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Polymer 43 (2002) 6415–6420

polymer

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Polycarbonate networks. Part 2. Cure study and determination of mechanical, adhesive, and crystallization properties

Daniel M. Knauss[1], Tae-Ho Yoon[2], James E. McGrath*

Department of Chemistry and Materials Research Institute, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061-0344, USA

Received 3 October 2001; received in revised form 10 July 2002; accepted 19 July 2002

Abstract

Vinylphenylcarbonate terminated oligocarbonates were thermally cured into insoluble three-dimensional networks. The cure reaction of the functional oligomers with varied molecular weights was studied under different reaction temperatures and cure times. The K_{1c} fracture toughness was determined for the cured samples and the values obtained show that the polycarbonate networks retain some of the toughness of linear thermoplastic polycarbonate. Dynamic mechanical analysis was performed on the uncured, partially cured, and fully cured samples and a shift in glass transition temperature (T_g) to higher values was observed with extent of cure. The low temperature secondary relaxation peaks were observed to broaden toward higher values with extent of cure. Tensile measurements of cured samples demonstrated an increase in tensile strengths for the cured materials relative to low molecular weight oligomers, but with no change in modulus, while the tensile elongations of the cured samples showed an improvement over oligomers. The crystallizability of the cured materials was examined and it was determined that a significant improvement in solvent resistance to crystallization was obtained over that of linear polycarbonate. The materials also show potential as structural adhesives. © 2002 Published by Elsevier Science Ltd.

Keywords: Polycarbonate; Vinylphenylcarbonate; Network

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1. Introduction

The synthesis and characterization of vinylphenylcarbonate terminated oligocarbonates of bisphenol A were described in the previous paper [1]. These oligomers were demonstrated to undergo a thermal cure reaction into insoluble networks during DSC measurements. While polycarbonate networks from functional oligomers and polymers have been previously described [2–23], relatively little information is available on the mechanical, adhesive, or crystallization behavior of polycarbonate networks. Furthermore, oligomers and networks using vinylphenylcarbonate functional groups have not been previously described except in preliminary communications [24,25]. The purpose of the work reported in this paper was to study the cure of different molecular weight vinylphenylcarbonate terminated oligomers and the properties of the resulting networks. The crosslinked polycarbonates were expected to retain some of the mechanical properties of linear polycarbonate with improved solvent resistance properties.

2. Experimental

Polycarbonate networks with different crosslink densities were prepared by the thermal cure of vinylphenylcarbonate terminated oligomers of different molecular weights. The functional oligomers, as well as non-reactively terminated oligomers, were prepared as described in the previous paper [1]. Lexan 150 was obtained from General Electric and Calibre 300-3 was obtained from the Dow Chemical Company. Molecular weights of samples were determined by GPC and ^{1}H NMR spectroscopy. The synthetic method and target molecular weights of the samples are indicated by the code numbers for the individual samples. More detail about the characterization of the oligomer samples is given in the preceding paper. Films were prepared either by compression molding followed by curing at elevated temperatures or by the subsequent oven curing of solution

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* Corresponding author. Tel.: +1-540-231-4457; fax: +1-540-231-8517.
E-mail addresses: jmcgrath@vt.edu (J.E. McGrath),
dknauss@mines.edu (D.M. Knauss).

[1] Present address: Department of Chemistry, Colorado School of Mines, Golden, CO 80401, USA. Tel.: +1-303-273-3625; fax: +1-303-273-3629.

[2] Present address: Department of Materials Science and Engineering, Kwangju Institute of Science and Technology, Kwangju 506-303, Korea.

0032-3861/02/$ - see front matter © 2002 Published by Elsevier Science Ltd.
PII: S0032-3861(02)00509-8

cast films. Plaques 75 mm × 40 mm × 3.2 mm were molded from the vinylphenylcarbonate terminated oligomers by the repeated filling of a stainless steel mold with these dimensions. The different oligomers were compression molded on a PHI Melt Press at different temperatures ranging from 120 to 180 °C, depending on the molecular weight of the oligomer. The oligomers were then thermally cured without added initiator at temperatures from 180 to 300 °C for different lengths of time at 10,000–20,000 lb of pressure.

