A Study on the Mechanism of the Curing of Larc–TPI High Temperature Adhesive

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Synopsis

A study of the changes in a LARC–TPI adhesive during a three-stage thermal curing process has been conducted. The multistage curing conditions followed commonly used industrial curing specifications. Using thermogravimetric analysis plus gas chromatography plus mass spectrometry, the gasses involved in the curing were identified. Water analysis was performed by two separate techniques and supplementary information gathered using Fourier transform infrared spectroscopy. These analytical studies permitted determination of the degree of cure at each stage and to determine whether any degradation is taking place under curing condition.

INTRODUCTION

High temperature-resistant adhesives are in high demand in recent years. Polymers that have been exploited as high temperature-resistant adhesives include epoxies, phenolics, polyimides, polyphenylquinoxalines, and polyimidazoles. Among those thermally stable polymers a class of adhesives that shows great promise is the polyimides.[1] LARC–TPI is a linear thermoplastic condensation polyimide. It contains a metasubstituted diamine and an ether solvent is used as the polymerization medium. LARC–TPI has a relatively low glass transition temperature. Unlike most linear polyimides, LARC–TPI can be processed after imidizing as a thermoplastic due to its molecular structure.[2] Hendricks et al.[3] evaluated adhesive resins including LARC-13, modified LARC-13, NRO56X, FM-34, polyphenylquinoxaline, and LARC–TPI. The evaluation was based on a combination of lap shear strength, crack extension, processibility, reproducibility, thermal stability, and environmental exposures. The test results showed that LARC–TPI has very good overall properties.

The linear condensation polyimide is prepared from the reaction between an aromatic diamine and a dianhydride. LARC–TPI is synthesized by reacting 3,3′-diaminobenzophenone (3,3′-DABP) with 3,3′, 4,4′-benzophenone tetracarboxylic dianhydride (BTDA) in a solvent bis(2-methoxyethyl) ether (diglyme). The reaction is shown in Figure 1. The polymerization product is a polyamic acid prepolymer solution which is very viscous. This polyamic acid can be applied on a substrate, dried, and thermally imidized to yield a linear high molecular weight polyimide.

The solvent used in the polymerization of polyamic acid prepolymer plays an important role in determining the adhesive properties.[4] An ideal solvent

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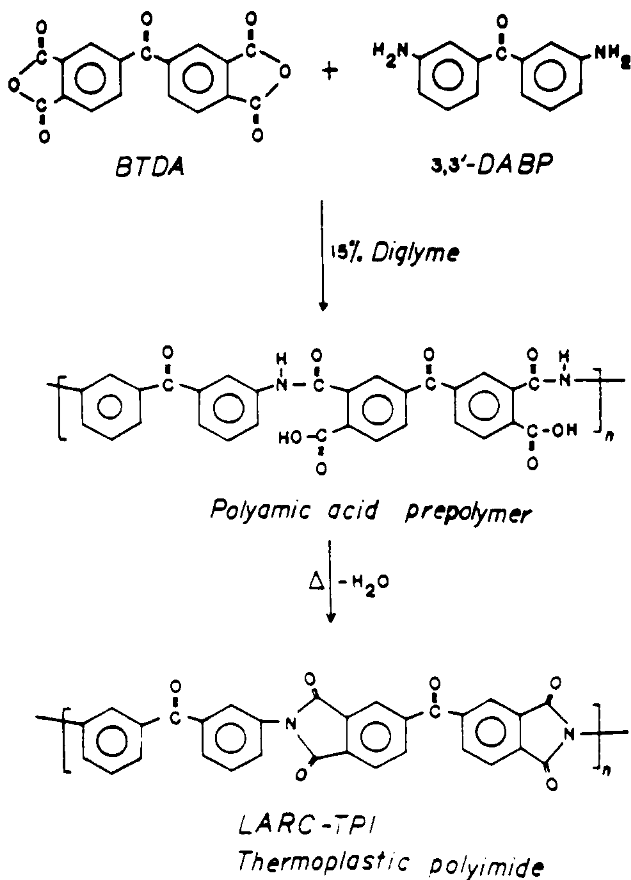

