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# Annealing of a Cyanurate Prepolymer Adhesive on Aluminium and Gold Substrates\*

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Two major effects are observed during annealing. First, some cyanate groups hydrolyze into carbamate structures on Al and Au. The reaction is driven by the metal surface and both hydroxyl groups and adsorbed water can be involved. On Al, where the carbamate production is most prominent, a part of the cyanate groups in the prepolymer is expected to react with substrate hydroxyl groups. The resulting carbamate coupling to the oxide provides a new chemical adhesion mechanism.

As a second effect, an unexpected strong loss of monomer molecules from the prepolymer layers is observed on both substrates at elevated temperatures. It is concluded that the monomer molecules are pushed out of the interphase layer with the substrates due to negative adsorption. Hence, the less mobile, bulky oligomers remain on the substrate and thermal curing of the adhesive must result in a polycyanurate network which is much weaker than in the bulk polymer. This could reduce the mechanical strength of an adhesive joint made with pure polycyanurates and could afford additional chemical modification for practical applications.

**Keywords:** Polycyanurates; Adhesion; Postcuring; IR reflection spectroscopy; Ellipsometry

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## INTRODUCTION

For thermosetting adhesives, the influences of the adherend surface may considerably affect the curing reaction and, hence, the properties of the final network in the bondline. Several papers have been published on this topic (see for example [1–5] as an arbitrary selection) but the picture is still very incomplete. This holds especially for the processes on the molecular level.

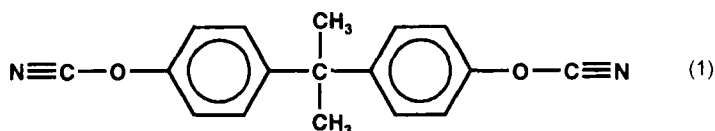
In this paper, a prepolymer of the Bisphenol A dicyanate (DCBA) is utilized as a model adhesive. This thermosetting monomer forms a polycyanurate network in a cyclotrimerization reaction. Polycyanurates possess a very good high temperature stability and favourable low-loss dielectric properties. The bulk curing reactions have been well studied (see *e.g.* [6, 7] and the references therein) and applications as matrix polymers for high performance composites have also been reported (*e.g.* [7, 8]). It has also been suggested that polycyanurates should be of interest as high-temperature adhesives [7, 9]. In [10–15], we reported on extended experimental studies of the basic adhesion mechanisms of a DCBA prepolymer on silicon and aluminium, respectively. The results led to detailed models for the spontaneous chemical adhesion processes [15, 16] *before* final curing and it was found that the DCBA monomer does not adhere spontaneously to the substrates. Strong adhesion is provided by specific donor – acceptor interactions between the trioxotriazine units in the oligomers and substrate surface states.

To the best of our knowledge, the curing reaction in the vicinity of a substrate has not yet been studied for polycyanurates. In this paper, the results of sample annealing at elevated temperatures are investigated for thin DCBA prepolymer layers on two substrates (Al or Au) by IR reflection spectroscopy, ellipsometry and other techniques. These annealing experiments model the curing reaction in a real adhesive bond.

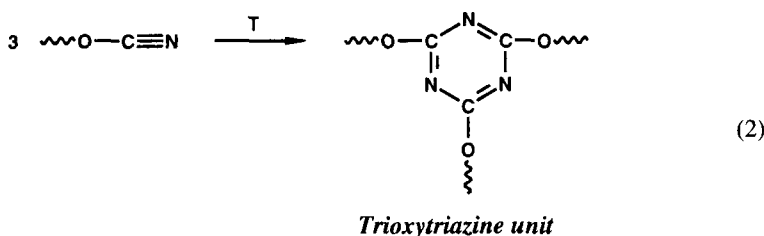
It will be shown that a part of the cyanate groups undergoes chemical conversion due to the influence of the metal substrates. Moreover, it turns out that the annealing is accompanied by a monomer loss out of the adhesive bond which is considerably stronger than the loss observed from the prepolymer bulk in the thermogravimetric measurement.

## MATERIALS AND SAMPLE PREPARATION

Dicyanate of Bisphenol A (DCBA)



was cyclotrimerized at 180°C in a nitrogen atmosphere. Schematically, the cyclotrimerization of the cyanate groups can be written as



The trioxotriazine units are the chemical links in a tight three-dimensional network if the reaction were to go to completion. No side reactions or intramolecular cyclizations are reported [7].

