

Rheological Investigation of Cure Kinetics and Adhesive Strength of Polyurethane Acrylate Adhesive

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ABSTRACT: In this work, we used rheological techniques to study both the cure characteristics and the degree of cure of polyurethane acrylate adhesive, a type of reactive adhesive used in hard disk component assembly. These results were then correlated with the tensile shear strengths of adhesives. Here, the cure characteristics of polyurethane adhesive were investigated at isothermal conditions ranging from 25 to 120°C. From the rheological results, the gelation time, the vitrification time, as well as the time required to reach the maximum degree of cure, decreased when increasing the curing temperature. The cure rates of adhesive increased with temperature in three temperature ranges, which were retardation zone, vitrification zone, and reaction-controlled zone. The cure rates in these zones were controlled by slow diffusion, fast diffusion, and the rate of reaction, respectively. From the temperature sweep of fully-cured adhesives, we found that

the crosslinking level of adhesives increased with curing temperatures at different rates depending on the temperature zones as well. Moreover, the adhesive strength measured by tensile shear test was found to also increase correspondingly with the adhesives' T_g , indicating that the crosslinking level directly affected the adhesive strength. The strong dependence of adhesive strength with crosslinking level indicates that the crosslinking level was essential for high adhesive strength. The correlation of cure characteristics and adhesive strengths at various curing temperatures performed in this study can further provide useful information for planning appropriate curing schemes of polyurethane acrylate adhesives used in electronic and other industries. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2344–2350, 2012

Key words: adhesives; rheology; curing of polymers

INTRODUCTION

Polyurethane acrylate adhesive is a thermosetting material which is used in many industries such as automotive and electronic industries for assembly of components.¹ The polyurethane acrylate adhesive used in this study is a reactive adhesive-like epoxy, but with significantly low viscosity. As a result, this adhesive is suitable for encapsulation applications, where adhesives must flow easily into narrow cavities before curing reactions take place. Even though the applications of polyurethane acrylate adhesives are becoming more widespread, the literature on curing characteristics of these adhesives has not been found. Therefore polyurethane acrylate adhesive is of great interest and was used in this study.

For thermosetting adhesives, gelation and vitrification are two important events that occur during the crosslinking polymerization reaction characterized by the transformations of liquid-to-rubber and liquid

or rubber-to-glass states, respectively.² When curing reaction begins, the small molecules of adhesive precursors react and become larger. This process continues until the reaction reaches the gelation point, where the molecules are sufficiently large and become interconnected. At this point, the first crosslink structure occurs, and the adhesive then undergoes phase change from liquid (sol) to solid network (gel).³ The curing reaction continues to create a denser crosslinking network until it reaches the maximum level at that curing condition. The schematic of crosslink network growth during the curing reaction between parallel plates can be illustrated in Figure 1.

The rate of curing reaction depends on the curing temperature and the T_g of adhesive. Since the glass transition temperature (T_g) of the adhesives is dependent on the state of cure, the cure rate of adhesive is high and can proceed to completion when the curing temperature is above the maximum T_g of adhesive. On the other hand, if the curing temperature is lower than the maximum T_g of adhesive, the curing reaction will proceed quickly as long as the curing temperature remains higher than the immediate T_g of adhesive. Once the curing temperature is below its T_g , the reaction is significantly retarded.

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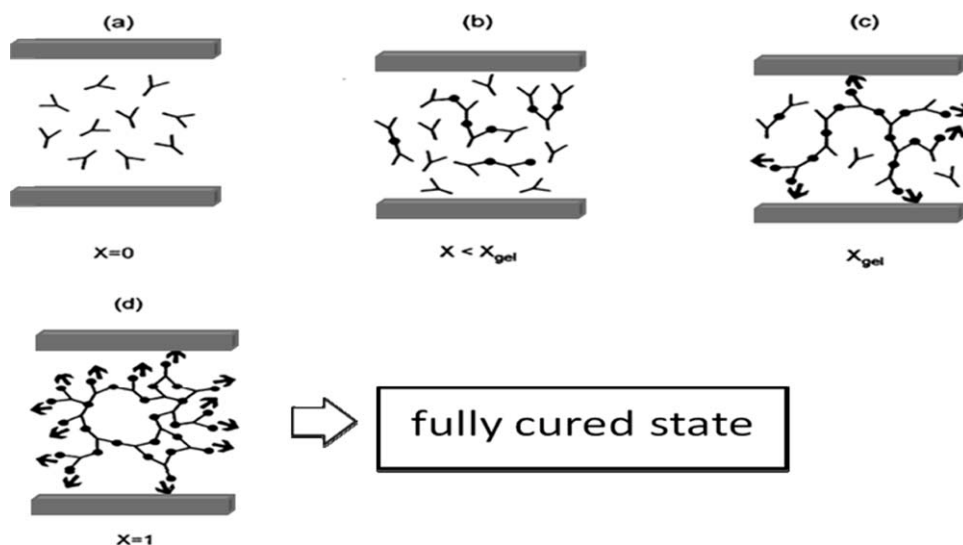


