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SYNTHESIS AND CHARACTERIZATION OF NEW ALUMINA AND TITANIA-CONTAINING HYBRID NETWORK CERAMER MATERIALS FROM SOL-GEL PROCESSING

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ABSTRACT

Transparent hybrid materials have been prepared by incorporating either an alumina or titania alkoxide sol with triethoxysilane endcapped polytetramethylene oxide (PTMO) oligomer. In order to avoid undesirable precipitation after the addition of water, a β-dicarbonyl ligand, ethyl acetoacetate, was used. Triethoxysilane endcapped polytetramethylene oxide with a molecular weight of 2000 (g/mol) was chosen to react with either the alumina or titania sol to demonstrate the features of the reaction scheme. The extent of reaction leading to network formation has been qualitatively followed by infrared spectroscopy. A series of solid films were prepared by varying the molar ratio of either aluminum tri(*sec*-butoxide) or titanium tetraisopropoxide to ethyl acetoacetate, and the weight fraction of alumina or titania to that of PTMO. The refractive index as well as the general structure–property behavior of these hybrid materials were studied.

INTRODUCTION

A novel route of preparing organic/inorganic hybrid network materials has been developed by the sol-gel approach [1–4]. As reported in previous publications from this laboratory, these novel hybrid sol-gel materials, which can be made transparent, exhibit interesting structure-property behavior. To date, tetraethoxysilane (TEOS) has been employed in most cases as the inorganic component due to its relatively slow and controllable rate of reaction (hydrolysis/condensation). Triethoxysilane capped poly(tetramethylene oxide) (PTMO) has been generally used as the organic oligomeric compound. However, this combination by no means limits the possibility of preparing other types of hybrid systems as has been discussed elsewhere [5].

Guglielmi and Carturan have pointed out that hydrolysis is the main step in the transformation of metal alkoxides to oxides [6]. From this point of view, the facility of these alkoxides to undergo hydrolysis is the most important factor for their success as precursors of the sol-gel process [6]. In addition, the rate of hydrolysis is also crucial in sol-gel processing [6–8]. In order to obtain a clear sol for these nonorganic-containing metal alkoxide systems based on aluminum, titanium, zirconium—all three of which show a relatively fast hydrolysis rate—chelating ligands such as glycols, organic acids, and β-dicarbonyl ligands have been utilized to control the reaction rates [6]. It is well known in coordination chemistry that multidentate ligands have a higher formation constant with the metal center than the monodentate ligands in a similar environment. The entropy effect also favors multidentate systems from a thermodynamic point of view [8]. After forming a complex with the chelating ligand, the species between metal and chelating agent is less easy to hydrolyze [8]. By controlling the ratio of metal alkoxide to chelating ligand and the amount of water which promotes hydrolysis, one should be able to obtain a clear sol. Based on the complex formation of acetylacetonate or acetate with titanium alkoxide, the hydrolysis rate can be slowed down so that no precipitation appears and homogeneous sols or gels can be obtained according to LaCourse and Livage [10, 11]. Also, infrared spectroscopy studies indicate that the interaction between acetylacetonate and acetate to titanium is bidentate [11].

By using the β-diketone chelating approach, a series of new systems based on aluminum tri(*sec*-butoxide) or titanium tetraisopropoxide coupled with triethoxysilane-capped PTMO has been prepared in this laboratory, as will be discussed. The β-dicarbonyl ligand, ethyl acetoacetate (EACAC), has been used to modify these metal alkoxides and produce a clear sol after hydrolysis and partial condensation. EACAC has been chosen because it shows better solubility in our systems than acetylacetone. In this study, several variables, including the ratio of EACAC to metal alkoxide and the organic/inorganic composition, have been investigated. The coordination of aluminum and titanium with EACAC and the formation of M—O—Si linkages, where M represents the metal species, were studied by infrared spectroscopy. Following the preparation of these materials, the structures of the final materials were also studied by using small-angle x-ray scattering (SAXS). Furthermore, the stress-strain and dynamic mechanical behavior, as well as the refractive index of these new hybrid systems, were also measured.

EXPERIMENTAL

Materials

Aluminum tri(*sec*-butoxide) ($Al(OBu)_3$) and ethyl acetoacetate (EACAC) from Aldrich Chemical and titanium tetraisopropoxide ($Ti(OPr)_4$)) from the Akzo corporation were used without further purification. Hydroxyl endcapped PTMO of molecular weights 650 and 2000 g/mol were obtained from Polyscience Inc., while 3-isocyanatopropyltriethoxysilane from Petrarch Systems was used to cap the hydroxyl functionalized PTMO systems.

Procedure

i) Alumina-Based Sol. $Al(OBu)_3$ was first mixed with isopropanol (IPA) using a molar ratio of 1:10, then an appropriate amount of EACAC (depending on the Al/EACAC ratio desired) was added to the solution. The mixture was stirred for 30 min followed by addition of deionized water using a molar ratio of 1:1 with respect to $Al(OBu)_3$. The resulting solution was stirred for another 60 min, then a clear alumina based sol was formed.

ii) Titania-Based Sol. $Ti(OPr)_4$ was mixed with IPA using a molar ratio of 1:10. Then an appropriate amount of EACAC (depending on the Ti/EACAC ratio desired) was added to the solution, at which point a yellow color developed. Denionized water was added to the system after stirring for 30 min (molar ratio of 1:1 with respect to metal alkoxide). The solution was stirred continuously for another 30 min, which led to a clear yellow titania-based sol.

iii) Triethoxysilane-Endcapped PTMO. The procedure of preparing these materials was similar to that previously reported [4]. First, a 1:1.06 equivalent molar ratio of PTMO to 3-isocyanatopropyltriethoxysilane was mixed in a three-neck round-bottom flask under nitrogen. This system was stirred and maintained at a constant temperature of 60°C. Infrared spectroscopy was used to monitor the extent of reaction by following the reduction of both the isocyanate (2270 cm^{-1}) and hydroxyl (3500 cm^{-1}) groups, which disappeared eventually with the formation of the urethane linkage (3350 cm^{-1}) and carbonyl group (1725 cm^{-1}). The reaction was continued for at least 5 days to ensure the completion of endcapping.

iv) Al/EACAC-PTMO and Ti/EACAC-PTMO Hybrid Materials. An appropriate amount of triethoxysilane endcapped PTMO (depending on the weight ratio under study) was added to the alumina-based sol or titania-based sol and stirred for 3–5 min. The final solution was cast into polystyrene petri dishes and covered for further drying and curing at room temperature. Films were removed from the dishes after 3 days, and the drying procedure was continued for at least 3 more days at ambient conditions prior to testing.