Fig. 1. The chemistry of LARC–TPI.

has to have a good wetting for the adherends and be easily removed before the bonding process and inert at elevated temperature. The residual solvent in the polymer causes harmful voids and the reactivity of the solvent at the elevated temperature needed for bonding may result in degradation of the adhesives. Comparing several different solvents used for preparing LARC–TPI, St. Clair and Progar[5] found that diglyme affords the highest lap shear strength (6000 psi for titanium alloys). This may be because diglyme is a better wetting agent for titanium.[6] One more advantage in using diglyme as the polymerization medium is that the commercially available reagent grade solvent needs no additional purification to obtain high molecular weight polymer.[5]

Typically in industrial applications the film of adhesive is cured in several stages of increasing temperature in order to permit the water that is evolved to diffuse out of the film thus avoiding voids. A typical curing sequence is:

First stage: 80°C 30 min in air
Second stage: 180°C 30 min under nitrogen
Third stage: 270°C 60 min under nitrogen

The problem then in studying the curing mechanism is to determine the degree of cure at each stage. Additionally it is of great importance to know whether any degradation of the adhesive is taking place under curing conditions. In order to determine the degradation, if any, it is necessary to determine the compounds in the evolved gasses.

EXPERIMENTAL

A 15–20% LARC–TPI solution was cast into films on glass plates. These plates were dried overnight in a vacuum oven at 40°C.

The dried film was cured in three stages as described above. The thermal analyses were made using a DuPont 990 DSC cell attached to a 990 thermal analyzer console; measurements were made in open aluminum cups with the instrument purged with nitrogen carrier gas to remove the volatiles. An Omnitherm QC-25 thermogravimetric analyzer was used in both the dynamic and isothermal modes in both air and nitrogen environments. The isothermal mode followed the temperatures times and gases indicated under curing conditions. A Hewlett-Packard 5985 GC–MS system was used to analyze the gases evolved at each stage of curing. The final experimental conditions adapted were to set the injection temperature at 80°C, insert the sample in a glass container into the injector, and flush for 30 min with the GC column temperature at −10°C to trap all materials. The gas chromatograph was then programmed at 15°C min up to 250°C. Analysis was made by comparison with the library included in the computer instrumentation.

Moisture analysis was run separately at each stage of curing, using both a DuPont 903 moisture analyzer and Mitsubishi CA-02 meter.

RESULTS AND DISCUSSIONS

A temperature-programmed DSC thermogram for LARC–TPI film is shown in Figure 2. The large endotherm between 125 and 220°C for the LARC–TPI sample is associated with the reaction between amide and acid groups. Figure 2 also shows that the glass transition temperature of the cured LARC–TPI film is about 250°C.

TGA thermograms in a dynamic mode under nitrogen and oxygen atmosphere respectively show a very small amount of weight loss for temperatures under 125°C. For temperatures above 150°C, the weight loss increases markedly. Films decomposed gradually when the temperature went above 400°C and decomposed totally above 550°C under oxygen. Under nitrogen atmosphere, the film is more stable at high temperature and decomposed gradually over a wide temperature range.

The values of the weight loss percentage at 80°C are scattered from 0.86 to 3.0%. This is due to the fact that the film absorbs moisture from air after the preparation of dried film. The weight loss for the 180°C curing is about 11.5 and 7% for curing at 270°C. The variances of the last two temperatures are considered as the difference in the thickness of films. The diffusion is more difficult for thicker films which trap more compounds.