Figure 1 The schematic of crosslink network growth from liquid to fully-cured state.

The transition point when curing temperature becomes lower than the T_g is called the vitrification point.⁴ At this point, the adhesive structure will transform from rubbery gel to glassy gel. This transformation can be illustrated schematically in Figure 2. Therefore, for the curing conditions that experience vitrification, the curing reaction would not be able to reach the fully-cured state.

In the past, DSC (differential scanning calorimeter) was extensively used for obtaining the cure kinetics of reactive adhesive.^{5–8} This technique provides information on cure rate from the amount of heat released from the curing reaction.⁹ Nevertheless, the technique cannot be easily used to identify the vitrification point. Moreover, the typical DSC technique cannot indicate the actual gelation time, especially of anaerobic adhesives, due to poor convective heat transfer in the DSC chamber and lack of metal contact on one side of the adhesive. Since the polyurethane acrylate adhesive used in this study is anaerobic adhesive, the contacts with metals, especially with active metals (e.g., aluminum, bronze, nickel and steel), in the ab-

sence of oxygen or air are essential.¹⁰ As a result, the onset of curing reaction obtained from a DSC is significantly delayed. Another way to investigate the cure behavior of adhesive is by using rheological techniques. This rheological experiment proceeds with intimate metal contact on both sides of adhesive, thus imitating the contacts that are found in encapsulation and underfill applications.

In this work, we used rheological techniques to study both the cure characteristics and the degree of cure of reactive adhesives by the increase in storage modulus (G'), where the gelation and vitrification points are probed by the crossover in the storage modulus (G') and loss modulus (G'') and the peak in $\tan \delta$, respectively.²

The adhesive strength of thermoset adhesives depends on two important factors, which are cohesion and adhesion properties.¹¹ The cohesion properties depend on the strength of crosslink structures, whereas the adhesion properties depend on the surface wettability, interpenetration and mechanical interlock between the adhesive and the adherends, as well as the type and cleanliness of adherends. The wettability of adhesive can be described by two activities: (1) a lateral spreading of the film and (2) a penetration of the adhesive fluid into the surface cavities, generated by the inherent surface roughness.¹² In this study, the adhesive strengths measured by the tensile shear tests¹³ at various curing temperatures were correlated with the cure properties obtained experimentally.

EXPERIMENTAL

Material

The adhesive used in this research was the AS 5505[®] polyurethane acrylate adhesive produced by ASEC,

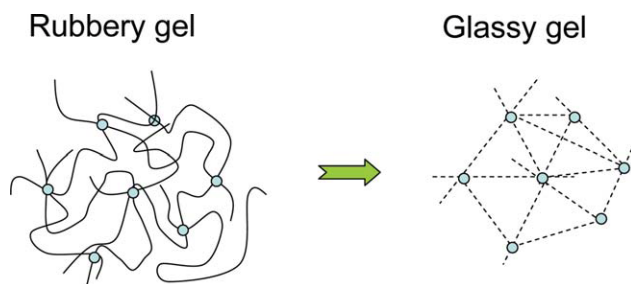


Figure 2 The schematic of adhesive structure transformation from rubbery gel to glassy gel. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Japan. This adhesive is an anaerobic adhesive used with metal parts. The curing of this adhesive occurs by the proprietary reaction of 56.5% urethane-methacrylate oligomer with 38.5% hydroxyl-alkyl methacrylate in the presence of organic hydroperoxide and acrylic acid. The viscosity of this adhesive precursor is 500–800 mPa with the gap filling ability of 0.15 mm. The T_g and the tensile shear strength of the fully-cured adhesive reported by the manufacturer are 55°C (by TMA) and 17.6–19.6 MPa, respectively. The recommended operating temperature is between 55 and 120°C.