After 8 hours, we stopped the cyclotrimerization at ca. 45% conversion of the cyanate groups (according to IR transmission spectroscopy) in order to maintain the solubility of the prepolymer. HPLC analysis provides the oligomer number distribution which is depicted in Figure 1 together with the chemical structure of the prevailing oligomers in our product.

It can be seen that the DCBA monomer and the cyclotrimer dominate the distribution. Hence, a large amount of cyanate groups is still present in the prepolymer.

As the first substrate, polycrystalline Al films (99.999% Al,  $d_{\text{Al}} > 100 \text{ nm}$ ) are evaporated onto Si (100) single crystal wafers. According to our scanning force microscopy (SFM, Nanoscope III, contact mode) images, the Al surface is smooth with a root mean square roughness  $R_{\text{RMS}} \approx 4 \text{ nm}$  (depending on the evaporation conditions) and a maximum local inclination angle of about 20°.

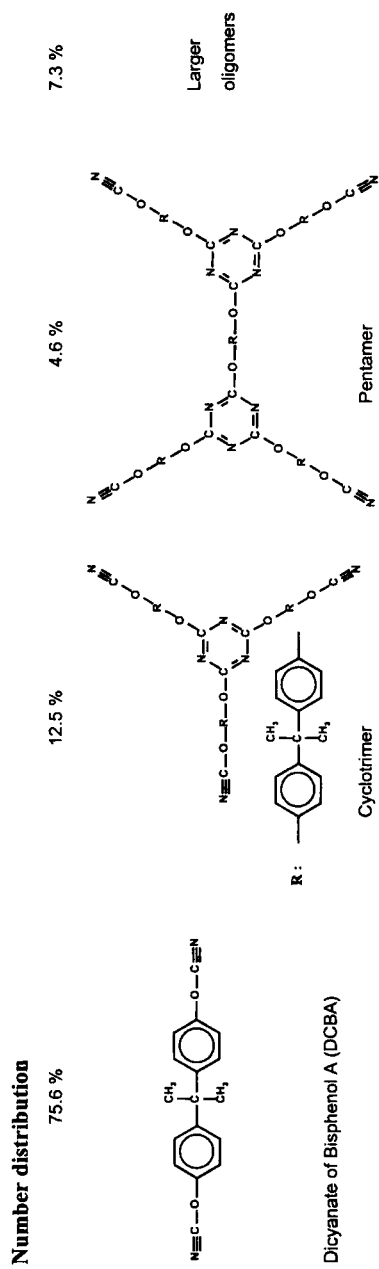


FIGURE 1 Chemical structure and number distribution of the oligomers in the DCBA prepolymer.

It was shown by XPS [15, 16] that the Al surface is covered by a continuous amorphous layer of native oxide which consists of  $\gamma$ -Al<sub>2</sub>O<sub>x</sub> ( $d_{O_1} = (2.7 \pm 0.3)$  nm, bearing OH groups). XPS also provided an oxygen ratio of OH : oxide  $\approx$  43 : 57 in the ultra-high vacuum (UHV). As a second substrate, smooth polycrystalline Au evaporation layers ( $R_{RMS} < 2$  nm) were produced on the Si wafers. Strips of a technical aluminium alloy containing 3% Mg (the so-called "AlMg3") are also included in the experiments for comparing the results on the ideal substrates with the situation on a technical surface.

The evaporated metal surfaces were used as prepared. The AlMg3 strips were polished and cleaned with acetone prior to use. They were covered with a few nanometers of a continuous Al oxide layer which also contains a great number of OH groups.

In the thickness range from  $\approx 10$  nm to about 100 nm, the ultra-thin prepolymer films were prepared by spin coating on the metal evaporation layers from a solution in tetrahydrofuran. The thickness was determined by ellipsometry (Wollam M-44). The SFM images (tapping mode) revealed that the fresh prepolymer films were continuous and very smooth ( $R_{RMS} = 0.36$  nm).

Compounds with thin adhesive layers (about 50–100  $\mu$ m) were obtained by pressing the prepolymer melt between two AlMg3 strips. This kind of sample represents directly a model adhesive joint.

