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Study on Relationships between Curing Pressures and Mechanical Properties for Epoxy Adhesive Films

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In this paper, the effects of different curing pressures on the mechanical properties of epoxy adhesive films were investigated. When the curing pressure increases from 0 MPa to 0.5 MPa, Nano-indentation analysis shows that the elastic modulus of the cured adhesive films increases from 2.92 GPa to 3.49 GPa, the tensile strength increases from 42.0 MPa to 43.7 MPa, and the breaking elongation increases from 2.61 % to 3.73 %. It was indicated that the microscopic and macroscopic mechanical properties of the cured adhesive films were improved. DMA results showed that, as the curing pressure increases, the Tg of the cured product does not change significantly, but the crosslinking density is significantly improved. These results indicate that a higher modulus of the cured product could be gained by increasing the curing pressure appropriately.

1. Introduction

High temperature curing epoxy adhesive films show high toughness, high strength, and high durability properties (Awaja et al., 2009; Barnes and Pashby, 1998). Due to their excellence, they are indispensable important bonding-repair materials in aerospace industry (Danielson and Berg, 1967; Archer and Mcilhagger, 2015). This technology can transmit large static and dynamic loads, and make the aircraft work reliable in a long-term. The Redux series of phenolic-acetal high-performance structural adhesives were first used to bond the aircraft metal structures in the UK from the 1940s. High-temperature curing structure adhesives have been improved with the continuous development of aerospace technology. Some commercial adhesives, such as Redux 319 (Hexcel), FM-300 (Cytec), AF311-5M (3M), and so on, had passed airworthiness certification in the aircraft bonding maintenance due to their good bonding performance (Higgins, 2000; Comyn, 2006).
For the bonding repair, the adhesives were the medium that transferred the loading between the patch and the repaired structures (Cagle et al., 1973; Radley, 1964). The choice for the type of adhesive, the curing process, and the compatibility of the patch structure had significant effects on the repairing effects. Curing pressure was an important factor affecting the final adhesive properties, while few studies were focused on this area (Khan et al., 1964; Khan et al., 2007; Morganti et al., 2016; Wang et al., 1992). The main research on adhesives mainly focused on further improving product quality precision, process performance, high heat resistance and high durability. In order to design the best curing process of adhesives, some scholars studied the curing mechanisms of adhesives through the curing dynamics (Katnam et al., 2013; Lei and Frazier, 2015; Baker and Jones, 1988). The evaluation criteria for the performance of adhesives were generally characterized by macroscopic mechanical properties, few studies reported the relationships between the nano-mechanical properties and macroscopic mechanical properties. In this paper, the micro-mechanical properties of adhesives under different curing pressures were studied by nano-indention analysis. The tensile properties of adhesive films under various curing pressures were studied by universal testing machines. Through the above analyses the mechanism of the influence of the curing pressure on the mechanical properties of adhesives was proposed.

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2. Experimental

2.1 Material

METLBOND 1515-4M epoxy adhesive film, manufactured by German company, Cytec Industries Inc., was adopted in the test.

2.2 Preparation of cured adhesive films

A was cured at 175 ℃ for 2 hours in a thermocompression between glass plates on which a release agent (75-95 % aliphatic hydrocarbon and <20% dibutyl ether) had been spread with various pressures: 0 MPa, 0.075MPa, and 0.5 MPa. The 0 MPa group was cured as a non-pressurized sample for comparison, while the 0.075 MPa and 0.5 MPa samples were used during the curing processes being related to actual industrial usage. The corresponding cured products were labeled as poly(A)-0, poly(A)-0.075, and poly(A)-0.5.

