showed an increase in adhesion on the oxygen-plaxma-treated polycarbonate surface (see Table 2).

Abrasion Resistance

The abrasion resistance values of the functionalized DDS and DETA systems with different curing temperatures and inorganic contents are shown in Figs. 5–7. Figure 5 shows the dependence of the abrasion resistance with curing temperature for the Zr50-DETA coated polycarbonate samples prepared at two different temperatures. Also shown is a polycarbonate control (uncoated) sample that had been heat treated at 150°C—this response serves as a reference to compare the abrasion resistance with the coated samples. The results clearly indicate that the optical abrasion resistance of the coating is much higher for the higher curing temperature. The effect of the added zirconium *n*-propoxide in conjunction with functionalized DETA on the optical abrasion resistance is shown in Fig. 6. The results indicate that samples with higher zirconium alkoxide contents display somewhat higher optical resistance as might be expected, but it is particularly noted that just the functionalized DETA (which therefore contains silicone alkoxy groups) provides nearly the same optical abrasion resistance as 30 and 50% of zirconium *n*-propoxide in the

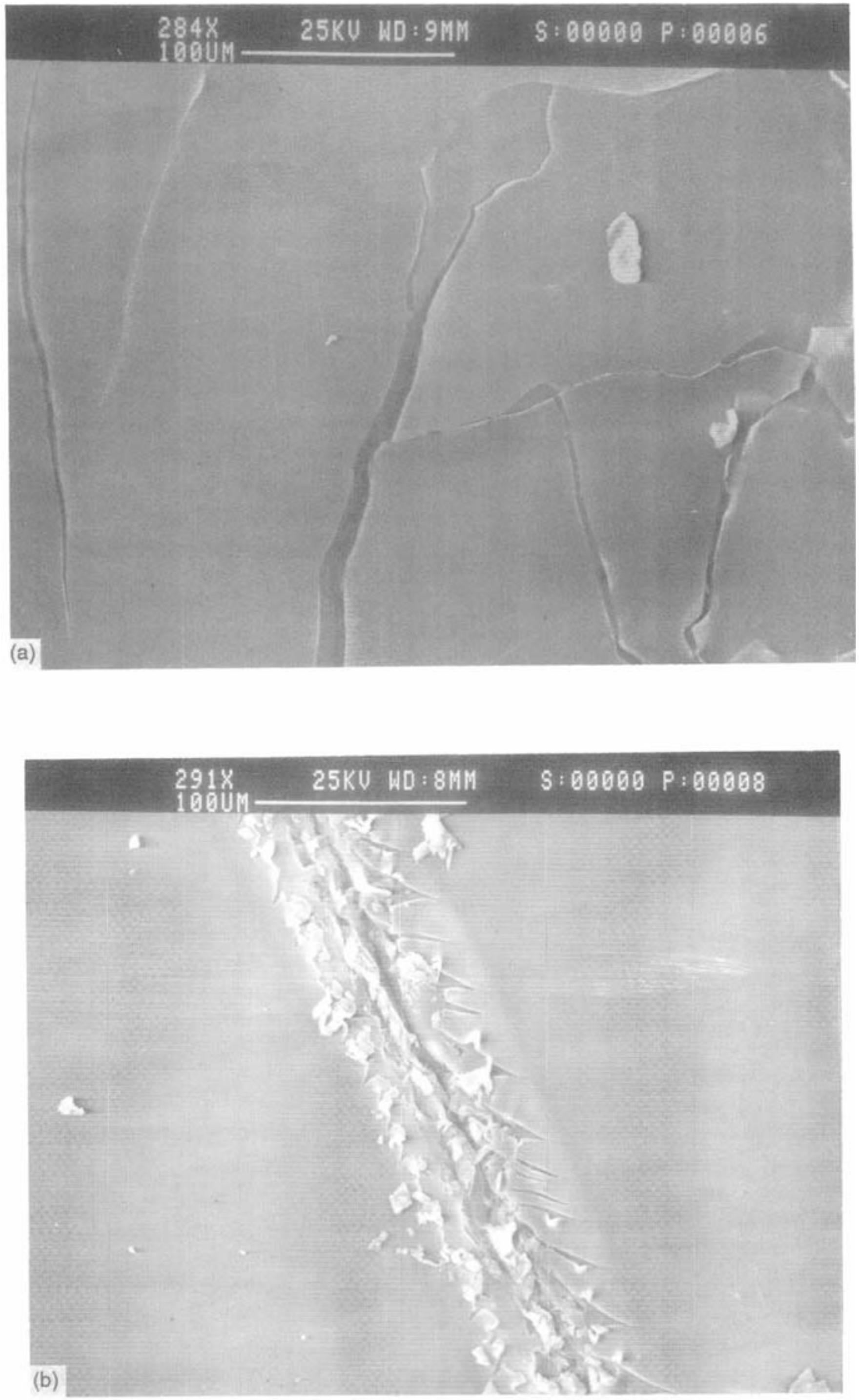

FIG. 4. SEM of Zr30-DETA coated polycarbonate. (a) Tape surface after peel for the 60°C cure sample; note coating flakes. (b) Coating surface after peel and scratch with indentor for the 145°C cured sample.

