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Ceramers: Hybrid Materials Incorporating Polymeric/Oligomeric Species with Inorganic Glasses by a Sol-Gel Process

2. Effect of Acid Content on the Final Properties

Hao-Hsin Huang, Bruce Orler, and Garth L. Wilkes*

Department of Chemical Engineering and Polymer Materials and Interfaces Laboratory,
Virginia Polytechnic Institute and State University, Blacksburg, VA 24061-6496, USA

ABSTRACT

A sol-gel process has been successfully utilized to produce hybrid materials incorporating polymeric/oligomeric components of polydimethyl siloxane(PDMS) with silicon glasses. All the samples made were transparent and flexible. Dynamic mechanical studies indicate that a portion of the siloxane species is phase-separated while the remainder is well dispersed. The effect of acid content were proven to be significant on the dispersion of the siloxane components and on the structure and properties of final products.

INTRODUCTION

The chemical reactions of the sol-gel process were reported almost two decades ago[1], and this technique has since gained increasing interest. Instead of fusing metal oxides under high temperatures, glasses can now be produced by reacting metal alkoxides with water followed by pyrolysis at relatively low temperatures. The structure of the final product is comparable to those made by conventional methods[2-4]. Besides the feature of low temperature synthesis, the sol-gel process makes it possible to produce glasses with high purity and high homogeneity. Furthermore, some of the multicomponent systems which cannot be made by conventional methods due to crystallization can now be produced[2]. Although shrinkage and fracture during the curing process limit the widespread application of this technique, some success has been achieved recently in producing monolithic solids by controlling the diffusion rate of volatile components in the system[5].

The general scheme for the sol-gel process is a hydrolysis reaction of metal alkoxides followed by a polycondensation reaction to form a three dimensional network. Due to the nature of this chemistry, it seems possible to incorporate some polymeric or oligomeric species into the glass network if these components have appropriate functional groups to undergo cocondensation. Materials made this way, which the authors have termed ceramers[6], should reflect some of the properties of the sol-gel glass and the incorporated polymeric components. With the success of this reaction scheme, some properties of glasses, e.g. brittleness and

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* To whom offprint requests should be sent.

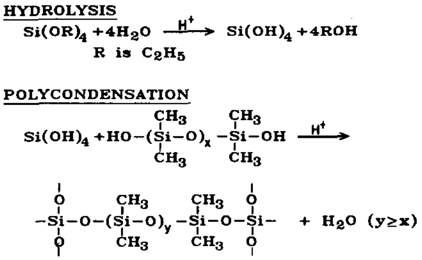
optical characteristics, could then be modified by properly choosing the polymeric species. Furthermore, this may provide a successful bridging between organic and inorganic compounds.

Several variables are crucial in the sol-gel process, four of these being: (1) the metal alkoxide used, (2) the stoichiometric amount of water added, (3) the pH value of the environment, and (4) the reaction temperature. For the hybrid system mentioned above, the situation may become even more complicated. Part of this is due to the difference between the reactivities and solubilities of the alkoxide and the polymeric component, and this difference may affect the final structure of the ceramers produced. In addition, the weight ratio of the alkoxide to the polymer, the chemical nature of the polymer, and the solvents used will likely play important roles in this new system.

Preliminary work reported from the authors' laboratory has shown promising results, and this is now being followed by a systematic investigation currently undertaken to study the effects of several important variables on the properties and structure of ceramers. Tetraethoxysilane(TEOS) was the alkoxide employed for the present work, and polydimethyl siloxane(PDMS) was the polymeric component. The latter was chosen due to its good thermal stability and the similarity between the Si-O backbone of PDMS and the sol-gel glass matrix. In this paper, the effect of the acid content is presented for two different weight ratios of TEOS/PDMS ---1:1 and 3:2. However, higher sol-glass contents have been studied and will be reported upon in a future communication[7].

EXPERIMENTAL

The basic reaction scheme for the present work is shown below:



$$Si(OR)_4 + 4H_2O \xrightarrow{H^+} Si(OH)_4 + 4ROH$$

R is C_2H_5

$$Si(OH)_4 + HO-(\overset{CH_3}{\underset{CH_3}{Si}}-O)_x-\overset{CH_3}{\underset{CH_3}{Si}}-OH \xrightarrow{H^+}$$

$$-\overset{O}{\underset{O}{Si}}-O-(\overset{CH_3}{\underset{CH_3}{Si}}-O)_y-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{O}{\underset{O}{Si}}- + H_2O \quad (y \geq x)$$

These reactions are highly schematic and they are not stoichiometrically balanced. A few points with regard to these reactions should be noted:

(1) The completion of the hydrolysis reaction depends on the amount of water added to the system. Hence, residual ethoxy groups may exist.