Characterization

Infrared spectra were obtained by using a Nicolet 5DXB FTIR spectrometer. Alumina (Al/EACAC) and titania (Ti/EACAC) based dried gels were ground with KBr and then pressed into pellets. These Al/EACAC–PTMO and Ti/EACAC–PTMO networks were prepared by direct casting of the sols onto a NaCl window. The refractive index was determined on 2–3 mil films of the final solid materials by using a Reichert ABBE Mark II refractometer at room temperature (sodium line). Dynamic mechanical experiments were performed by using an automated Rheovibron DDV-III dynamic viscoelastometer at an operating frequency of 11 Hz. The temperature range studied was from −100 to 200°C at a heating rate of 1–2°C/min. Small-angle x-ray scattering (SAXS) was measured by using a Kratky camera (Anton-Paar) in conjunction with a Braun position sensitive detector from Innovative Technology Inc. The absolute smeared scattering intensity of the sample was plotted vs the scattering variable, s, which is defined as

$$s = 1/d = 2 \sin \Theta/\lambda$$

where d is the pseudo-Bragg spacing which can be used to estimate the correlation distance between regions of comparable electron density. Θ is one-half of the radial scattering angle, and λ is the wavelength utilized (1.54 Å).

Stress-strain experiments were carried out with an Instron 1122 model at a crosshead speed of 2 mm/min. Samples were cut by using a dogbone die with an initial gauge length of 10 mm and 2.6 mm width. All species were tested at 25 ± 2°C. Young's modulus, stress at break, and strain at break were determined for four to six specimens of each composition. The mean and standard deviation of these test results are reported.

Extraction

To gain information on any remaining unincorporated sol fraction, the Al/EACAC–PTMO and Ti/EACAC–PTMO dried gels were extracted with methylene chloride (HPLC grade) in a Soxhlet apparatus for 48 h.

Nomenclature

The format for sample designation is illustrated in Table 1 for both the alumina and titania systems. The loading of the "inorganic" component (metal alkoxide) is expressed as a percentage of the total weight of the metal alkoxide and oligomeric component used. However, two other quantities are also important in defining the system: (i) the molar ratio of metal alkoxide to EACAC and (ii) the molecular weight to PTMO.

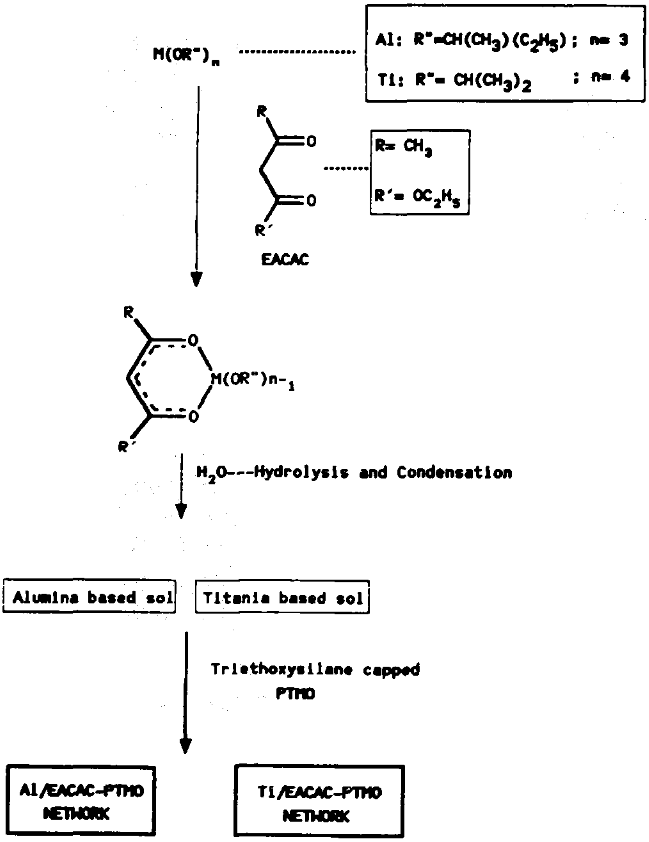
RESULTS AND DISCUSSION

The Network Reaction of the Al/EACAC–PTMO and Ti/EACAC–PTMO Systems

The mechanism of forming a coordination complex between either aluminum or titanium alkoxide with EACAC is shown in Scheme 1. As

TABLE 1. Nomenclature Used for Describing the EACAC Hybrids: [x] M/EACAC (y)–PTMO (z)-w-a

Notation	Description
[x] M/EACAC	x is the molar ratio of the metal (M) to EACAC (mol)
(y)	Wt% of metal alkoxide used
PTMO (z)	Functionalized oligomer (molecular weight)
w	Percentage of stoichiometric amount of water to the alkoxide
a	Molar ratio of the acid (HCl) to the alkoxide


M(OR")n
Al: R"=CH(CH3)(C2H5) ; n= 3
Ti: R"= CH(CH3)2 ; n= 4
R
R'
R= CH3
R'= OC2H5
EACAC
M(OR")n-1
H2O---Hydrolysis and Condensation
Alumina based sol
Titania based sol
Triethoxysilane capped PTMO
Al/EACAC-PTMO NETWORK
Ti/EACAC-PTMO NETWORK

SCHEME 1.

expected, the formation of this complex is an exothermic reaction for both alumina and titania systems and occurs rapidly after mixing the metal alkoxide with EACAC. The β-dicarbonyl group chelates to the metal center as a bidentate complex. The infrared spectra provides strong evidence for the formation of these bidentate complexes. The strong band of a doublet showing the free EACAC carbonyl vibration in the range of 1710–1750 cm^{-1} is not observed in the spectra for either the Al/EACAC gel or the Ti/EACAC gel. Two new bands due to the carbonyl and the C=C of the enolic form are present at 1628 and 1523 cm^{-1}, respectively. These results agree with previous literature reports [15, 16].

The general hydrolysis and condensation that takes place after adding the water to these systems is also shown in Scheme 1. Following hydrolysis and condensation, a clear viscous sol is formed. The molar ratios of aluminum alkoxide to EACAC used were in the range of 1–2. When the ratio is greater than 2, precipitation is observed after adding a 1:1 mole ratio of the aluminum alkoxide-containing system to water. When the ratio of titanium isopropoxide to EACAC is greater than 0.8, precipitation also occurs after adding a 1:1 mole ratio of water to the system. If the molar ratio of water to either titanium or aluminum is greater than 2, undesirable precipitation occurs for both systems. The infrared spectra of both the aluminum and titanium gels indicate that the EACAC component is chelated to the metal center.