## EXPERIMENTAL

Infrared spectroscopy was mainly conducted with *s*- or *p*-polarized light in the external reflection arrangement for the vibration spectra of the ultrathin spin coating layers. Information on chemical conversion and on strong molecular interactions can be extracted. We applied a Bruker IFS 66v equipped with a MCT detector and the Bruker A 513 specular reflection unit. The spectrometer was operated both in the purged and in the evacuated mode. Moreover, usual transmission IR spectroscopy is used for the analysis of annealed prepolymer taken out of the AlMg3 model adhesive joints.

Thickness changes in the spin coating layers due to annealing were recorded by ellipsometry, with SFM images depicting the corresponding changes in the layer morphology.

## RESULTS AND DISCUSSION

### Annealing of AlMg3 Adhesive Joints

Polished and cleaned AlMg3 plates of  $4 \times 4 \text{ cm}^2$  were joined with the DCBA prepolymer adhesive. As depicted in Figure 2, these sandwich specimens were placed in an oven as is done for a real thermosetting adhesive joint. The oven was covered by a silicon wafer with an evaporated aluminium mirror – the “Al cover”.

A heater provides the temperature necessary for the curing reaction of the prepolymer in the adhesive bond, while the cooled Al cover serves to condense any volatile material which might evaporate out of the bond during the annealing process.

The samples were heated to  $100^\circ\text{C}$ ,  $150^\circ\text{C}$  or  $200^\circ\text{C}$  for up to 20 min. At all temperatures, the Al cover collects considerable amounts of volatile products as it is easily seen by eye. Figure 3 presents an example of the IR reflection spectra obtained on the Al cover after sample annealing at  $200^\circ\text{C}$ .

The spectrum of the condensed material coincides with the spectrum of the DCBA monomer. Obviously, the monomer molecules evaporate quickly and massively out of the thin adhesive layer in the *closed* joint. The monomer content in the bond is strongly reduced even at  $100^\circ\text{C}$ , which is well below the temperature range for a sufficiently fast cyclotrimerization. Such a high volatility is very unexpected. For comparison, the bulk prepolymer (with open surface!) loses only minor amounts of mass in the thermogravimetric analysis at the same

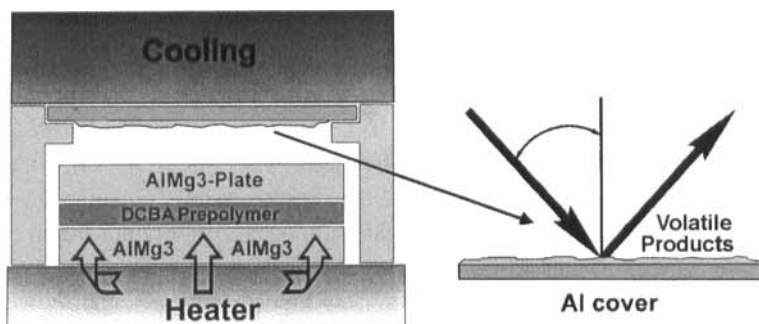


FIGURE 2 Sketch of the experimental set-up (left) for the annealing of AlMg3 plates adhesively bonded with the DCBA prepolymer. Right: Scheme for the IR external reflection spectroscopy of the condensed volatiles on the Al cover.

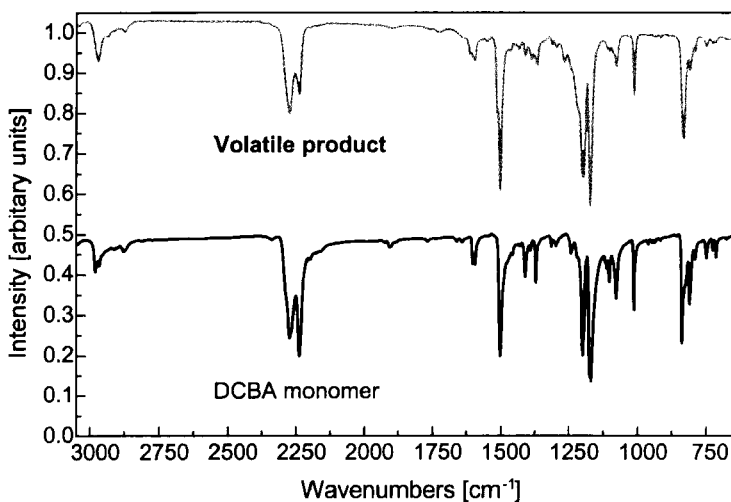


FIGURE 3 Spectroscopic identification of the products which evaporate out of the prepolymer adhesive joint with AlMg3 substrates. *Top*: IR external reflection spectrum of the condensed volatile products out of a 10  $\mu\text{m}$  thick bond line after 15 min. annealing at 200°C. *Bottom*: IR transmission spectrum for the bulk DCBA monomer.