Cured samples with dimensions of 6 mm × 20 mm × 3.2 mm were cut from larger samples and extracted with chloroform for four days using a soxhlet extraction apparatus. The amount of extracted material was measured by evaporating the chloroform and weighing the residue to determine the percent of soluble products.

Swelling experiments were performed on cured samples with the dimensions of approximately 6 mm × 20 mm × 3.2 mm. The cured samples were weighed and placed in 1,1,2,2-tetrachloroethane at 25 °C for 24 h. The swollen samples were weighed to determine the solvent uptake. The samples were then dried under vacuum for 24 h at 50 °C, reweighed, and the process repeated.

Tensile tests were performed on an Instron 1123 equipped with a strain gauge extensometer (Instron 2630-013). Five to ten dog-bone shaped samples (ASTM D-638 #5) were cut from compression molded films with thicknesses from 3 to 10 mil. The samples were tested at room temperature with a crosshead speed of 0.5 in./min consistent with ASTM D-638. The results of statistically consistent samples were averaged to determine the values.

Fracture toughness measurements were conducted in accordance with ASTM D-5045-91 (E-399-90). 10–12 K_{1c} test samples with dimensions 6 mm × 40 mm × 3 mm were cut from the larger plaques. The individual samples were notched at the center to a depth of approximately 0.5 mm with a reciprocating saw. Sharp cracks were then initiated by gently tapping a liquid nitrogen cooled razor blade within the notch, taking care to ensure that the crack had evenly propagated into the sample. The pre-cracked samples were then loaded on a three-point-bend fixture attached to an instron and tested at a rate of 0.05 in./min.

Dynamic mechanical analyses (DMA) were performed on a Perkin Elmer DMA-7 analyzer in the three-point-bending mode. Tests were conducted on the fracture toughness samples at a frequency of 1 Hz under a dynamic temperature scan rate of 5 °C/min.

The fracture surfaces of the broken fracture toughness samples were exposed to solvent for different amounts of time. The morphology of the fracture surface was determined with an International Scientific Instruments Model SX-40 SEM at 20 kV. Samples were mounted on aluminum substrates with silver paint and the fracture surface was sputtered with approximately 100 Å gold film from a Bio Rad Polaron Model E 4500 sputter coater. Samples were observed at 2000 × magnification.

The adhesive bond strengths of crosslinked polycarbonates to aluminum were examined by performing single lap shear tests at 25 °C according to ASTM D-1002. Aluminum coupons with dimensions 1 in. × 5 in. × 1.5 mm were prepared according to ASTM D-2651-79 with a sulfuric acid/dichromate etch. A primer coating of 5 wt% polymer in chloroform was applied to the surface of the coupons. Melt pressed films of reactively terminated oligomers were formed by compression molding at 160–190 °C for 5 min. The 'pre-cured' films were placed between aluminum coupons in a single lap shear orientation and cured at 500 lb of pressure and at 180–220 °C for 30 or 60 min. The samples were tested on an Instron Model 1123 at a crosshead speed of 0.05 in./min. Single lap shear samples were similarly prepared of non-reactively terminated polycarbonates for comparison.

3. Results and discussion

3.1. Synthesis of crosslinked polycarbonate networks

Vinylphenylcarbonate terminated oligocarbonates were synthesized to various molecular weights as described previously [1]. Crosslinked polycarbonate networks could be obtained from the reactive oligomers. The formation of the crosslinked networks could be effected through a thermally initiated cure reaction of the styrene-like end groups. The mechanism of the thermal initiation was considered to be similar to the thermal self-initiation of styrene [26]. This mechanism of styrene initiation has been widely debated, but nevertheless results in the formation of free radicals that initiate the polymerization of the remaining styrene monomer. In the case of the end functionalized polycarbonate oligomers, free radical generation causes initiation of the styrene-like end groups. In order to obtain the largest processing window possible, free radical initiators were not added to the reactive oligomers.