Rheological test

The Bohlin Gemini HR Nano rheometer from Malvern Instruments, with parallel plate fixture was used to investigate the rheological properties of the adhesive. The plate diameter and gap size between the parallel plates were 25 and 0.15 mm, respectively. Time sweep test by oscillation method was applied for studying the cure characteristic of the isothermal curing system at 25–120°C. The degree of cure at a specified curing temperature was detected by the increase in storage modulus (G') until the maximum curing capacity was reached. The cross-linking levels of adhesives were qualitatively evaluated from the T_g of the cured adhesive. To evaluate the cure conversion at this stage, the curing temperature was ramped up to 100°C and maintained at this temperature until the adhesive was fully-cured. The system was then cooled down to the initial curing temperature to compare the final storage modulus after being fully cured at 100°C (State 2) with the maximum G' of the initial temperature (State 1). The curing scheme described above is illustrated in Figure 3.

The cure conversion at any time (t) can be obtained from the G' values of State 1 and State 2 indicated in Figure 3 by

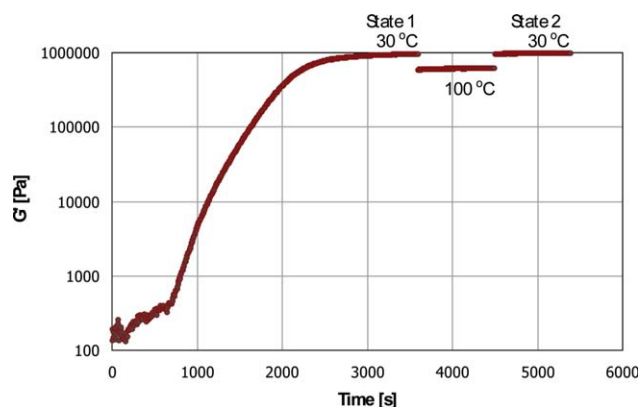


Figure 3 The storage modulus G' (log scale) of the polyurethane adhesive cured at 30°C, with the temperature ramp-up to 100°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

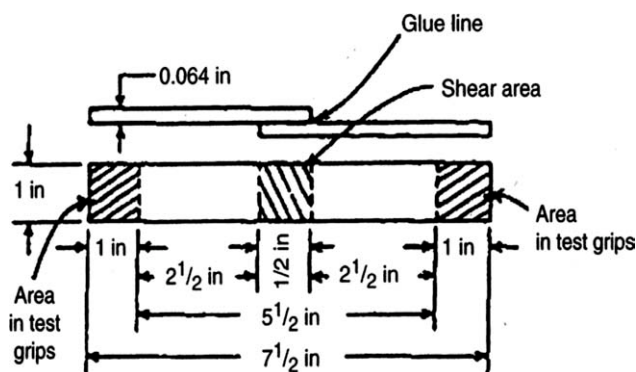


Figure 4 Standard design of tensile shear test specimen (ASTM D 1002).

$$\text{Cure conversion } (t) = \frac{G'(t)}{G'_{\text{state2}}}$$

The adhesive was first completely cured at the specified temperature and then tested by temperature sweep from room temperature up to 100°C. Note that the adhesive cured to the equilibrium level at 100°C was chosen to be the fully-cured adhesive (G'_{state2}) in this study because this temperature is considered sufficiently high without requiring too much expansion compensation when ramping from much lower temperatures. However, to attain a more accurate value of G' for fully-cured adhesive, the adhesive should have been cured to the highest possible temperature before degradation occurred.

Tensile shear test

The substrates used for conducting tensile shear test were aluminum pieces with 1.5 mm thickness. The test specimens were prepared according to ASTM D 1002, as shown in Figure 4.¹⁴

The dimensions of the substrates were 4 in. long and 1 in. wide. The glue line length between the two substrates was 0.5 in. A compression mold was used to control the adhesive thickness at 0.15 mm and to supply heat for the curing process. The tensile shear tests of the prepared specimens were carried out using the Dak System universal testing machine series 9000 with the tensile speed of 1.3 mm min⁻¹. The tensile shear strength was calculated from the ratio of peak load (F_{max}) and the glued area (A_s). For reliable test results, the average values obtained from five specimens were used for each curing condition.