2.3 Measurements and Characterization

Universal testing machine: the films used were around 100 μm-thick and were rectangular in shape (50*10 mm). Testing of the mechanical properties of the cured resins was performed using a KQL KD-5 testing machine according to ASTM D882 at room temperature. A gauge length of 20 mm and a crosshead speed of 2 mm/min were set for the test.
Differential scanning calorimetry (DSC) was performed on a TA Instruments Q20 model at a heating rate of 10 ℃/min under nitrogen atmosphere at a flow rate of 60 ml/min.
The dynamic mechanical properties of the cured films were obtained using TA instruments DMA Q800 dynamic mechanical analyzer (DMA) with a sample dimension of 12 mm × 9 mm × 0.2 mm in a controlled strain tension mode with an amplitude of 20 μm and a temperature ramp rate of 5 °C/min from 40 ℃ to 300 ℃ at a frequency of 1.0 Hz.
Nano-indentation instrument: NHT2, the berkovich diamond Mitsubishi cone indenter was pressed into the samples with the loading rate of 60 mN / min from 0 mN to 30 mN, the maximum depth of indentation was 2900 nm. Hold for 10 s to eliminate the creep effect before unloading, and then unload at a rate of 60 mN / min. The loading-time curves please see Figure 1.

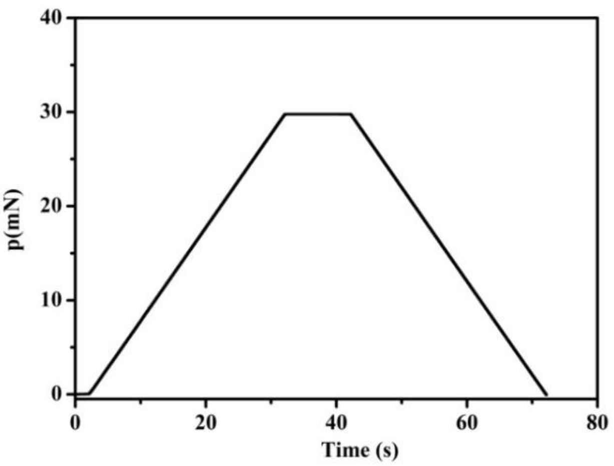


Figure 1: Loading-time curves from Nano-indention analysis.

3. Results and Discussion

3.1 Curing behavior of the cured adhesive films

The DSC curve of uncured A was shown in Figure 2(a). The onset temperature T_{onset} and the peak temperature T_{peak} were 134 ℃ and 159 ℃ respectively. The total heat enthalpy was 268 J/g. After curing for 2 hours at 175 ℃, the exothermic peaks disappeared, and the residual heat enthalpy became zero. These results indicated that the cured samples were cured completely and adding curing pressure had little effects on the curing of the adhesive films.

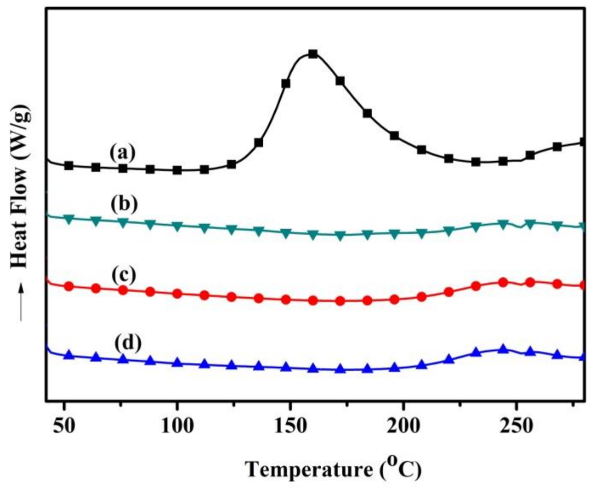


Figure 2: DSC curves of A (a), poly(A)-0 (b), poly(A)-0.075 (c), and poly(A)-0.5 (d)

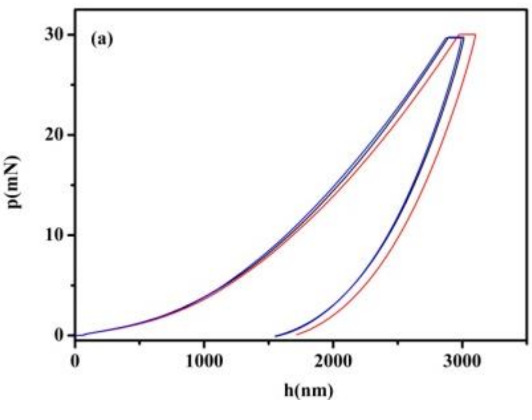
3.2 Nano-indentation test and analysis

Loading and displacement curves of the films under different curing pressures were shown in Figure 3. The load displacement curves of the three samples were easily reproducible. According to the computational model proposed by Waugh (2016), the hardness and elastic modulus of the samples could be derived from equations 1 and 2.