The M (Al or Ti)/EACAC–PTMO ceramer network is formed after mixing either the alumina or titania-based sol with the triethoxysilane-capped PTMO. For the Al/EACAC–PTMO system, infrared absorption peaks at 1070 and 1040 cm^{-1} are observed as shown in Fig. 1. There is no absorption for these bands for the triethoxysilane-capped PTMO or Al/EACAC components. These new bands are believed to be due to the Si—O—Al linkage, which is in agreement with that reported in the literature [17]. For the Ti/EACAC-PTMO system, a peak at 920 cm^{-1} is observed as shown in Fig. 2. Neither tri-ethoxysilane-capped PTMO nor the Ti/EACAC component displays this absorption in the respective infrared spectrum. Therefore, this peak is believed to be due to the Si—O—Ti linkage, an assignment that again agrees well with that reported in the literature for the Si—O—Ti bond [18, 19]. A suggested schematic of the generalized Al/EACAC–PTMO network is shown in Fig. 3; a similar network is postulated for Ti/EACAC–PTMO. Clearly this illustration is oversimplified, but it assists in picturing the generalized network formed.

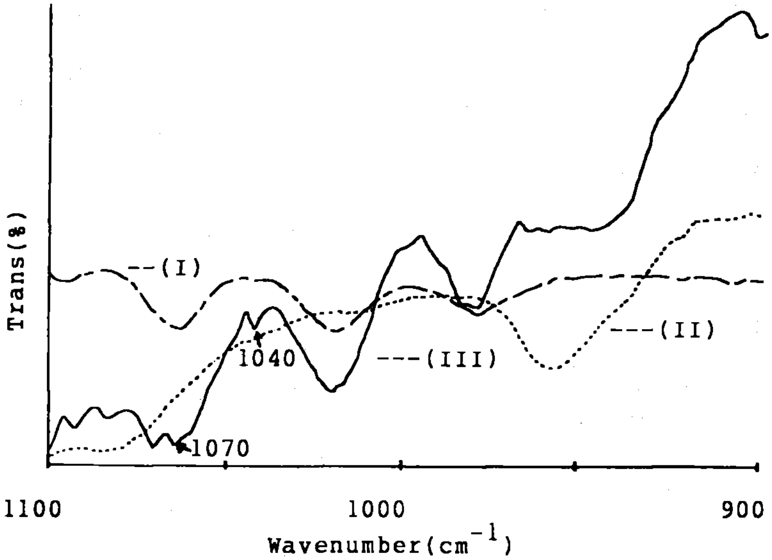


FIG. 1. IR spectra of (I) Al/EACAC based sol; (II) triethoxysilane capped PTMO; (III) final Al/EACAC-PTMO network material.

These final network products were surveyed by extraction. For the Al/EACAC systems, when the Al/EACAC ratio was 1.0, an 18–20% weight loss was observed. Systems with an increased Al/EACAC ratio from 1.5 to 2.0 had a lower weight loss of 14–16 to 10–12%, respectively. Analysis of the extractants by infrared spectroscopy shows that most peaks match the spectra of the Al/EACAC component. A much lower absorption band around 3500 cm^{-1} (due to some Al—OH groups), which has a much lower intensity, suggests that most of the extractables are likely cyclic products from a side reaction. In contrast to the Al/EACAC systems, only a 1–3% weight loss is observed following extraction for the Ti/EACAC system. This lower content of extractables is tentatively believed to arise from the fact that titanium possesses a valence of four while aluminum is only three. With the chelating agent EACAC, it is more probable for the aluminum system to form a cyclic product than it is for the titanium system, thereby leaving no reactive site for these Al/EACAC cyclics. Therefore, network formation is believed to be more facilitated for the titanium systems than for the aluminum systems.

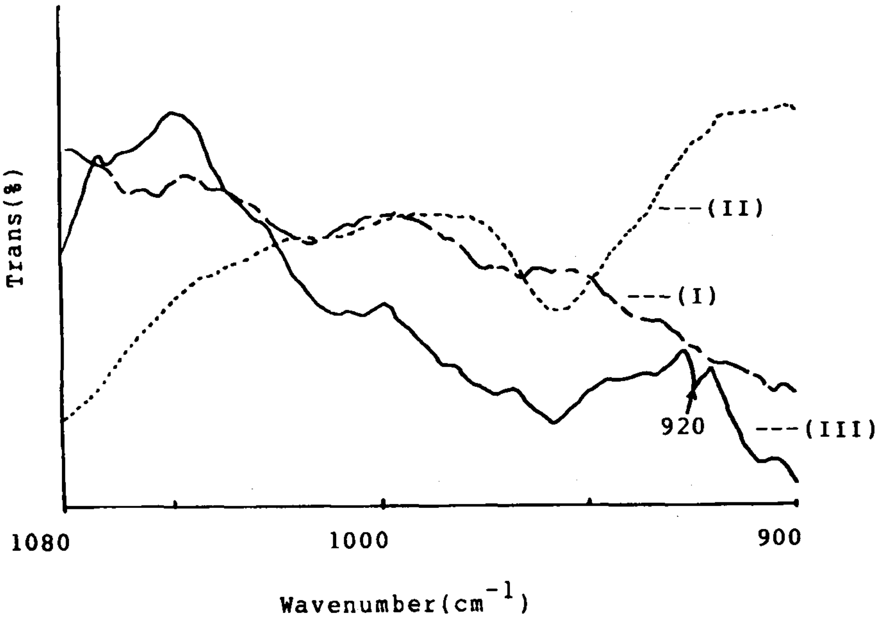


FIG. 2. IR spectra of (I) Ti/EACAC based sol; (II) triethoxysilane capped PTMO; (III) final Ti/EACAC-PTMO network material.

Optical Properties of the Al/EACAC-PTMO and Ti/EACAC-PTMO Networks

All the materials produced in these studies are in the form of transparent films (∿2-10 mils), which indicates the absence of large-scale phase separation or precipitation of any component. Photographs of typical samples are shown in Figs. 4(a) and 4(b) for the Al/EACAC-PTMO and Ti/EACAC-PTMO network systems, respectively. The light yellow color observed for the titania systems is believed to be due to either a charge transfer between titanium and EACAC, an intervalence charge transfer between Ti^{3+} and Ti^{4+}, or a combination of these two cases [14].