RESULTS AND DISCUSSION

In this study, the cure characteristics of a polyurethane acrylate adhesive at various curing temperatures were investigated and correlated with adhesive strength.

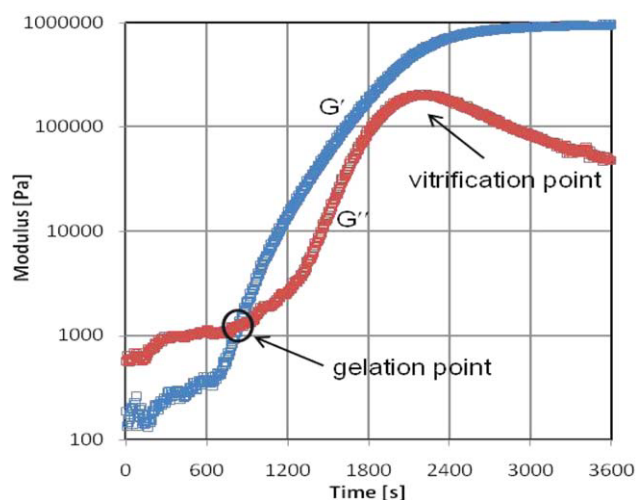


Figure 5 The plot of G' and G'' measured during the curing process at the curing temperature of 30°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Cure characteristics

The cure characteristics of polyurethane acrylate adhesive used in this study were investigated by rheological techniques, where the nondestructive oscillatory mode has been used. By this technique, the transitions occurring during the curing process were observed by the changes in the storage modulus (G') and loss modulus (G''). An example of G' and G'' curves during a curing process at the curing temperature of 30°C is shown in Figure 5.

From the figure, the gelation and vitrification points were obtained from the crossover point between G' and G'' and from the maximum point of the G'' curve, respectively.

The cure kinetics at various cure temperatures were monitored by the increase in storage moduli (G'), as illustrated in Figure 6. From the figure, the

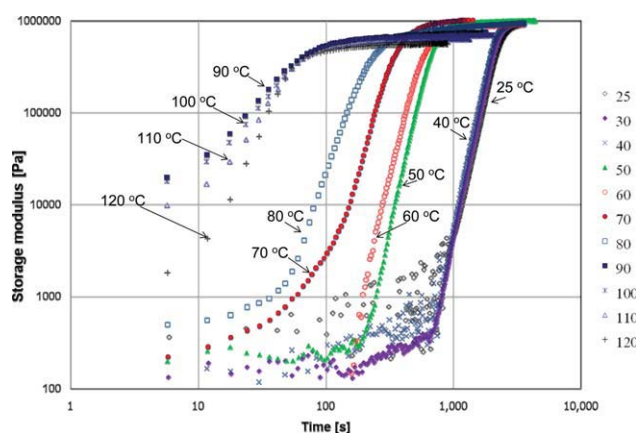


Figure 6 The increase in storage modulus (G') during curing at various curing temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

cure rate of adhesive increased with temperature in three temperature ranges in the order of cure rate, which are retardation zone at temperatures below 50°C, vitrification zone during the glass-to-rubber transition, and chemical reaction zone beyond the T_g of fully-cured adhesives. The cure rate at cure temperatures below 50°C was possibly low due to the effect of reaction inhibitor together with the vitrification effect. At higher temperatures but still lower than the T_g of fully-cured adhesive (89°C), the reaction rate increased monotonically with temperature as the reactions were controlled by vitrification. Beyond 90°C, the vitrification effect disappeared and the cure rate increased further as the reactions were mainly controlled by the rate of reaction.

The gelation, vitrification, and cure times at different curing temperatures are summarized in Figure 7. From Figure 7, the gelation time, the vitrification time, as well as the time required to reach the maximum degree of cure, decreased when increasing the curing temperature corresponding to the cure rate. At curing temperatures above 70°C, the adhesive curing was so rapid that the gelation times could not be detected. Also, the vitrification peaks disappeared at 90°C and above indicating that these curing temperatures were above T_g of the fully-cured adhesives.