TABLE I Isothermal mass reduction of the DCBA prepolymer in bulk as measured by TGA in  $\text{N}_2$  atmosphere, sample weight  $\approx 5$  mg

<i>TGA temperature</i>	<i>TGA time</i>	<i>Relative mass reduction</i>
100°C	$\gg 24$ h	< 1%
150°C	12 h	5%
200°C	1.5 h	6%

temperatures (see Tab. I). Moreover, these mass losses of a few per cent from the prepolymer bulk occur over a much longer time than the curing experiment with the adhesive bonds. The forced DCBA loss out of the adhesive joint deserves attention since these molecules are no longer available for the curing reaction. The lack of small, mobile monomer molecules will result in a PCU network that is weaker than the usual bulk network.

As the next step, the annealed specimen is destroyed at room temperature by an appropriate shear force. The force is relatively low in this case since the curing is not at all completed within 20 min. The fracture fully proceeds in the adhesive. Some material from the fracture face is prepared from solution as a film on a KBr pellet for IR transmission spectroscopy. Figure 4 compares the spectrum of the annealed adhesive with the spectrum of the original prepolymer.



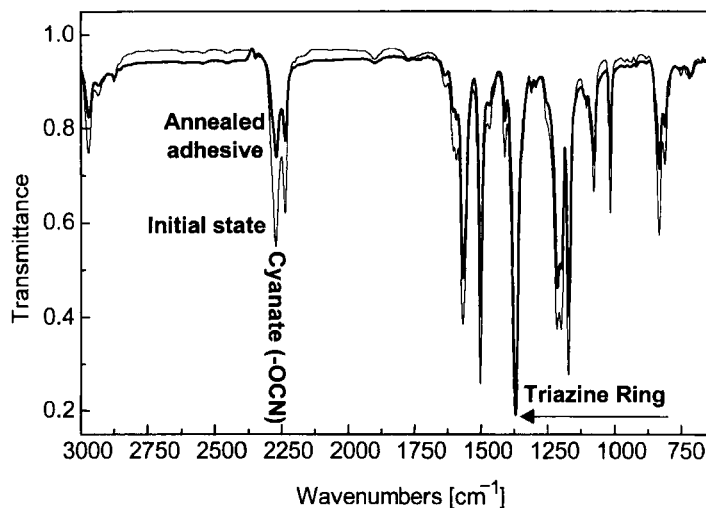


FIGURE 4 IR transmission spectra of the prepolymer in its initial state (thin line) and of the annealed prepolymer from the fracture face of the AlMg3 joint (thick line). Prior to fracture, the AlMg3 joint ( $\approx 100 \mu\text{m}$  thick) was annealed at  $200^\circ\text{C}$  for 15 min. Both spectra are normalized to the triazine ring vibration at  $1368 \text{ cm}^{-1}$ .

The doublet at  $2271 \text{ cm}^{-1}/2236 \text{ cm}^{-1}$  and several other bands clearly indicate that the cyanate content and, hence, the monomer concentration is reduced in the annealed adhesive. Formation of trioxotriazine rings due to cyclotrimerization cannot be excluded but it is not easily established from the spectra because of the massive monomer evaporation. No new reaction products are found in the material from inside the thick adhesive layer.

### Annealing of Ultrathin Prepolymer Films

This part of the study reveals the changes that might be induced in the interphase between substrate and prepolymer by annealing.

Figure 5 provides a sketch of the set-up for the annealing experiment with prepolymer ultrathin films (about 15–20 nm or 65–75 nm thick) on the surfaces of the evaporated Al or Au layers.