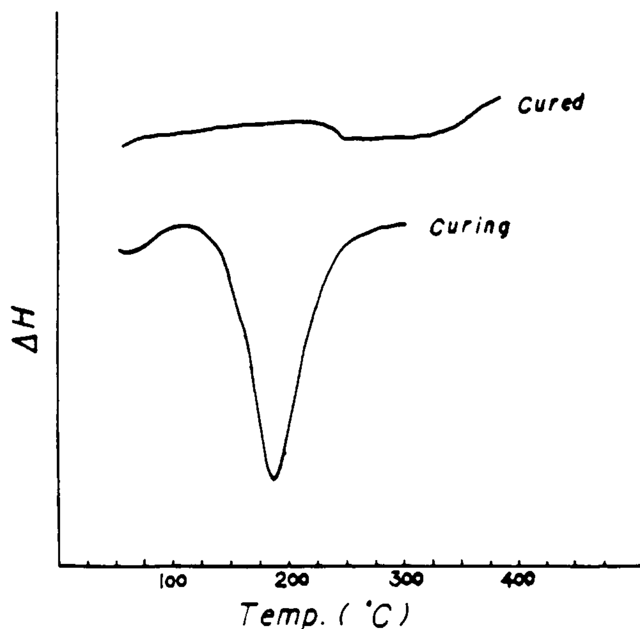

Fig. 2. Temperature-programmed DSC thermogram.

The data for the determination of moisture in the LARC–TPI sample in the curing process are given in Table I from the DuPont 903 instrument and Table II from the Karl–Fischer method.

As seen from the result obtained from the two moisture analysis methods, there is little consistency. One probable reason for the discrepancy of results may be due to the variation of thickness for each trial. A more detailed study needs to be made to determine the reason for such low consistency.

The following results were obtained in a series of experiments on TGA–GC–MS. The identification of the gas components were checked with

TABLE I
Water Analysis for LARC–TPI by the DuPont 903 Instrument

%	80°C	180°C	270°C
Trial 1	0.52	2.2	0.76
Trial 2	0.58	2.0	0.47
Trial 3	0.36	2.9	0.44

TABLE II
Water Analysis for LARC–TPI by the Karl–Fischer Method

%	80°C	180°C	270°C
Trial 1	1.9	3.9	0.93
Trial 2	2.4	3.6	0.64
Trial 3	2.4	3.5	0.55

TABLE III
Gas Components Evolved from the Curing of LARC–TPI Cast Film at 80°C

1. Diglyme
2. Diglyme + its isomers
3. α,α-Dimethyl-benzenemethanol

TABLE IV
Gas Components Evolved from the Curing of LARC–TPI Cast Film at 180°C

1. 2-Methoxy ethanol
2. 2-Methoxyethoxy ethene
3. 2-(2-(Ethenyloxy)ethoxy)-ethanol
4. Diglyme
5. 1-Phenyl-1-hexanone
6. α,α-Dimethyl-benzenemethanol

TABLE V
Gas Components Evolved From the Curing of LARC–TPI Cast Film at 270°C

1. Diglyme
2. Diglyme isomers
3. Trimethylene glycol dimethyl ether
4. 1,1′-Oxybis(2-ethoxy)-ethane
5. 2-(2-Methoxyethoxy)ethanol
6. 1-Phenyl-1-hexanone
7. α,α-Dimethyl-benzenemethanol

both computer library and reference standards. The background was subtracted when required. The identification cannot be considered as conclusive; it was consistent with the mass spectra and the possibility of components present. It appears that the evolved gases from the curing of the films are mostly diglyme and its isomers and impurities. The results in Tables III–V indicate that there is no evidence of decomposition under the conditions used here.

On combining the TGA and moisture analysis data, one can draw the following conclusion. The total weight loss for 180°C is about 11.5%, which contains about 3% of water and that for 270°C is about 7% containing approximately 0.7% water. The dynamic DSC thermogram shows that the imidization reaction occurs at about 185°C. The detection of water at 270°C indicates that the imidization was not complete after curing to 180°C for 30 min and that the water was trapped in the film after the imidization reaction. The results show that solvent and its isomers and impurities were detected. This indicates that the LARC–TPI film was not decomposed by the curing. A longer curing time may be required to complete the imidization reaction and a vacuum system coupled with the heating system for the curing process would ease the elimination of water.

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