Propagation is undoubtedly limited by the viscosity increase that is encountered during the formation of the crosslinked network, as well as by the steric requirements of linking multiple oligomers. For this reason, it is expected that the oligomerization of the end groups should not continue beyond a few repeat units.

The reactive oligomers could be cast from solution and subsequently heated to 200–300 °C under vacuum in order to effect a thermal cure. After this thermal treatment, the samples were found to be partially or totally insoluble depending on the temperature and length of time at elevated temperature. Since the low molecular weight oligomers were also found to flow at relatively low temperatures relative to the temperature of the cure reaction, specimens with a variety of sample geometries could be formed by compression molding. Reactions were done at different temperatures for varying amounts of time in order to determine the effects on the formation of a three-dimensional network.

Table 1
Effect of cure time on percent extractable material

Sample	30 min[a]	60 min[a]	90 min[a]	120 min[a]
A(2.5K)	0.5	–	–	–
A(5K)	12	6	4	2
A(7.5K)	14	13	2	1
A(10K)	26	15	11	1

[a] Cure time at 220 °C.

The curing reaction was examined by subjecting the different samples to different time/temperature profiles. Initial samples were held at 220 °C for times ranging from 30 min to 2 h. The samples from different molecular weight oligomers were examined by soxhlet extraction to determine how the molecular weight of the oligomers affects the extent of the cure reaction or the time required to cure the samples (Table 1). From the data, it can be seen that the lower molecular weight oligomers require less time to become 100% insoluble. The higher molecular weight oligomers require more time at this temperature, but do become 100% insoluble by the end of 2 h.

Samples were also analyzed by soxhlet extraction after curing at 300 °C for 40 min. A similar trend could be observed at this temperature, where the higher molecular weight samples did not become 100% insoluble after this reaction time (Table 2).

The soluble portion extracted from the cured B(5K) oligomer was analyzed by GPC and by ^{1}H NMR in order to probe how much reaction had taken place. GPC analysis determined that the molecular weight was similar to that of the initial uncured oligomer. ^{1}H NMR on the other hand, indicated a lower concentration of vinyl end groups present in the sample. This may indicate that some non-reactive end groups are present in this sample, or that termination of the reactive end groups occurred before propagation could take place. The latter explanation is backed up by the observance of new peaks in the aliphatic region of the ^{1}H NMR spectrum. Some vinylphenyl end groups still remain, also indicating that the reaction time was insufficient to complete the cure.

3.2. Fracture toughness

Fracture toughness was determined by single edge notched bending (K_{1c}) for samples cured at 220 °C for 30 min and for samples cured at 300 °C for 40 min. Linear, non-reactive *t*-butylphenylcarbonate terminated polycarbonate oligomers (similar to the molecular weights of the reactive oligomers before cure) as well as commercial polycarbonate were also tested for comparison. The results of the fracture toughness tests are compiled in Table 3.

Table 2
Percent extractable material after cure at 300 °C for 40 min

Sample	Amount of extractable material (%)
B(1.5K)	2
B(2.5K)	3
B(5K)	14
B(7.5K)	22

Table 3
K_{1c} fracture toughness values

Sample	K_{1c} fracture toughness (MPa m$^{1/2}$)
Cured at 220 °C/30 min	
A(5K)	3.09 ± 0.23
A(7.5K)	3.31 ± 0.27
A(10K)	3.46 ± 0.19
Cured at 300 °C/40 min	
B(1.5K)	1.04 ± 0.15
B(2.5K)	2.35 ± 0.23
B(5K)	3.52 ± 0.17
B(7.5K)	3.54 ± 0.31
Non-reactively terminated	
t-Bu-A(2.5K)	2.43 ± 0.24
t-Bu-A(5K)	3.06 ± 0.23
t-Bu-A(7.5K)	3.39 ± 0.25
t-Bu-A(10K)	3.37 ± 0.26
Lexan 150	3.44 ± 0.19
Calibre 300-3	3.39 ± 0.08