The refractive index of the films is found to increase with an increasing weight fraction of the inorganic component for both systems, as would be expected. By plotting refractive index vs weight percent of Al/EACAC-PTMO or Ti/EACAC-PTMO, where it is assumed that the condensation reaction goes to completion, a linear relationship is obtained for either system-see Figs. 5 and 6. For the Al/EACAC systems,

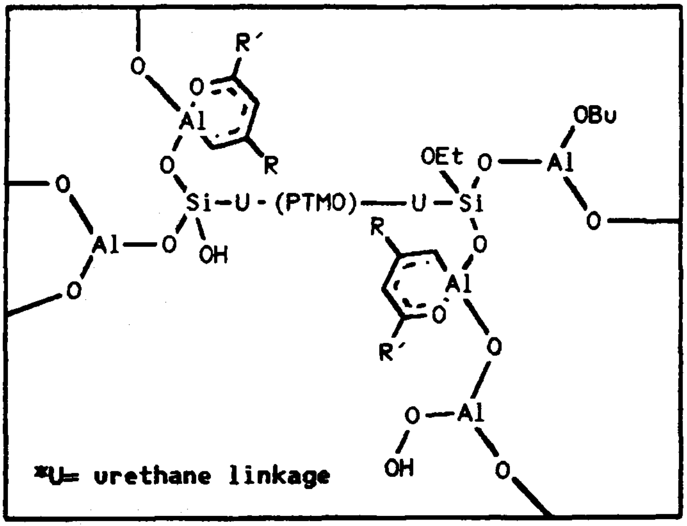


FIG. 3. Simplified schematic for the Al/EACAC–PTMO hybrid network.

the values range from 1.459 to 1.491 for the different weight fractions of Al/EACAC composition. Compared to the Al/EACAC–PTMO systems, the Ti/EACAC–PTMO systems display much higher values of refractive index, as would be expected based on the properties of titanium oxides. The values of these refractive indices increase from 1.45 to 1.64 with an increasing weight fraction of the Ti/EACAC component as shown in Fig. 6.

Structure–Property Behavior of the Hybrid Materials

The dynamic mechanical spectra of a series of samples with three different Al/EACAC ratios are shown in Fig. 7. The data illustrate that at temperatures below −80°C, the hybrid materials are clearly in the glassy state with a modulus that corresponds to this regime, ∿1 GPa. However, the materials then begin to soften, but over a wide temperature range beginning near −80°C. This is illustrated by the tan δ response where the molecular dispersion ends at about 0°C for the highest Al/EACAC ratio and is considerably broader for the system with the highest EACAC content. The initiation of dispersion at −80°C extends from the PTMO component where it begins to undergo its glass transition. However, due to the great width of the relaxation, which extends from −80 to 0°C,

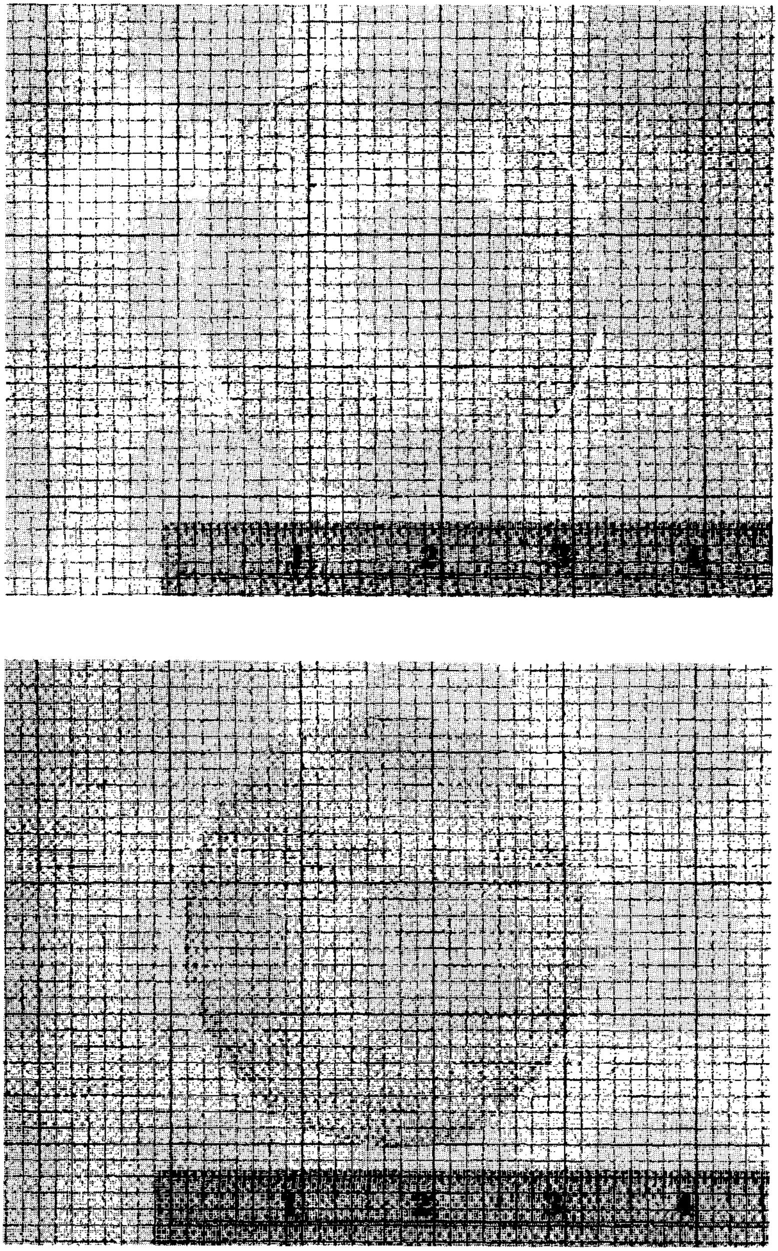


FIG. 4(a) (top): Photograph of a [2] Al/EACAC(50)–PTMO(2K)-33-0 hybrid material. 4(b) (bottom): Photograph of a [0.8]Ti/EACAC(50)–PTMO(2K)-25-0 hybrid material.