(2) Self-condensation of the silanol terminated PDMS can take place, and this will affect the network structure.

(3) Solvent(s) used may affect the mobilities and relative solubilities of all the incorporated components. Consequently, this may affect the structure and properties of the final product.

The nomenclature used in this work can be illustrated using the following example:

TEOS(48)--PDMS(1700)--50--0.045--80C

silane used(wt%) oligomer(m.w.) reaction temp.

% stoichi. amount water added molar HCl/TEOS

Appropriate amount of solvents, distilled water, and hydrochloric acid were first added to a 100 ml round-bottomed flask. Then, TEOS and PDMS(MW=1700) were simultaneously poured into the solution. The flask was rapidly put into a water bath at 80°C and the reaction took place under reflux with fast agitation for 20 minutes. Then, the solution was poured into a Teflon coated petri dish and covered with Parafilm to allow the gelling process to occur. After 24 hours, all of the samples gelled and the Parafilm was removed to allow further network development of the samples. The drying process lasted for at least 48 hours before carrying out any characterization tests.

Dynamic mechanical data were obtained utilizing a DDV-IIC Rheovibron Dynamic Viscoelastometer. The materials were run at 110 Hz with a heating rate of 2-4°C/min. Stress-strain experiments were carried out with an Instron 1122 model. Dogbone samples of 10 mm in length were used, and the strain rate was 2mm/min.

RESULTS AND DISCUSSION

As shown in Fig. 1, ceramers with high transparency were obtained for this study. Most samples can be bent considerably to display significant flexibility, while pure silicon glasses which were made for comparison are very brittle. This results strongly suggests that the rubbery siloxane components have been incorporated into the network. Since the samples are transparent, there is most likely no phase separation in the dimension of the wavelength of visible light. However, the existence of some microphase separation is indicated by the results shown below, and it is significantly dependent on the acid content of the system.

Dynamic mechanical experiments were carried out on a series of ceramers made with different ratios of HCl/TEOS, and the results are shown in Fig. 2. The pH values of

Fig. 1. Ceramer samples made with 48wt% TEOS and 52wt% PDMS(MW=1700)

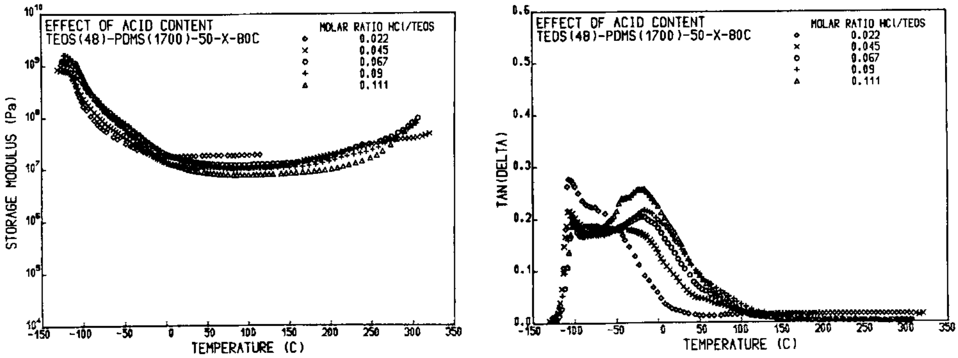


Fig. 2. Effect of acid content on the dynamic mechanical properties of ceramers made with 48wt% TEOS. (a) storage modulus spectrum (b) tanδ spectrum.

all the reactions were between zero and one. The storage modulus shows a plateau region with a magnitude of 10^9 pascals beginning at very low temperatures. As the temperature increases, the modulus decreases gradually and finally reaches another plateau region, which has a magnitude of the order of 10^7 pascals. This is the first indication of the incorporation of PDMS. The plateau region of 10^7 pascal extends over a very wide temperature range --- about 200°C. Such a long and almost constant modulus region is rather unusual for polymeric compounds, and it should become an important feature for the applications of these hybrid materials. After approximately 200°C, the modulus starts to increase. This increase may be attributed to a combination of further curing and a "rubber elasticity" effect[6]. In Fig. 2b, a tanδ peak near -106°C is observed for all cases, and its magnitude decreases with increasing acid content. In addition, a peak near -10°C begins to appear as the acid content increases.