The K_{1c} fracture toughness measurements show that the cured samples retain some of the inherent toughness properties of high molecular weight linear polycarbonate. However, the toughness of the networks was found to decrease with a decrease in the initial oligomer molecular weights. The lower molecular weight between crosslinks obtained from these lower molecular weight oligomers is most likely not able to absorb the energy as well as the samples with higher molecular weights between crosslinks. It further appears that to a first approximation, the fracture toughness of the network material corresponds closely to that of the low molecular weight *t*-butylphenyl terminated oligomers; although the effect of residual linear material not incorporated into the network structure cannot be ignored in these results.

3.3. Dynamic mechanical analysis

The dynamic mechanical spectra of uncured, semi-cured, and fully cured samples were examined to determine if a shift in the secondary relaxations could be detected, and how this might correlate to the fracture toughness values. Samples were analyzed at a frequency of 1 Hz in three point bending mode and the tan δ peak was plotted versus temperature for samples with different cure histories. Vinylphenylcarbonate terminated oligomers B(5K) and B(7.5K) were of sufficient molecular weight to form three point bending samples by compression molding. Uncured oligomers of lower molecular weight could not be measured, as they did not have sufficient molecular weight to form suitable samples. To determine the DMA spectrum

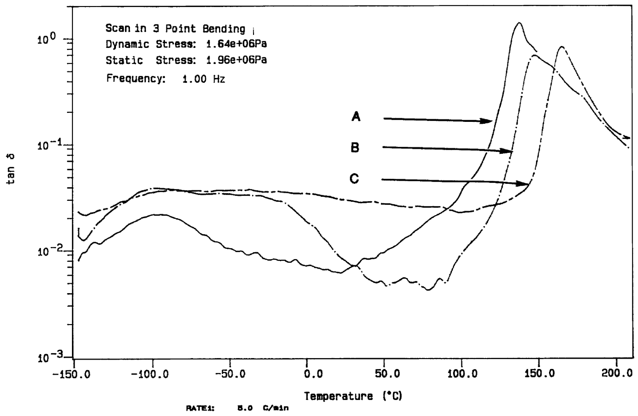

Fig. 1. DMA spectra (5 °C/min; 1.0 Hz) for B(5K). (A) Uncured oligomer; (B) cured at 300 °C for 40 min; (C) cured at 250 °C for 3 h.

of fully cured networks of these samples, the compression molded oligomers were cured in an oven under nitrogen atmosphere at 250 °C for 3 h (soxhlet extraction of these samples yielded 100% insoluble materials). DSC was also performed on these cured samples and showed an increase in the T_g from that of the uncured oligomers, as described in the previous paper [1]. The fully cured B(5K) sample showed a T_g of 162 °C, while the fully cured B(7.5K) sample showed a T_g of 160 °C.

DMA spectra of uncured B(5K), B(5K) cured at 300 °C for 40 min, and B(5K) cured at 250 °C for 3 h are depicted in Fig. 1, while the DMA spectra of similar samples of B(7.5K) are depicted in Fig. 2. The DMA spectrum for linear Dow Calibre 300-3 polycarbonate is represented in Fig. 3 for comparison.

From Figs. 1 and 2, it can be seen that the glass transition increases with the extent of cure. Furthermore, the low temperature relaxation peak changes with network formation. The 5K samples in Fig. 1 represent this change, as the cure causes a broadening of the secondary relaxation peak toward higher temperatures. The same effect can be seen in the 7.5K sample in Fig. 2, but to a lower extent than in the 5K sample.