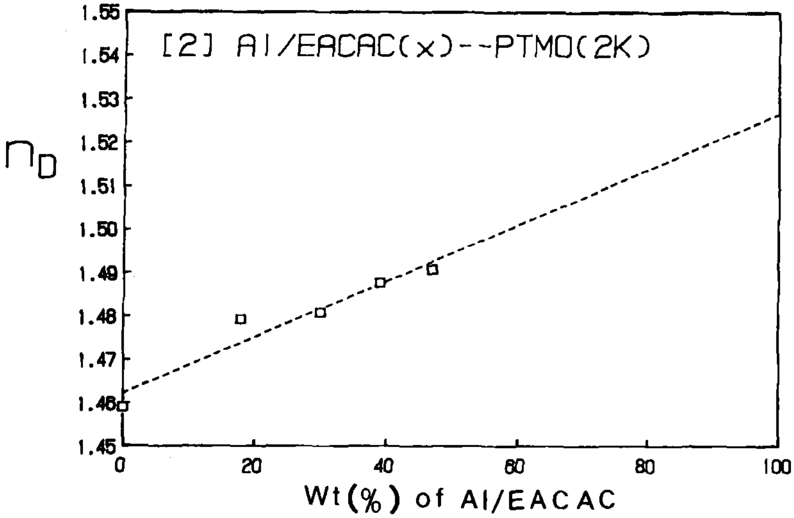


FIG. 5. Refractive index vs weight fraction of Al/EACAC in the Al/EACAC-PTMO hybrid systems.

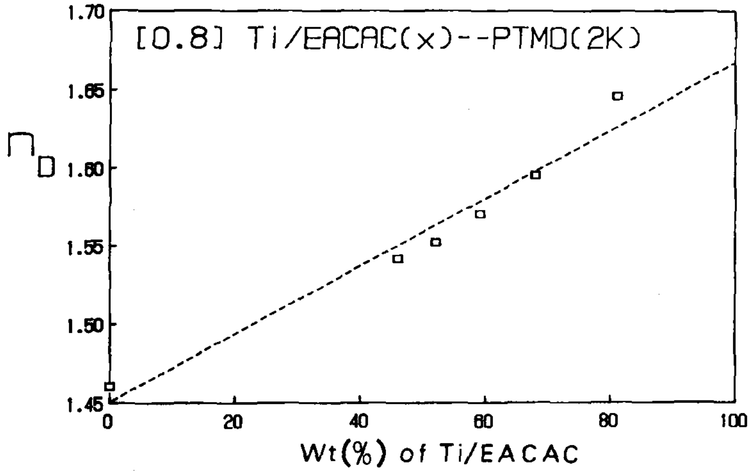


FIG. 6. Refractive index vs weight fraction of Ti/EACAC in the Ti/EACAC-PTMO hybrid systems.

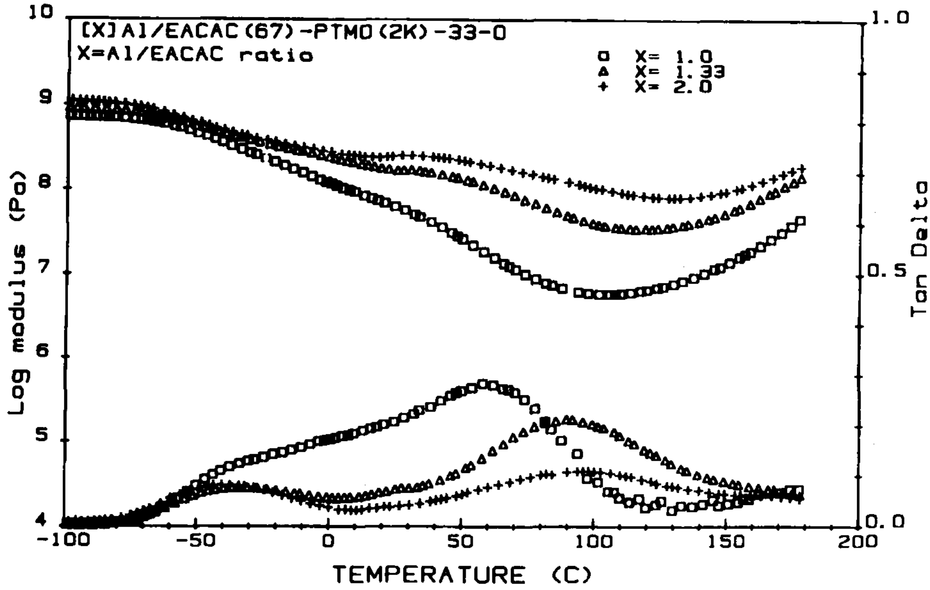


FIG. 7. Storage modulus and tan δ spectra of three Al/EACAC-PTMO systems with various ratios of aluminum alkoxide to EACAC.

these results clearly suggest that some level of mixing occurs between the PTMO and the inorganics. This further restricts mobility of the PTMO chains and raises the glass transition temperature accordingly (pure endlinked PTMO of this molecular weight would illustrate a glass transition tan δ peak at about −70°C for a frequency of 11 Hz) [4].

Another notable feature of the storage modulus curves in Fig. 7 is a distinct upturn in the range of 90 to 170°C. This behavior can be accounted for on the basis of further development of the network (i.e., curing) with higher temperature. Similar trends have been observed in related systems based on silicon alkoxides studied in this laboratory [2].

Increasing the level of EACAC gives a correspondingly higher loss behavior, as indicated by the tan δ behavior. This can be explained either as the result of a poorly developed network or the existence of a low molecular weight species acting as a platicizer within the matrix. The reader will recall that the extractables from the Al/EACAC-PTMO hybrids are believed to be cyclic by-products of the Al/EACAC-based component. The dynamic mechanical behavior of the extracted sample indicates that the removal of this by-product does not influence the

PTMO-rich regions nearly (∼ − 80 to ∼0°C) as much as the Al/EACAC-based phases (∼20 to 170°C). There is a slight decrease and shift to a higher temperature for the molecular loss in the PTMO phase, whereas the loss dispersion at the higher temperature range, ∼20 to 170°C, is practically eliminated altogether for the extracted sample.