The actual T_g of the adhesive was measured using rheological techniques by applying a temperature sweep after the adhesive was fully cured. The plots of $\tan \delta$ versus temperature and G' versus temperature obtained from the temperature sweep test on the adhesive fully-cured at 100°C are shown in Figure 8(a,b), respectively. The T_g curve in Figure 8(a) indicates that the glassy structure of the crosslinked adhesive was gradually softened at a temperature of around 70°C and became totally rubbery at the temperature of 120°C. The average T_g indicated by the

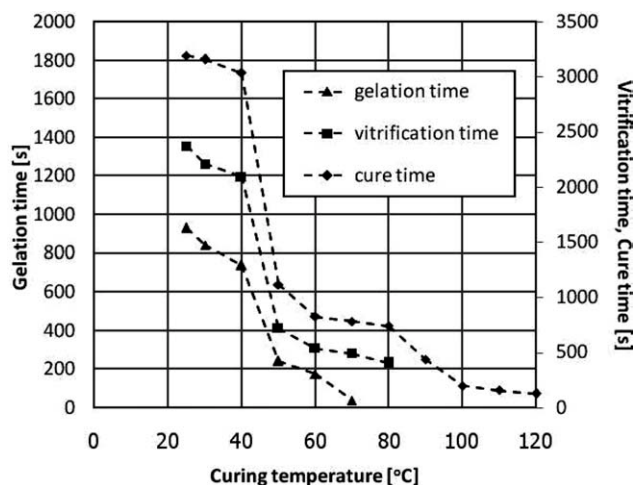


Figure 7 Gelation and vitrification times at various curing temperatures.

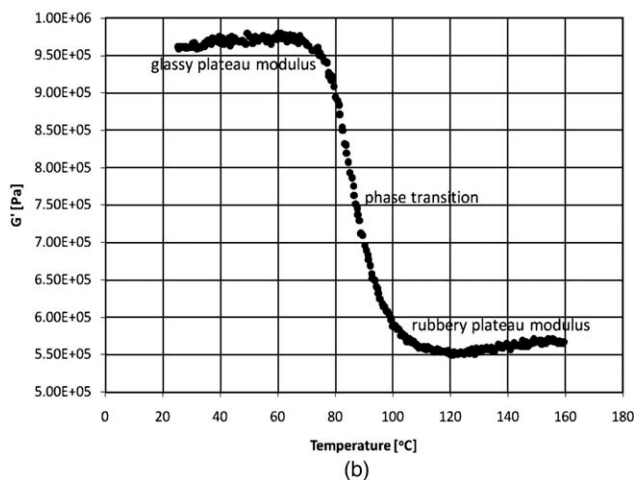
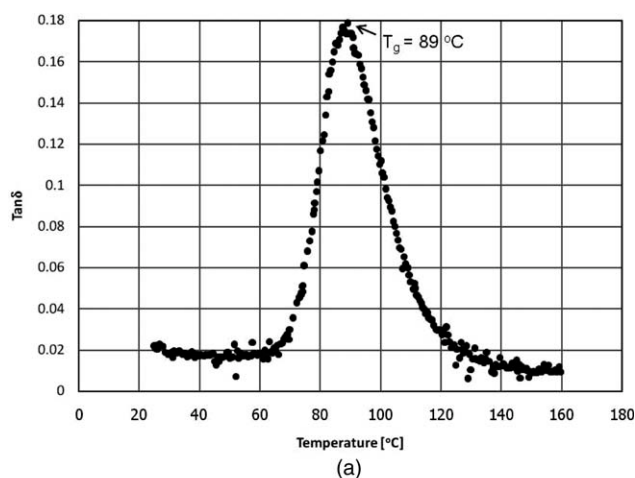


Figure 8 The changes of $\tan \delta$ with temperature (a) and of G' with temperature (b) for fully-cured adhesive at the curing temperature of 100°C.

peak in $\tan \delta$ ^{6,15} was found to be 89°C, consistent with the disappearance of the vitrification peaks at curing temperatures above this point. The change in G' during the glass-to-rubber transition is shown in Figure 8(b). The plateau in storage modulus at the temperatures below T_g is called a glassy plateau modulus (G_{glass}^0), whereas the plateau in the storage modulus at temperatures above T_g is called a rubbery plateau modulus (G_N^0).¹⁶ The magnitude of G_{glass}^0 is dependent on the segmental modulus of adhesive, which is inherent to the molecular nature of adhesive. On the other hand, the rubbery plateau G_N^0 is dependent on the crosslink level of the adhesive structures.