From the earlier reaction scheme, the network is formed by condensation reactions of silanol groups. Therefore, the relative concentration of the silanol group from the PDMS versus that from the hydrolysis of TEOS will be crucial to the structure of the final product. At the beginning of the reaction, all silanol groups present extend from the PDMS , hence, the self-condensation would be favored. This results in a chain extension of the PDMS and promotes some phase separation. The T_g for these phase-separated siloxane regions would be close to the T_g of the siloxane rubber --- around -120°C. However, the silanol groups from the hydrolysis reaction would increase with time and, hence, the cocondensation of the silanol terminated PDMS and the hydrolyzed TEOS would gradually become the dominant reaction of the system. Such a transition would result in the following:

(1) The phase-separated siloxane species, i.e. those with longer chains, would eventually be bonded to the glassy matrix at both ends. This bonding within the sol-gel matrix would somewhat restrict the mobility of these chains and cause their T_g to possibly shift to a higher

temperature. This may explain the existence of the tanδ peak near -106°C.

(2) The remaining initial short oligomeric chains of siloxane would be incorporated into the glassy matrix and cause the T_g of these well dispersed siloxane species to shift to even higher temperatures than the phase-separated regions. This is believed to be the origin for the broad peak near -10°C

Based on the mechanism suggested above, the effect of the acid content may now be rationalized. As its concentration increases, the rate of the hydrolysis reaction would also increase. Therefore, the period of time that the self-condensation is favored would be shortened. This would reduce the amount of the phase-separated siloxane regions and thus cause the low temperature tanδ peak to decrease. Since the total amount of siloxane components is constant for all samples in Fig. 2b , less phase separation implies that more oligomeric chains would be dispersed into the sol-gel glass matrix. Consequently, the magnitude of the tanδ peak near -10°C, which was attributed to the dispersed siloxane species, would increase as is indeed noted.

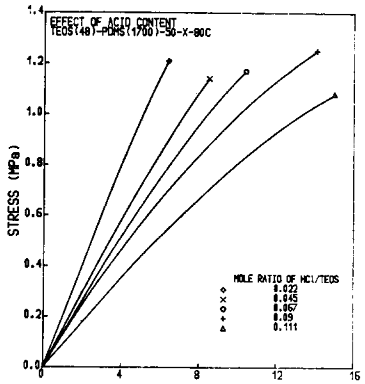


Fig. 3. Effect of acid content on the stress-strain behavior of ceramers with 48wt% TEOS.

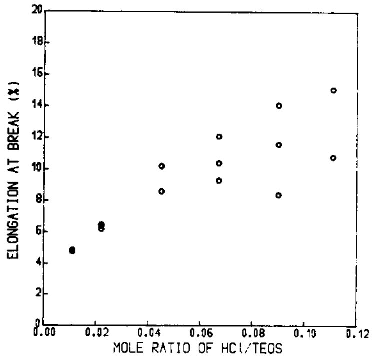


Fig. 4. Effect of acid content on the elongation at break of ceramers with 48wt% TEOS.

Figure 3 shows the results of stress-strain experiments carried out on these samples. The elongation at break, which ranges from about 6% to 15%, indicates the incorporation of rubber molecules into the network since pure glasses would not display such extensibility. The Young's modulus shows a systematic decrease with increasing acid content with its general magnitude being around 10^7 pascals. This is consistent with the results of the dynamic mechanical experiments.

According to the mechanism suggested above, less acid content would promote phase separation while more acid would cause more oligomeric chains of siloxane to disperse and bond within the glassy matrix. In terms of the network structure, the latter should show a more uniform crosslinking pattern than the former. Therefore, when one strains the sample made with low acid content, the chance of stretching a rigid bond from the glassy matrix would be greater than if one strains the sample made with higher acid content. This would obviously result in a higher modulus for the former than that

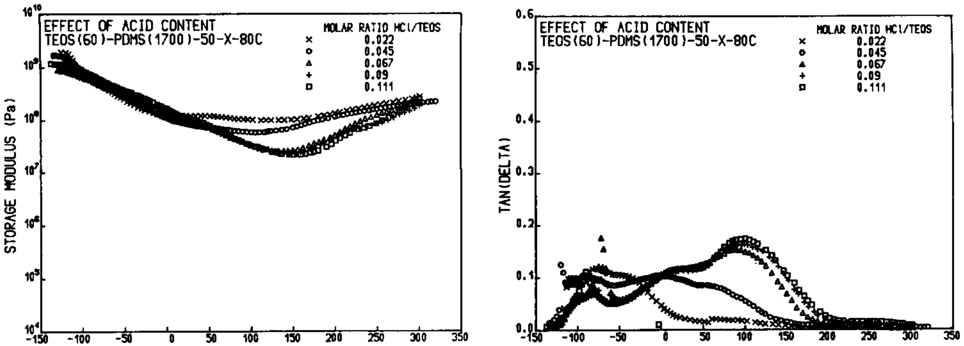


Fig. 5. Effect of acid content on the dynamic mechanical properties of ceramers made with 60wt% TEOS.(a) storage modulus spectrum (b) tanδ spectrum.

for the latter, which is directly in line with the experimental results. Following the same argument, one would expect that the elongation at break should increase as the acid content increases. Figure 4 shows the effect of the acid content on the elongation at break. Although some degree of scattering was observed, the anticipated trend is clear.