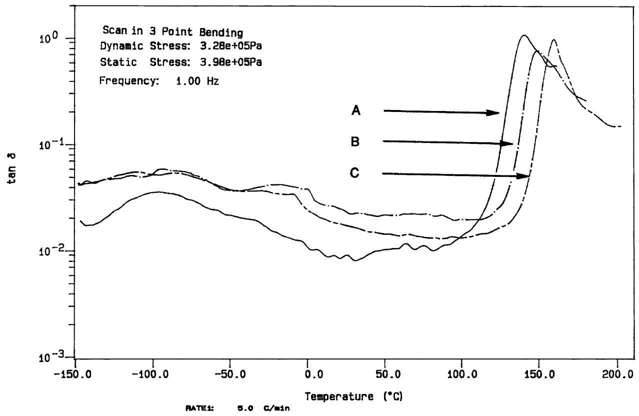

Fig. 2. DMA spectra (5 °C/min; 1.0 Hz) for B(7.5K). (A) Uncured oligomer; (B) cured at 300 °C for 40 min; (C) cured at 250 °C for 3 h.

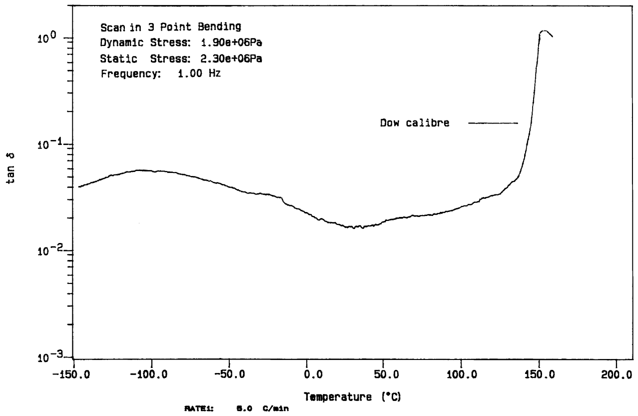

Fig. 3. DMA spectrum (5 °C/min; 1.0 Hz) for Dow Calibre 300-3 linear polycarbonate.

3.4. Tensile properties

The tensile mechanical properties were determined from stress–strain analysis of cured samples and non-reactive *t*-butylphenylcarbonate terminated oligomers. The data obtained for these samples is contained in Table 4. For the network materials, the testing was done on samples that were not completely cured in all cases.

The tensile strengths of the cured samples are increased over that of the uncured oligomers, while the modulus was not observed to change significantly. It was expected that the tensile moduli for the cured samples would have increased, but this was not observed. The tensile elongations of the cured samples are observed to be greater than those of the low molecular weight, non-reactively terminated oligomers, although the cured samples from very low molecular weight oligomers show the nature of the highly crosslinked network with rather low elongations at break. Comparative tensile elongations of higher molecular weight samples were inconclusive due to the limits of the extensometer.

Table 4
Tensile mechanical properties

Sample	Tensile strength (MPa)	Tensile modulus (GPa)	Tensile elongation (%)
B(1.5K)[a]	86.3	2.6	7.5
B(2.5K)[a]	96.7	2.7	>30[b]
B(5K)[a]	82.1	3.2	>30[b]
A(7.5K)[c]	78.6	2.7	>30[b]
A(10K)[c]	75.2	2.8	>30[b]
Non-reactively terminated oligomers			
t-Bu-A(2.5K)	73.5	2.8	3.2
t-Bu-A(5K)	74.7	2.9	4.9
t-Bu-A(7.5K)	77.6	2.9	>30[b]
t-Bu-A(10K)	77.1	2.8	>30[b]

[a] Cured at 300 °C for 40 min.
[b] Not broken due to limit of extensometer.
[c] Cured at 220 °C for 30 min.

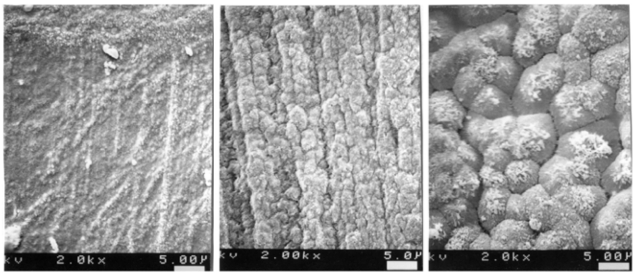

Fig. 4. SEM of polycarbonate (Calibre 300-3). Fracture surface after acetone exposure: (A) 1 s; (B) 30 s; (C) 60 s.