The prepolymer film surface has to be shielded against contact with the ambient atmosphere in order to simulate the conditions in a real adhesive bond. For that purpose, a Si wafer was coated with an

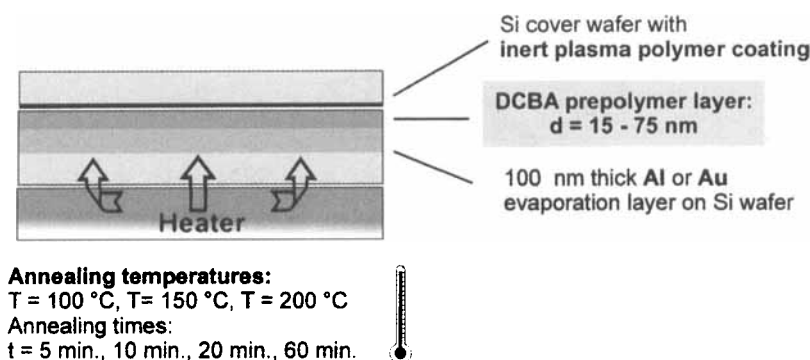


FIGURE 5 Experimental set-up for the annealing experiment with prepolymer thin film samples.

adhesive plasma polymer which completely repels the DCBA prepolymer. A sheet of such a coated wafer served as the cover for the ultrathin prepolymer film specimens during the annealing procedure. The IR spectroscopic checking of the Si sheet prior and after the experiment made sure that no material from the prepolymer film was transferred to the cover.

The SFM image in Figure 6 illustrates the small changes in film morphology induced by the thermal treatment.

The surface is slightly roughened as indicated by the darker areas of a few 100 nm in size in the image. The  $R_{\text{RMS}} = 0.38\text{ nm}$  is still in the same range as for the samples prior to annealing. Hence, the film still covers the substrate completely. The same behavior is found on aluminium.

Figure 7 depicts the integral thickness reduction as a function of the annealing time for several films on Al as measured by ellipsometry.

The films on Al lose about 30% of their initial thickness within the first 5 min. of annealing for all applied temperatures. Similar results are obtained on the gold substrates. In view of the results for the annealed AlMg3 adhesive joint, we interpret the thickness reduction as the result of monomer evaporation. As the DCBA contributes not more than 40% to the initial mass distribution of our prepolymer, the observed thickness reductions indicate a very intense monomer loss for the ultrathin prepolymer films, despite the fact that they are covered by the wafer sheet. Compare again the thermogravimetric data in

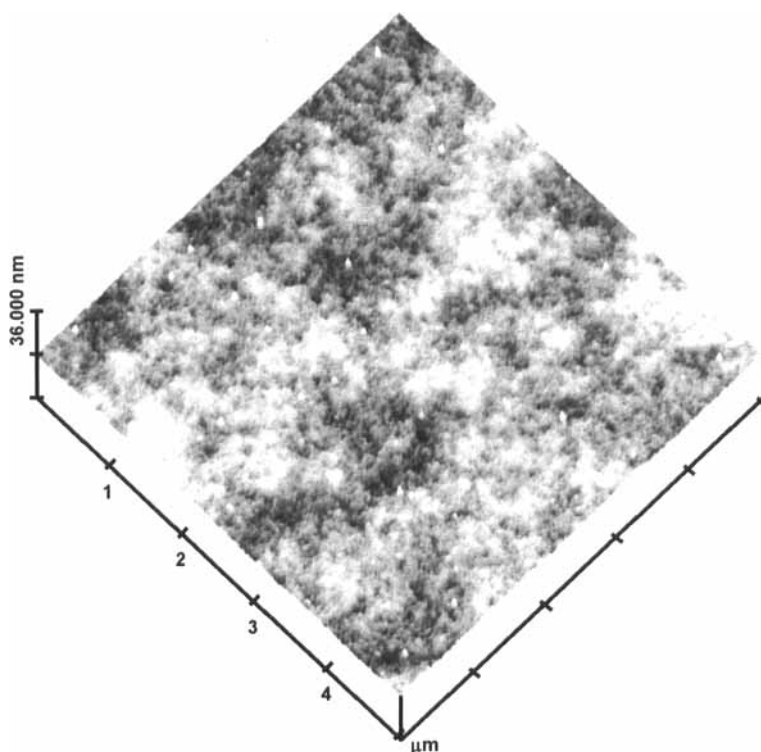


FIGURE 6 SFM tapping image of a 74 nm prepolymer film on an Au evaporation layer after 60 min at 150°C in the annealing experiment according to the set-up in Figure 5.

Table I where no such pronounced mass loss is found for the prepolymer in bulk.

Therefore, the thickness reduction of the ultrathin films can be explained by the assumption that the metal surfaces repel the monomer by some selective thermodynamic incompatibility (*i.e.*, a negative adsorption), thus, forcing its release even out of the very thin bond-line of the covered prepolymer layer.