Following the first series, which has a weight ratio of TEOS/PDMS approximately equal to unity, a second series of samples which has a ratio of 3:2 was synthesized to study the effect of the acid content. The molar ratio of TEOS/PDMS was changed from approximately 7:1 to 12:1, which implies that these materials should have a greater hardness and lower extensibility. However, results were not quite as expected. Figure 5 shows dynamic mechanical results of the second series of samples. At low acid content, the storage modulus shows a long plateau region as was observed previously. However, this feature disappears as the ratio of HCl/TEOS reaches 0.067. Instead of showing a plateau, the storage modulus further decreases to a minimum and then again increases. This may suggest that the siloxane components have dispersed into the network in the form of very short chains. This point is supported by the tanδ behavior which shows a broad peak, growing with increasing acid content, near 100°C. By comparing Figures 2b and 5b, one can see that the tanδ values are higher for materials with higher rubber content. This is reasonable since it is the PDMS which causes the loss behavior. For the second series, the magnitude of the low temperature peak of tanδ is only about one half of the tanδ peak near 100°C. In addition, the high temperature peak of this series is generally broader than that of the first series. This may imply that, with the same acid content, the sample with 60 wt% glass content would show a more uniform structure than the one with 48 wt% glass content. According to the mechanism suggested above, the lower the rubber content, the shorter the time needs for the cocondensation to become favored over the self-condensation of PDMS. In other words, siloxane molecules would have a shorter time to form rich phases and, therefore, the rubber component would be more dispersed. This better dispersion may explain the surprisingly

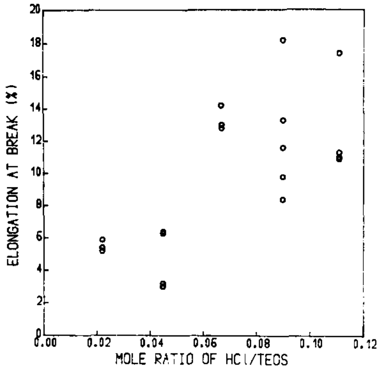


Fig. 6. Effect of acid content on the elongation at break of ceramers with 60wt% TEOS.

high extensibility observed in the stress-strain experiments (Fig. 6).

From these two series, one realizes that the extensibility is related not only to the rubber content of the sample, but also to the dispersion of the rubbery components. A higher content of TEOS may mean more glass-like behavior, but it also may lead to a better dispersion of the rubber components. These two effects may interact and make it difficult to predict the extensibility of the sample.

In the suggested mechanism, an implication was made that the reactivities of the silanol groups are the same regardless of whether it is from the rubber or from the glass component. This assumption needs further verification through the kinetic study of the condensation reaction. The NMR technique has been proven to be rather powerful in this respect [8]. We are currently using similar approaches for better understanding of these aspects of our systems.

CONCLUSIONS

Ceramers, which incorporated polydimethyl siloxane with tetraethoxysilane, were successfully synthesized. All products were transparent and showed good flexibility.

The acid content of the system affects both the final structure and the properties of the ceramers. For the series of samples containing 48 wt% of TEOS, results of mechanical tests shows that the modulus decreases, but the extensibility increases with increasing acid content. Dynamic mechanical results show that a tanδ peak near -10°C grows with increasing acid content while, at the same time, a peak near -106°C decreases. All of these may indicate that more oligomeric chains of siloxane disperse into the network as the acid content increases. This better dispersion results in a more uniform structure and softer materials.

As the TEOS content is increased to 60 wt%, the modulus increases due to the higher glass content. However, the extensibility is somewhat the same as the samples with 48 wt% of TEOS. We suspect that this may result from a better dispersion of the siloxane species, which is indicated by a broad peak of tanδ around 100°C.

The mechanism suggested is based on indications obtained from mechanical tests. Direct evidence about the structure of ceramers is currently being pursued through other techniques, e.g. SAXS and SEM.

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