Temperature sweep tests of cured adhesives at different curing temperatures are shown in Figure 9. From the figure, the adhesives cured at high temperatures (>80°C) show the typical single and narrow peaks in the $\tan \delta$ -temperature plot. On the other hand, adhesives cured at low temperatures show broad spectra of $\tan \delta$, indicating that those adhe-

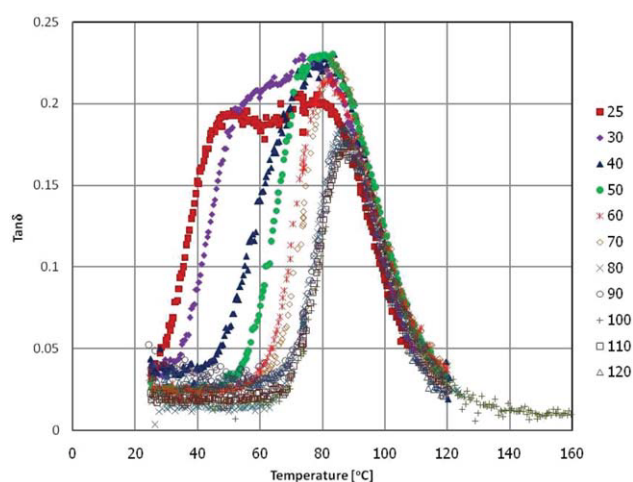


Figure 9 The temperature sweep of adhesives fully cured at various curing temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

sives were not fully-cured prior to the sweep tests. Therefore, the onset values of $\tan \delta$ peaks were used to indicate T_g in this study instead of the maximum point.¹⁷ The T_g values of adhesives cured at different temperatures are summarized in Figure 10. As can be seen, for curing temperatures in the range of 25–60°C, the T_g of adhesives increased with curing temperature. On the other hand, for the curing temperatures of 70–90°C, the T_g did not increase much with curing temperature. The curing mechanism in this temperature range might have been complicated by the transition of adhesive structures from glassy gel to rubbery gel. Beyond 90°C, the T_g increased slightly with curing temperature again indicating that denser crosslink networks were formed as the remaining part of the glassy structure turned into rubbery structure and might have been further cured.

By comparing $G'(t)$ to G' of fully-cured adhesive as explained in the experimental section, we can also convert from the plot of G' (Fig. 6) to that of cure conversion, as shown in Figure 11. The maximum conversion obtained at various curing temperatures could be characterized in three zones. At low

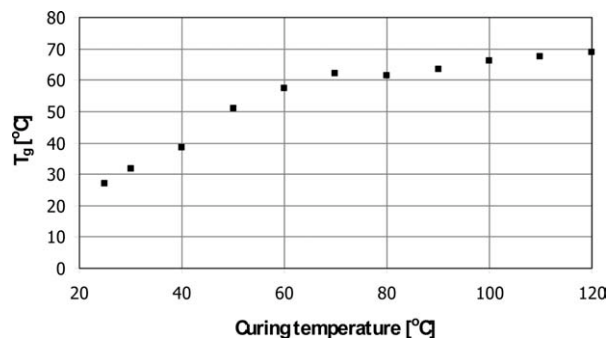


Figure 10 The correlation of T_g and curing temperature.

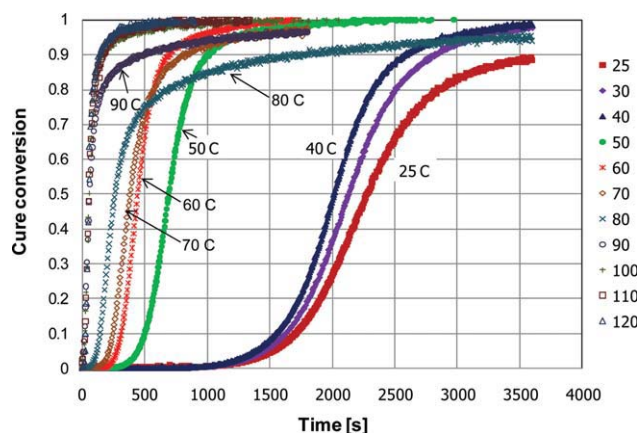


Figure 11 The correlation of cure conversion and time at various curing temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