Figure 8 presents two examples for the time-dependent changes in the IR external reflection spectra due to the annealing of the ultrathin film samples.

The spectra do not only depict the monomer loss. Depending on the annealing temperature, a new IR absorption band evolves around

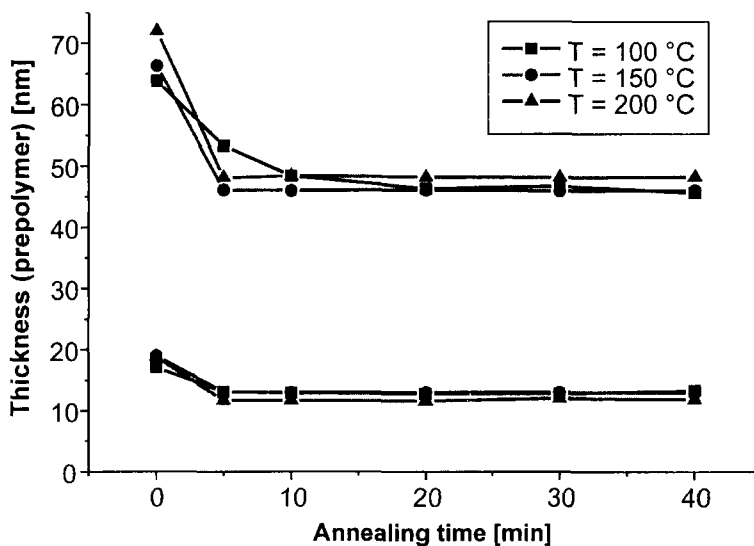
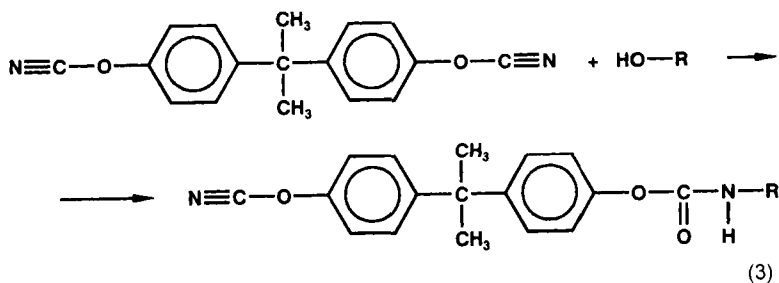


FIGURE 7 Ellipsometric thickness changes of prepolymer ultrathin films on Al evaporation layers as a function of annealing time.

$1750\text{ cm}^{-1}$  with annealing time. For  $100^\circ\text{C}$ , this is illustrated in Figure 8 for covered 79 nm and 73 nm prepolymer films on Au and Al, respectively. The  $1750\text{ cm}^{-1}$  band indicates that a new chemical species emerges in the thin prepolymer layers from a chemical conversion of cyanate groups. In the literature [7, 17, 18, 21], several reactions are discussed for cyanate groups in the prepolymer bulk. However, only the hydrolysis of the cyanate group by a hydroxyl group into a carbamate structure agrees with our reflection spectra:



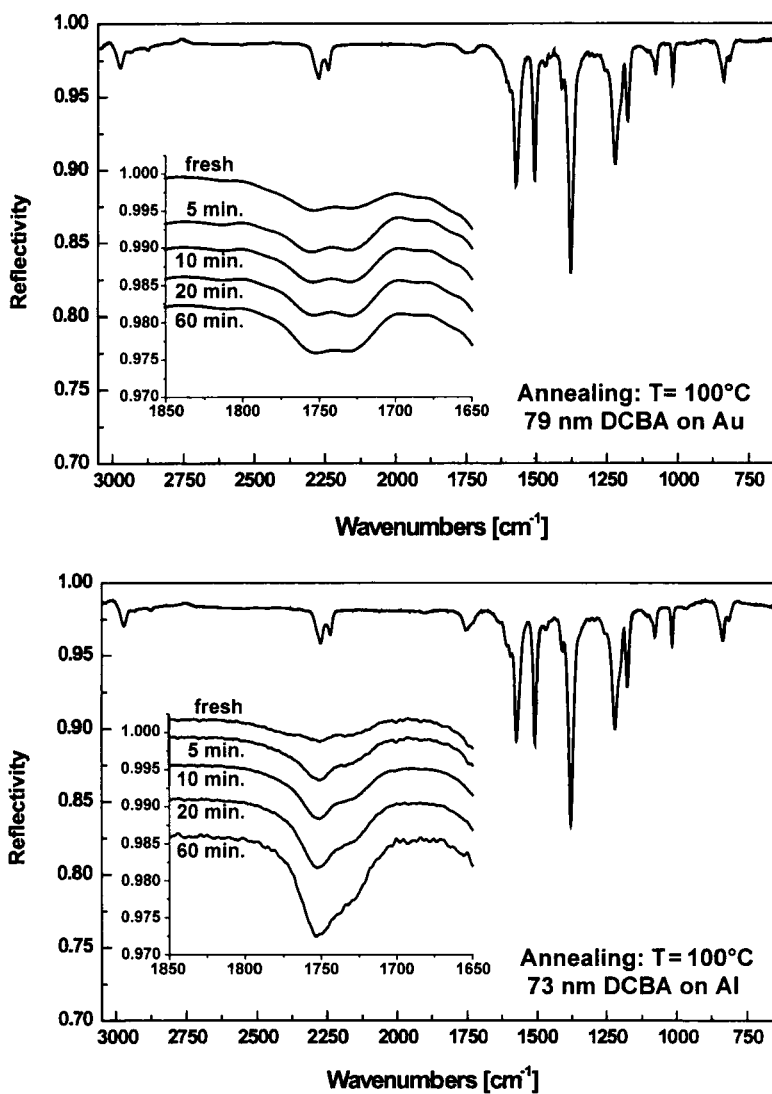


FIGURE 8 Time dependent external reflection IR spectra of a 79 nm prepolymer film on Au (top) and of a 73 nm prepolymer film on Al (bottom) at 100°C annealing temperature. The inserts depict the time-dependent evolution of the carbamate band around 1750 cm<sup>-1</sup>.

For bulk spectra of carbamate-containing compounds, the very strong (C=O) – stretching vibration for secondary as well as for primary carbamates is reported at 1683 cm<sup>-1</sup> – 1740 cm<sup>-1</sup> [19, 20, 22].

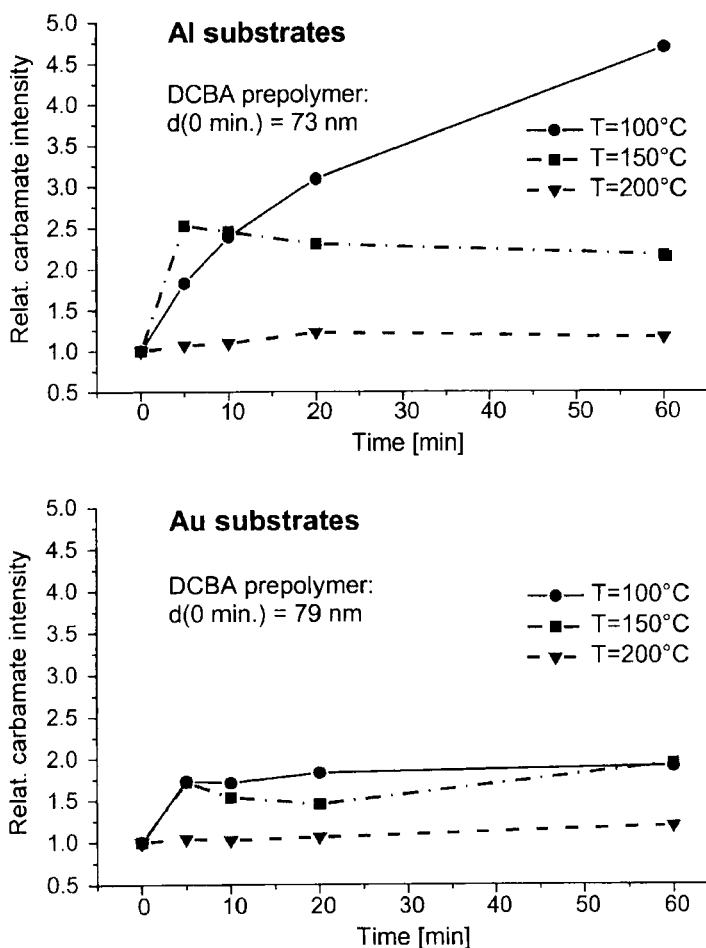


FIGURE 9 Evolution of carbamate with annealing time and temperature as referred to  $t=0$  according to IR reflection spectroscopy of ultrathin DCBA prepolymer films on Al (top) and on Au (bottom).