To gain further information on the structural features of these materials, the SAXS behavior of the same three systems are shown in Fig. 8. A broad maxima is observed in each of the scattering curves obtained for the three different Al/EACAC ratios, with the angular dependence and intensity not being greatly different for the three traces. The peak in these respective scans, which occurs at a value of s of ∼0.10 nm^{-1}, clearly indicates a correlation length of approximately 100 Å (based on the smeared SAXS data). This result is also expected on the basis of our earlier studies of TEOS-PTMO systems with a comparable PTMO weight fraction and molecular weight [2-4]. This general correlation

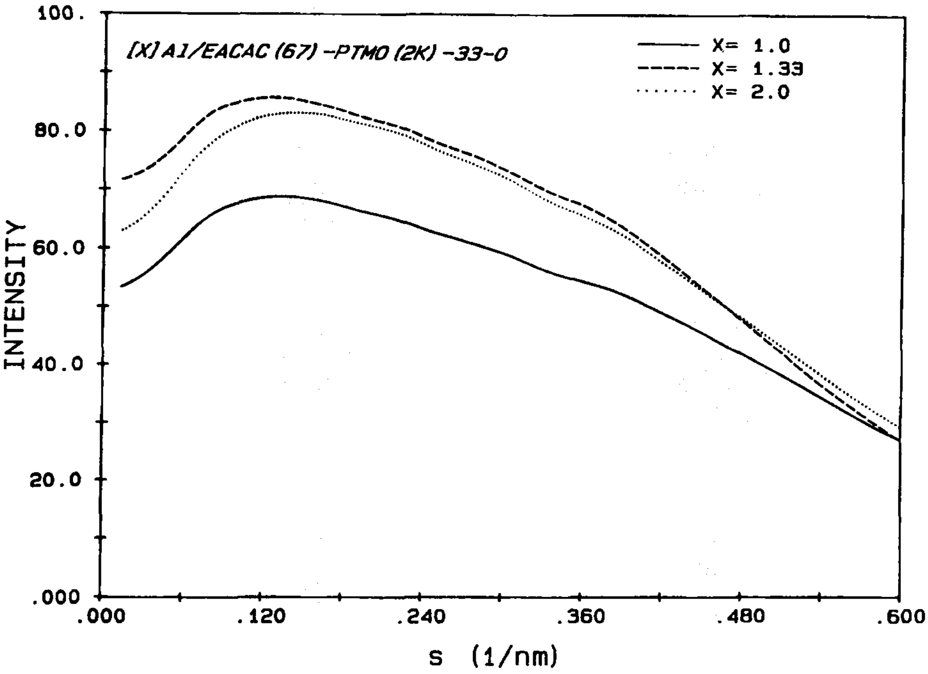


FIG. 8. SAXS scans of three Al/EACAC-PTMO systems with various ratios of Al/EACAC.

length relates to the average periodicity between regions of comparable electron density, as has been discussed in some of our previous papers [1–3]. However, the considerably greater breadth of the SAXS peaks for the Al/EACAC systems strongly suggests there are some distinct differences in structural behavior. In fact, a much greater degree of mixing of the components on a smaller dimensional scale is indicated, although it is not periodic in nature.

In view of the dynamic mechanical data, it would appear that the systems with greater amounts of EACAC may have poorer network development. Thus these materials were extracted with methylene chloride to determine if any solubles existed. In the earlier discussion it was shown that as the EACAC content increased, the extractables ranged from 10–12% up to 18–20% weight loss. The extent to which the extraction influences either the structure or related dynamic mechanical properties is illustrated in Figs. 9 and 10, respectively. As noted from Fig. 9, the SAXS

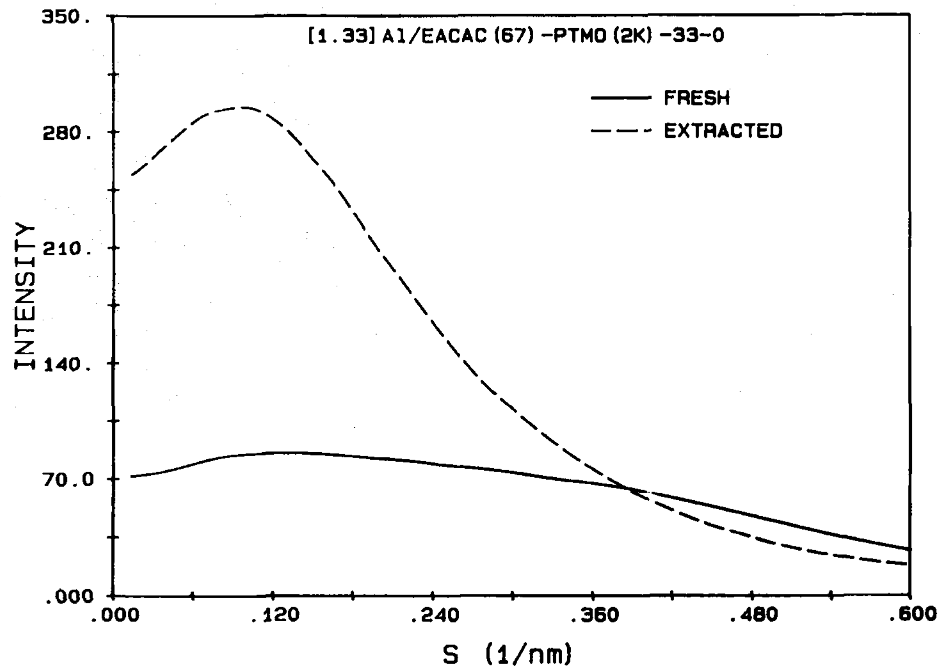


FIG. 9. SAXS behavior for the unextracted sample of [1.33]Al/EACAC(67)-PTMO(2K)-33-0 network material as well as the extracted form.

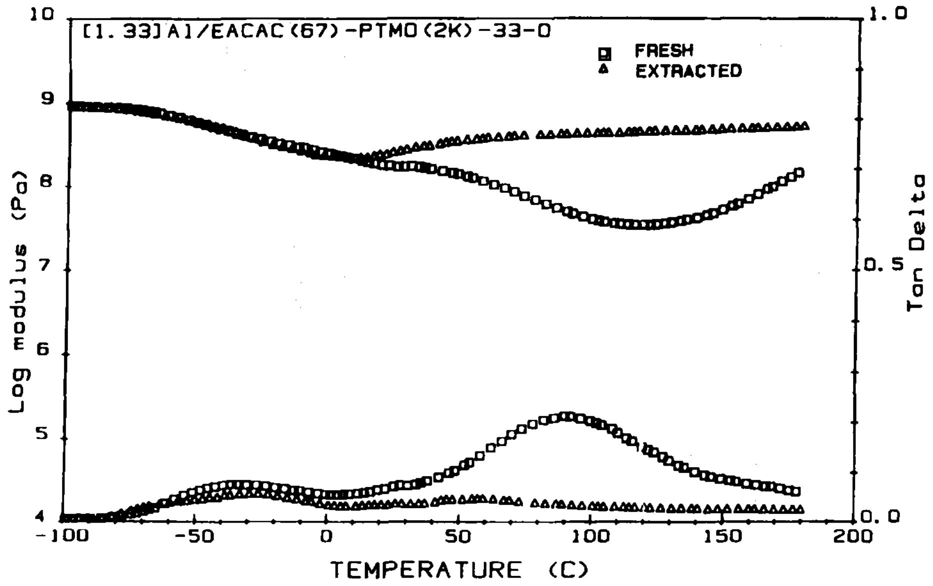


FIG. 10. The dynamic mechanical behavior for [1.33]Al/EACAC(67)-PTMO(2K)-33-0 network material and its extracted counterpart.