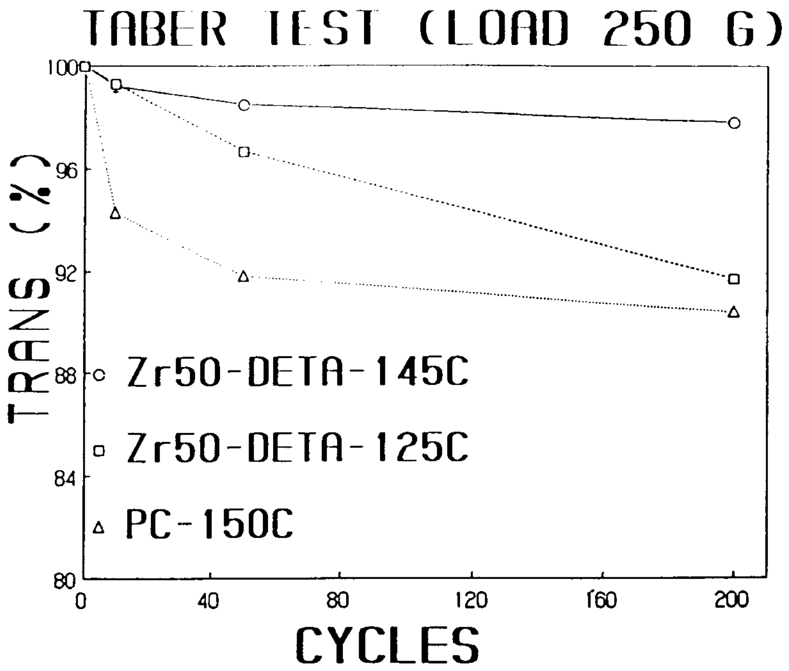

FIG. 5. Light transmittance vs number of wear cycles for Zr50-DETA coating on polycarbonate. The key provides the curing temperatures.

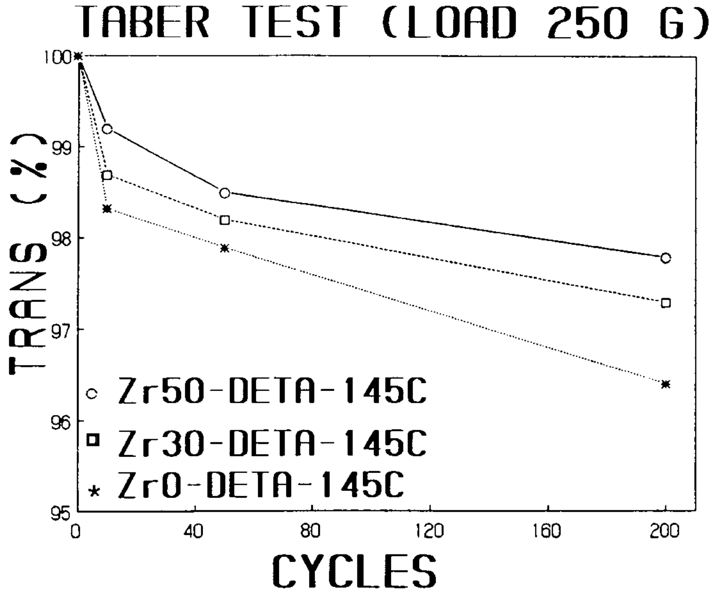

FIG. 6. Light transmittance vs number of wear cycles for Zr(X)-DETA on polycarbonate. The coating cure temperature was 145°C. X represents the initial weight percent of zirconium *n*-propoxide used relative to the weight of functionalized DETA. Note change in scale relative to Fig. 5.

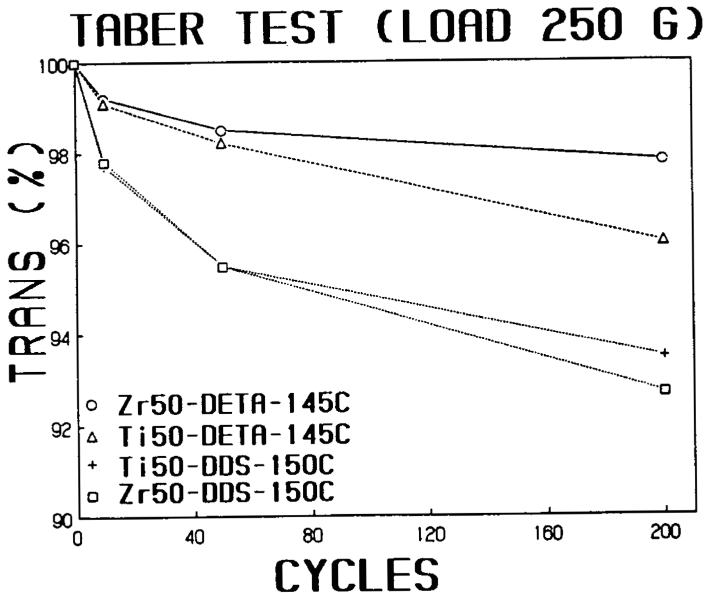

FIG. 7. Light transmittance vs number of wear cycles for Zr50-DETA, Ti50-DETA, Zr50-DDS, and Ti50-DDS on polycarbonate. The DETA coatings were cured at 145°C while the DDS coatings were cured at 150°C. Note change in scale from Figs. 5 and 6.

DETA materials. A summary of the behavior for the DETA and DDS systems is shown in Fig. 7. Based on the same 50% weight fraction of zirconium or titanium alkoxide, DETA-based-coating systems displays better optical abrasion resistance by our procedures than the corresponding DDS systems. Also, the Zr50-DETA systems perform slightly better than the Ti50-DETA systems. Further work will address the details of these differences.

CONCLUSIONS

New transparent hybrid inorganic–organic systems can be utilized as optical abrasion-resistant coatings on polymeric substrates. These coatings display promising results but the behavior is dependent on the cure temperature. The trifunctional organic DETA displays better optical abrasion resistance than the bifunctional DDS system. In addition, the level of adhesion can be improved by a prior oxygen plasma pretreatment of the substrate. Further work is continuing to investigate additional features of the structure–property response of these coatings.

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