The small frequency increase observed in our reflection spectra could be due to the optical properties of the thin film specimen or it may indicate the influence from the oxide surface. This surface activity could also be responsible for the doublet-like shape of the  $1750\text{ cm}^{-1}$  band in our reflection spectra. Note that the intensity ratio of the high-frequency peak (at ca.  $1753\text{ cm}^{-1}$ ) relative to the low-frequency peak (at  $1727\text{ cm}^{-1}$ ) is larger on Al than on Au.

Figure 9 summarizes the carbamate intensity development as a function of time obtained on Al and Au for three annealing temperatures.

Generally, much more carbamate is found on Al than on Au. This is another hint of the specific catalytic activity of the surface states on the different substrates.

The amount of carbamate also decreases with increasing annealing temperature. No carbamate rise is found with time during annealing at 200°C. That instability is an additional proof for the assignment of the band at  $1750\text{ cm}^{-1}$  as a carbamate because a decay of the carbamate above about 190°C is reported in [7] for the bulk.

## CONCLUSIONS

During short-time annealing at elevated temperatures, the IR spectra reveal that some cyanate groups hydrolyze into a carbamate that could appear in different structures in the interphase on the investigated metals. Both hydroxyls and adsorbed water could be involved in that chemical reaction. Although being most prominent on Al, the carbamate production is also detected on the Au. This indicates a substrate-specific catalytic activity.

On Al, carbamate coupling to the oxide *via* surface hydroxyl groups could serve as a new chemical adhesion mechanism. The details of that mechanism are not yet fully understood from our experiments. A few of the possible structures are illustrated by Figure 10.

On gold, the details of such a bond are not clear yet because the state of the adsorbed water on the surface is not so well known.

With respect to the practical application of polycyanurates as high temperature adhesives, the carbamate adhesive bond appears not to be very useful, however, because the carbamate is not formed at temperatures above 150°C or it decomposes quickly if it was produced by low temperature conversion of cyanate groups.

Further, the IR spectroscopic and ellipsometric results indicate an unexpected strong and accelerated loss of DCBA monomer from all investigated prepolymer layers on the metal substrates during annealing. Even enclosure of the prepolymer in an adhesive bond cannot stop these losses. We conclude that the substrates are

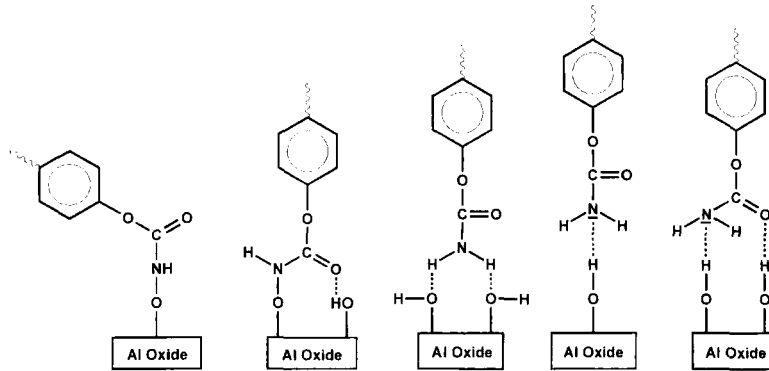


FIGURE 10 Schematic drawing for possible chemical links of DCBA prepolymer molecules to the Al oxide surface *via* a carbamate functionality resulting from the reaction of a cyanate with OH groups or with adsorbed water.

thermodynamically incompatible with the DCBA (*i.e.*, negative adsorption) which pushes the monomer molecules out of the interphase layer with the substrates. This interpretation also receives support from the observation that DCBA desorbs quickly and completely from the same substrates under vacuum conditions [16].

As a consequence, mainly the less mobile, bulky oligomers remain in the interphase on the substrate. These oligomers adhere at least in part to the surface by chemical adhesion bonds *via* the trioxotriazine units, as deduced in [16]. Hence, a thermal curing reaction in that interphase between such molecules with reduced mobility will result in a polycyanurate network which is much weaker than in the bulk polymer. This could exert a negative influence on the mechanical strength of an adhesive joint formed with pure polycyanurates and affords additional chemical modification for practical applications.

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