results for the extracted materials clearly indicate a more well-defined peak in the scattering curve with a considerably higher intensity. This scattering behavior implies a much greater constrast between the richer inorganic and richer organic phases. The tail of the scattering curve even drops below that of the unextracted material. Collectively, these features strongly indicate that the extractables likely resided somewhat uniformly in the matrix of the PTMO, thereby raising its electron density and causing lower contrast and therefore less scattered intensity. In fact, the SAXS curve from the extracted sample is very much in agreement with those seen from previous hybrid materials made with silicon alkoxides except for the fact that the scattered intensity is higher in the alumina-based systems, as would be expected due to its higher electron density.

Turning to Fig. 10, one also sees that the extracted materials show a loss dispersion behavior associated with the glass transition of the PTMO component. That again suggests some partial mixing with the inorganic (note the dispersion beginning at −80°C and extending to about 0°C). However, following this dispersion there is relatively little magnitude to tan δ, with the modulus only increasing somewhat above room temperature as some further curing takes place with heating. In fact, the extracted sample shows a considerably higher modulus than the unextracted material since the extracted network shows a higher level of crosslinking on a per unit volume basis. Hence, the results of the respective SAXS and dynamic mechanical studies on the extracted and unextracted samples clearly support the view that the by-products serve somewhat as plasticizers and are probably responsible for the difference in properties and altered structure.

The stress-strain behavior (Fig. 11) of a cast sample with an Al/EACAC ratio of 1.33 mixed with 33% of the 2000 g/mol oligomers of PTMO undergoes a sharp decrease in ultimate elongation following extraction with methylene chloride. Along with the decrease in overall elongation, the material no longer exhibits any yield behavior. This supports the concept of poorer network formation due to the presence of a loosely bonded species and/or some plasticization, i.e., extraction of the by-product leaves a less ductile material.

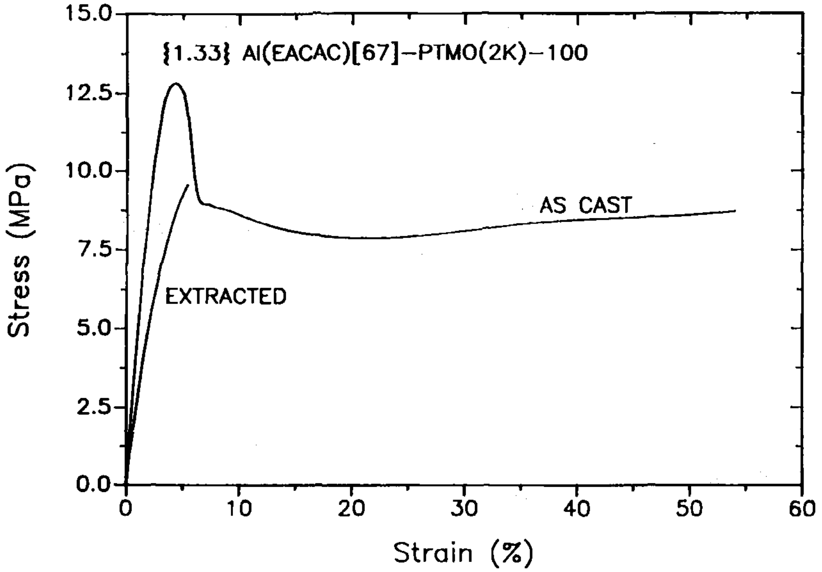


FIG. 11. The stress-strain behavior for the network material [1.33]Al/EACAC(67)-PTMO(2K)-33-0 and its extracted counterpart.

In contrast to the Al/EACAC systems, the Ti/EACAC materials were shown earlier to have very low extractables, e.g., on the order of 1 to 3 wt%. Indeed, looking at the dynamic mechanical results from the unextracted material for two different Ti/EACAC ratios (see Fig. 12), one notes that there is a response rather similar to the extracted Al/EACAC system in that there is principally only a glass transition dispersion of considerable breadth that begins at approximately −80°C and extends to about 0°C. There also seems to be some enhancement of this dispersion at lower temperatures, likely caused by even sharper phase separation of the PTMO component, i.e., less mixing with the inorganic species. There is a lower temperature dispersion at about −120°C which arises from the rotational features of the tetramethylene linkage in the PTMO component, as expected [20]. One also notes that there is some degree of loss behavior above 0°C; a portion of that dispersion is a result of some additional curing that takes place with further heating, but this is of relatively small magnitude and is as expected since the modulus is nearly constant up to ∿175°C as shown. Also, even at high temperatures the

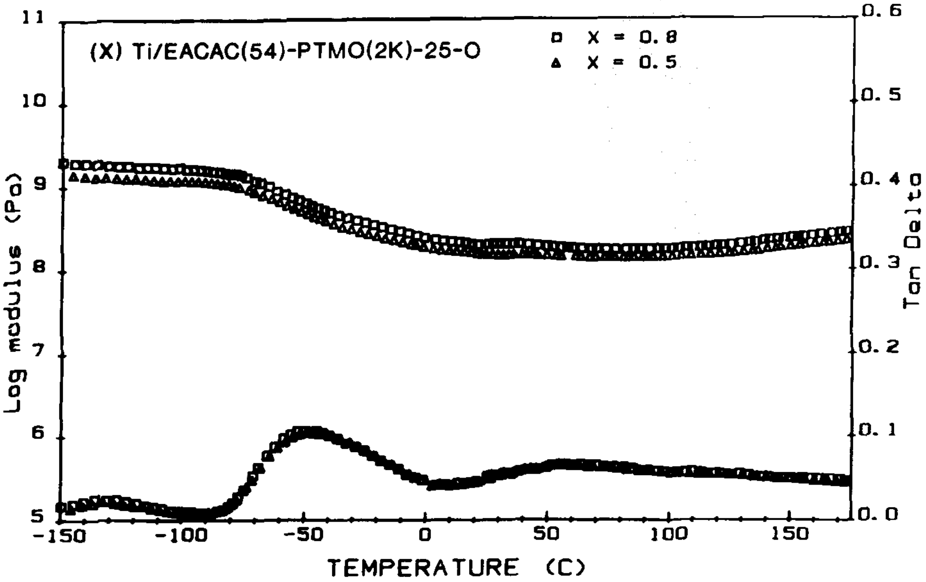


FIG. 12. Effect of the Ti/EACAC ratio on the dynamical mechanical behavior of Ti/EACAC–PTMO hybrid networks.