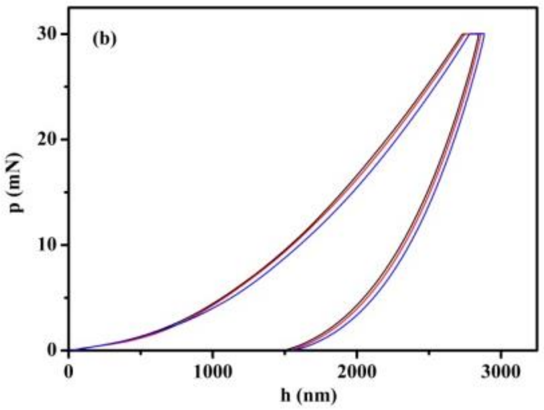
$$H_{iT} = \frac{P_{max}}{A_p} \quad (1)$$

$$E_r = \frac{\sqrt{\pi}}{2\beta} \frac{S}{\sqrt{A_p}} \quad (2)$$

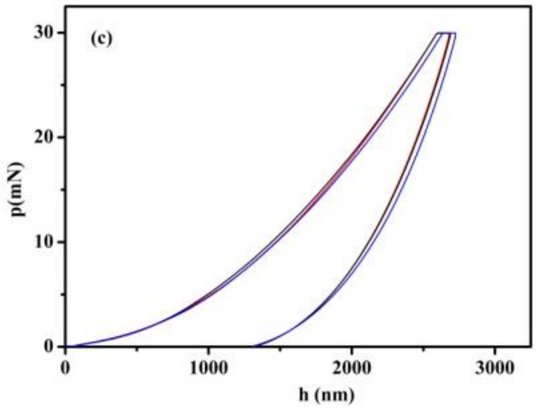
Where β related to the shape of the indenter, for berkovich indenter, β=1.034. A_p was the projection contact area.
The average hardness of adhesive films under different pressures was shown in Figure 4. The average hardness of poly (A)-0.5, poly (A)-0.575 and poly (A)-0.5 were 185.7 MPa, 206.2 MPa, and 243.9 MPa.
The hardness rates increased by 11.0% and 31.3% respectively within the increasing curing pressure. Meanwhile, the elastic modulus increased from 2.92 GPa to 3.49 GPa within the increasing curing pressure.
It was indicated that the cross-linking densities of cured adhesive films increased when the curing pressure increased, moreover, the strength of cured adhesive films also increased.



(a) poly(A)-0



(b) poly(A)-0.075



(c) poly(A)-0.5

Figure 3: The load-displacement curves

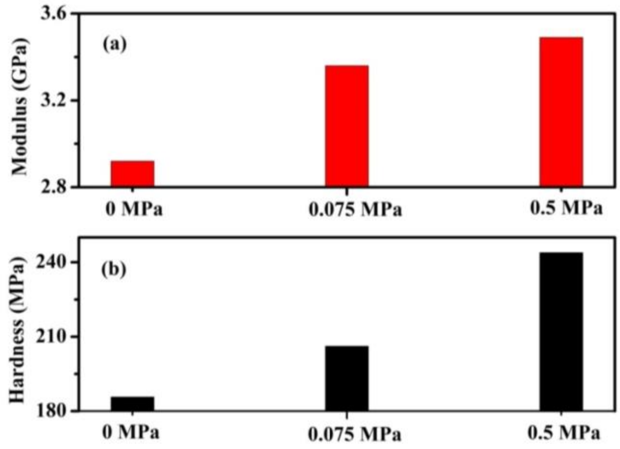


Figure 4: Elastic modulus and hardness of the cured adhesive films under different curing pressures

3.3 Tensile property analysis

The tensile properties of the cured adhesive films were shown in Table 1. The tensile strengths of poly(A)-0 and poly(A)-0.5 were 42.0 MPa and 43.7 MPa respectively. The breaking elongations of poly(A)-0 and poly(A)-0.5 were 2.61 % and 3.73 % respectively.