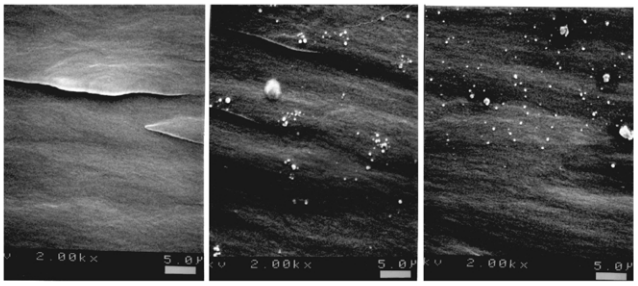

Fig. 5. SEM of B(1.5K) cured at 300 °C for 40 min. Fracture surface after acetone exposure: (A) 1 min; (B) 30 min; (C) 120 min.

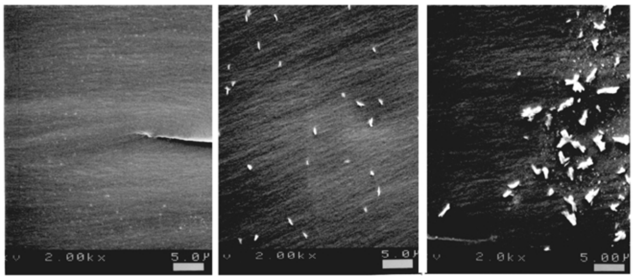

Fig. 6. SEM of B(2.5K) Cured at 300 °C for 40 min. Fracture surface after acetone exposure: (A) 1 min; (B) 30 min; (C) 120 min.

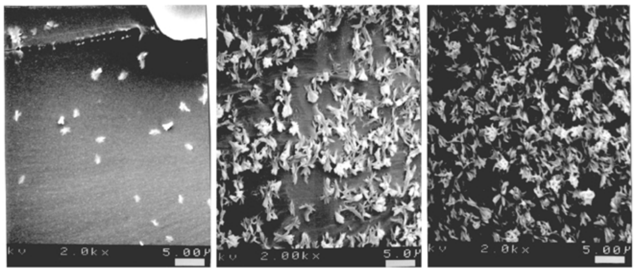

Fig. 7. SEM of B(5K) cured at 300 °C for 40 min. Fracture surface after acetone exposure: (A) 1 min; (B) 30 min; (C) 120 min.

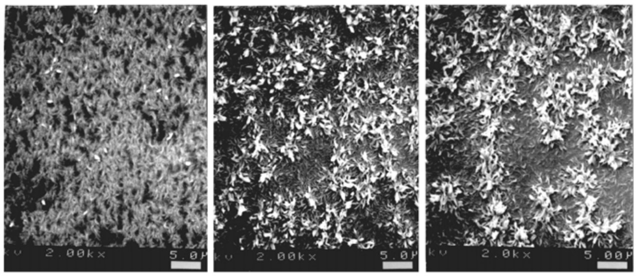

Fig. 8. SEM of B(7.5K) cured at 300 °C for 40 min. Fracture surface after acetone exposure: (A) 1 min; (B) 30 min; (C) 120 min.

3.5. Scanning electron microscopy (SEM)

Polycarbonates are known to crystallize when stressed samples are exposed to acetone [27]. The effect that network formation has on the ability of the polycarbonate to crystallize when exposed to solvent was investigated. Fractured K_{1c} sample bars of materials cured at 300 °C for 40 min were placed in acetone for 1, 30, and 120 min to determine how solvent exposure affected the fracture surface. The fracture surface of a polycarbonate control was exposed to acetone for 1, 30, and 60 s. The control and cured samples were analyzed by SEM to examine the morphology that developed. The scanning electron micrographs with 2000 × magnification are shown in Figs. 4–8.