modulus level is near that of a polymeric glass material, implying that there is considerable network structure developed within this hybrid system. Addressing the SAXS results shown in Fig. 13, one again notes a distinct maxima that provides a correlation length of the order of 100 Å as observed before for other hybrid systems. The level of SAXS intensity is also expected to be high, based on the high electron density of the titanium component. The fact that the scattered intensity does not rapidly decrease following the maxima also suggests that some level of mixing still does occur between the organic and inorganic components. This can help explain the broader dispersion of the glass transition response of the PTMO as discussed in previous publications [1, 2].

Figure 14 provides the stress-strain behavior of the titania-based hybrids for two different Ti/EACAC ratios. These results, as determined at ambient temperature, indicate that a reasonable level of elongation can

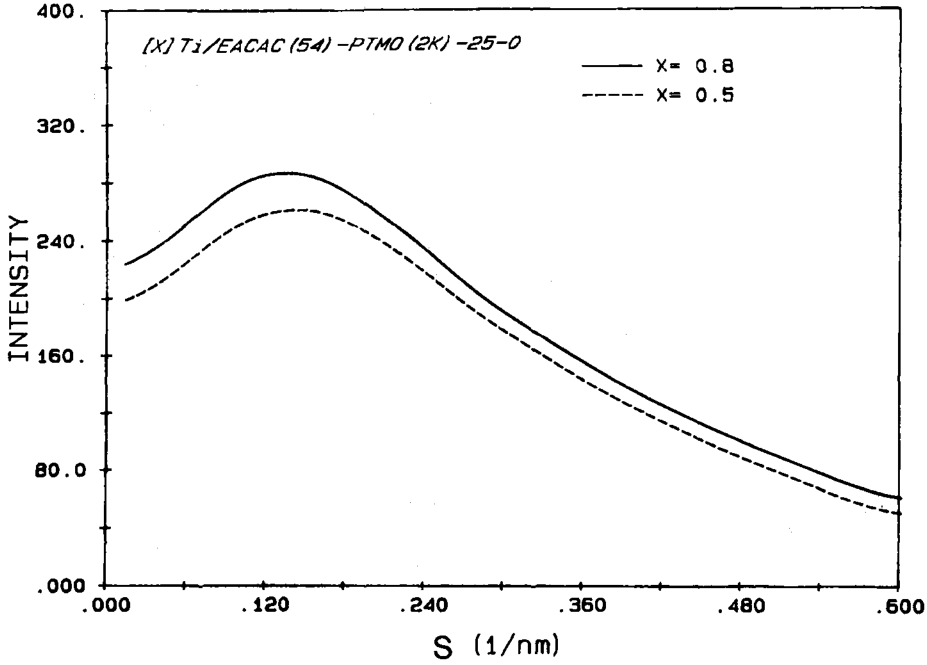


FIG. 13. SAXS scans of the Ti/EACAC-PTMO hybrid network systems with various ratios of Ti/EACAC.

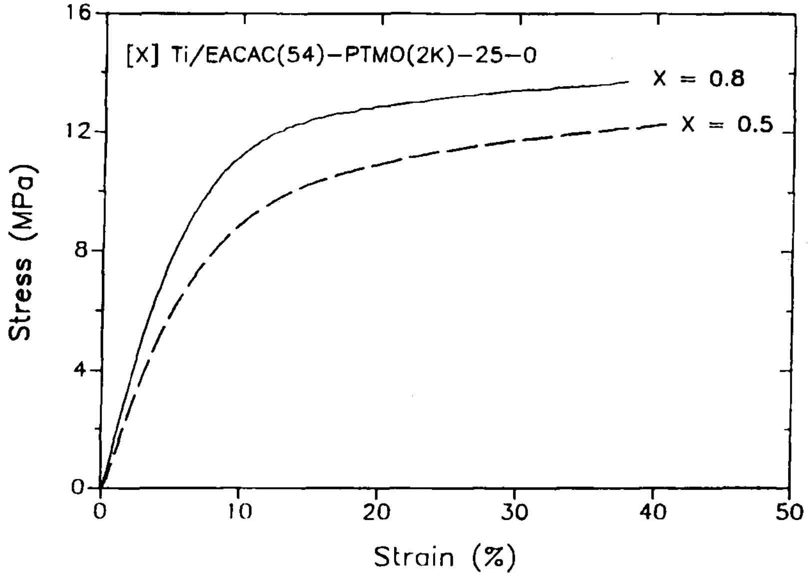


FIG. 14. Effect of the Ti/EACAC ratio on the stress-strain behavior for the Ti/EACAC-PTMO hybrid network systems.

be reached prior to failure with a substantial tensile strength of over 10 MPa. As expected, as the ratio of Ti to EACAC increases, the corresponding modulus and tensile strength are also enhanced, as would be anticipated due to the increased content of the inorganic network component.

CONCLUSION

In summary, a new route to prepare Al/EACAC-PTMO hybrid materials by using the sol-gel scheme has been successfully developed. Transparent films of these systems can be produced in a manner similar to the previous TEOS-PTMO systems described elsewhere [1-4]. However, the existence of unreacted Al/EACAC-based cyclic by-products does influence the final structure-properties response, but these components can be eliminated by solvent extraction. In contrast, much lower extractable hybrid systems can be prepared based on the Ti/EACAC-PTMO materials, with these systems illustrating no need for extraction. These latter systems are also of comparable structure to those discussed in earlier publications based on silicon alkoxide materials with similar endcapped PTMO components. Utilization of titanium alkoxide leads to materials that provide a higher refractive index, as would be expected. Efforts are underway to explore this area in more detail as a means of generating high transparency high refractive index flexible films, fibers, and coatings by utilization of other higher refractive index polymeric/oligomeric components.

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