temperatures in the range of 25–60°C, the maximum conversion increased with temperature to reach the fully-cured state. However, as the curing temperature approached the glass-to-rubber transition (between 70 and 90°C) the maximum conversion dropped below 1.0 and increased to 1.0 again at the curing temperatures beyond 90°C. It can be explained that adhesives fully cured at low temperatures are the complete structures of glassy crosslink and those cured at high temperatures are the complete structures of rubbery crosslink. The drop in conversion during the transition zone coincided with the slow increase in T_g in this zone (Fig. 12). The lower conversion and slow increase in T_g during this transition zone was still difficult to explain. At temperatures higher than 90°C, the T_g slightly increased with temperature, indicating that the adhesive might be further cured. This slight increase was not detected by the increase in cure conversion possibly due to the limitation of choosing 100°C as the referenced temperature for maximum cure.

Adhesive strength

The strength of adhesive appeared to increase in three steps. At temperatures below 70°C, we found

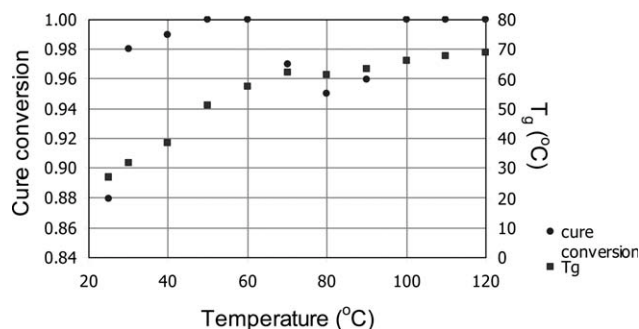


Figure 12 The relation of the cure conversion and crosslinking level at various curing temperatures.

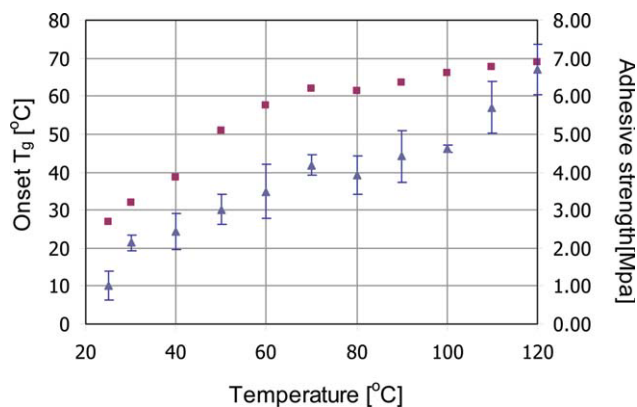


Figure 13 The relation of the crosslinking level and adhesive strength at various curing temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

that the tensile shear strength of adhesive increased with cure temperatures due to higher conversion. From the curing temperatures of 70–90°C, which were in the glass-rubber transition zone, the tensile shear strength was not much improved at higher curing temperature. However, when the temperature increased beyond the glass transition zone, the tensile shear strength of adhesive slightly increased with cure temperature again. By comparing the crosslinking level (implied by the T_g value) with tensile shear strengths of adhesives (Fig. 13), we found that the strength correlated remarkably well with the adhesive's T_g , especially at curing temperature below 90°C. Above 90°C, while the T_g s of adhesive increased only slightly with cure temperature, the tensile shear strengths were significantly improved indicating stronger networks found at higher curing temperatures.

CONCLUSIONS

Rheological techniques as proposed in this study can be applied to investigate the cure characteristic of polyurethane acrylate adhesives at various curing temperatures. From rheological experiments, the gelation time, vitrification time, cure rate, and cure conversion, as well as the T_g of adhesives, can be obtained. We found that the cure rate of the adhesive increased with temperature in three temperature ranges in the order of cure rate, which were retardation zone at temperatures below 50°C, vitrification zone during the glass-to-rubber transition, and reaction-controlled zone beyond the T_g of fully-cured adhesives. We also found that the cure conversions at cure temperatures in the glass-rubber transition zone (70–90°C) were less than those cured at slightly lower or higher temperatures. Moreover, the crosslinking level of adhesive indicated by T_g also correlated well with the cure conversion and adhesive strength, indicating that the strength of

adhesive in this case was controlled by cohesion property. The information obtained from this study can be applied in planning appropriate curing schemes of polyurethane acrylate and other thermosetting adhesives used in electronic industries.

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