The micrographs demonstrate the development of crystallinity with exposure time. While the linear polycarbonate control develops crystallinity immediately (requiring a different time scale to demonstrate the immediate crystallization), the cured samples show a decreased tendency towards crystallization.

The amount of crystallinity is observed to increase with the expected increase in molecular weight between crosslinks; although, these samples also have a greater amount of residual uncured material. The only sample in which no crystallinity can be detected to develop on the observed time scale is the cured B(1.5K) material. Although the micrographs do show some surface characteristics for this sample, it is believed to be either air bubbles or possibly demonstrates the extraction of low molecular weight uncured material. Although from this data it is difficult to ascertain whether the observed increase in crystallinity with initial oligomer molecular weight is due entirely to the residual uncured material or because of the higher molecular weight between crosslinks, it is postulated that some of the crystallinity is developed in the crosslinked network itself and not entirely from the soluble portion. Evidence of this is demonstrated by the fact that the cured B(1.5K) and B(2.5K) samples have similar percentages of residual insoluble portions (2 and 3%, respectively) determined from soxhlet extraction data (Table 2); yet the cured B(1.5K) sample develops no crystallinity while the cured B(2.5K) sample does crystallize slowly. Nevertheless, the cured samples do show a tremendous increase in solvent resistance compared to linear polycarbonate.

3.6. Adhesion properties

A cursory investigation of the adhesion properties of these new materials to aluminum was performed by single lap shear tests (Table 5). Adhesive failure was observed for

Table 5
Single lap shear strength of polycarbonate samples

Sample	Single lap shear strength (MPa)
Reactively terminated oligomers cured at 220 °C for 30 min	
A(2.5K)	33.7 ± 1.0
A(5K)	40.8 ± 2.5
A(10K)	37.9 ± 2.1
Non-reactively terminated polycarbonates	
t-Bu-A(2.5K)	13.5 ± 1.0
t-Bu-A(5K)	24.1 ± 1.2
t-Bu-A(10K)	30.9 ± 0.6
Lexan 150	24.5 ± 2.5

all samples except in the case of *t*-Bu-A(2.5K), where cohesive failure was observed. Compared with commercial polycarbonate (Lexan 150), the cured samples showed an increased adhesion to the aluminum substrate. This is possibly due to the fact that the low molecular weight of the reactive oligomers allows them to flow better than the high molecular weight material, and thus adhere better to the substrate before being cured into a network. Except for *t*-Bu-A(2.5K), the non-reactively terminated oligomers also demonstrated increased adhesion to the substrate relative to high molecular weight polycarbonate. Again, this is probably due to the better flow properties of the low molecular weight materials. From this work, it is apparent that the reactively terminated materials have potential for use as structural adhesives.

4. Conclusions

The rate of formation of a totally insoluble polycarbonate network, as determined by soxhlet extraction of thermally cured samples, was found to be dependent on the molecular weight of the reactive telechelic oligomers. Higher molecular weight carbonate oligomers required more time, or a higher temperature, to reach large extents of cure. The mechanical properties of the cured materials were examined and found to relate to many of the characteristics of linear high molecular weight polycarbonate. K_{1c} fracture toughness values increase with a decrease in the crosslink density, and crosslinked materials from carbonate oligomers larger than 5 kg/mol have a K_{1c} fracture toughness value similar to commercial linear polycarbonate. These materials show potential for application as structural adhesives, displaying significant single lap shear strengths when bonded to aluminum. The solvent resistance of the cured samples was greatly improved over linear polycarbonate. All cured samples showed significant improvement over linear polycarbonate in terms of the rate of crystallization upon exposure to acetone, while cured samples from low molecular weight carbonate oligomers showed no evidence of crystallization after 2 h of exposure to acetone.

Acknowledgements

The authors thank the Adhesive and Sealant Council and the Dow Chemical Company for financial support of this work.

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