The tensile properties of the cured products slightly improved when the curing pressure increased from 0 MPa to 0.5 MPa. This phenomenon may be related to the cross-linked structures of the polymers, as the degree of cross-linking increased with increasing cure pressure (see below table).
Meanwhile, the rules of change on the macro-mechanical properties were also consistent with those of the micro-mechanics analysis for the three cured adhesive films.

Table 1: Tensile properties of cured adhesive films prepared under different cure pressures

Sample	Maximum force (N)	Tensile strength (MPa)	Breaking elongation (%)
poly(A)-0.5	225.5	43.7	3.73
poly(A)-0	224.1	42.0	3.10

3.4 DMA Analysis

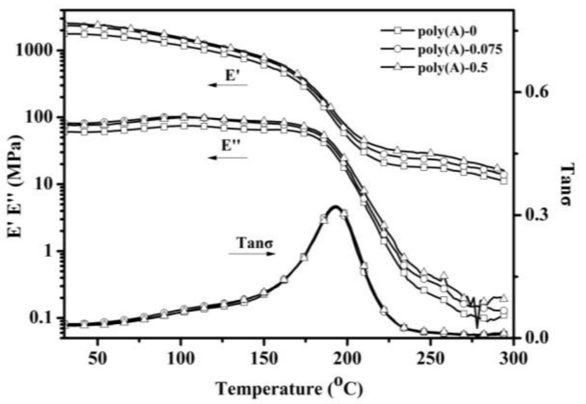


Figure 5: DMA curves of the cured adhesive films under different curing pressure

The DMA curves of the cured adhesive films under different curing pressure were shown in Figure 5. The E' values of poly(A)-0.5, poly(A)-0.075, poly(A)-0 at room temperature (40 °C) were 2.55 GPa, 1.94 GPa and 1.77 GPa. It was shown that the higher the curing pressure, the higher the E ' values of the cured products. These three cured adhesive films had only one peak temperature from the Tanσ curves, and the T_{peak} was 192 ℃.
In order to further explain the difference, the following equation (3) for the rubbery plateau storage modulus (T_g+40 °C) was used to anlysis the cross-link density (Ran et al., 2011; Xu et al., 2017; Chang et al., 2018):

$$d_{\text{cross-link}} = E'/2(1+\gamma)RT \quad (3)$$

Where E′ is the storage modulus (dyn/cm^2) of the polymer at temperature T, R was the gas constant, and **γ** was Poisson's ratio which was assumed to be 0.5 for incompressible networks. $d_{cross\text{-}link}$ was the cross-link density (mol/cm^3) of the polymer. The cross-link density of the poly(A)-0, poly(A)-0.075 and poly(A)-0.5 were calculated to be 3.0 × 10^{-3} mol/cm^3, 4.0 × 10^{-3} mol/cm^3, and 4.8 × 10^{-3} mol/cm^3. The results showed that, to some extent, the increased curing pressure could improve the cross-linking densities of the cured products.

4. Conclusions

In this paper, the effects of different curing pressures (0 MPa, 0.075 MPa, and 0.5 MPa) on the properties of METLBOND 1515-4 epoxy adhesive film were investigated. The results showed that the macro-mechanical properties and micro-mechanical properties of the cured products were improved as the curing pressure increased. The DMA results showed that the cross-linking densities of the cured products increased substantially within the increasing curing pressure. That was because the application of curing pressure promoted the collision of epoxy precursors in the probability of collision, thus increasing the cross-linking densities of the cured adhesive films.

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