

# A Dynamic Mechanical Thermal Analysis on Allylester Polymers and Composites Filled with Alumina

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## SYNOPSIS

A dynamic mechanical thermal analysis (DMTA) was performed on allylester polymers and composites filled with alumina. We determined the glass transition temperatures and the values of the storage moduli in both the glassy and rubbery states in each system and compared the mechanical-thermal behavior of pristine allylester polymers with that of composites filled with alumina. To supplement the result of DMTA, we also carried out viscometry, gel permeation chromatography, and differential scanning calorimetry. The molecular structures had an influence on the viscosity, the glass transition temperature, and the storage modulus. Allylester composite filled with 20 phr alumina showed peculiar mechanical-thermal behavior. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Allylester resin has many advantages, including a range of mechanical properties, long shelf-life, and thermal stability. It is cured after preparation of a prepolymer by transesterification, differently from other allyl system polymers.<sup>1-4</sup> It also has weathering stability, chemical resistance, heat resistance, corrosional resistance, distinguished optical properties, and excellent electric resistance at elevated temperature and high humidity. Therefore, allylester resin can be widely used in applications such as optical materials, building materials, artificial marble, and wire board.<sup>5,6</sup> Especially, as the prepolymerization is accomplished not by radical reaction but by transesterification, it is easy to change the content and types of polyol and diallyl ester. It is also easy to modify the molecular structure and performance of polymer at will.

It takes a long time to cure allylester systems completely, and that is its weakness. The possibility of new processing applications is expected, however.

Their utility lies in the extremely wide variety of chemical reactions that can be used for the curing and resulting properties. On the other hand, appli-

cations of allylester resins are restricted owing to limited information concerning the cure kinetics and the thermal behavior of reinforced composites as well as pristine allylester polymers, although many studies on other resins have been made.<sup>7-12</sup>

Therefore, it is important to verify the cure kinetics and the mechanical-thermal behavior of allylester polymers and composites for the various applications of this allylester. We have already accomplished the cure kinetics for allylester polymers and composites reinforced with alumina in our previous works by using the differential scanning calorimetry (DSC) technique.<sup>13-15</sup>

There are several techniques to monitor the thermal behavior, such as thermomechanical analysis, differential thermal analysis, DSC, and thermogravimetric analysis.<sup>9,10,16-22</sup> We used the dynamic mechanical thermal analysis (DMTA) to search for mechanical-thermal behaviors in this study.

The dynamic methods, in which the system is cured on constant heating rate, are simple and valuable for the study. The dynamic mechanical method assesses the structure and properties of solids and viscoelastic via their dynamic moduli and damping. This method has great sensitivity in detecting changes in internal molecular mobility and in probing phase structure and morphology. Secondary relaxations in the glassy state can be easily studied as

**Table I Chemical Structures of Monomers Used for Preparation of Allylester Prepolymers in This Study**

Nomenclature (Abbreviation)	Chemical Structure
Diallyl terephthalate (DAT)	
Diallyl isophthalate (DAIP)	
1,3-Butylene glycol (1,3-BG)	
Diethylene glycol (DEG)	HOCH2CH2OCH2CH2OH

well as the glass transition relaxation process. Many researchers reported their successful studies using the dynamic mechanical method.<sup>23-30</sup> It is known that DMTA is a powerful and useful method in making out the mechanical-thermal behavior.<sup>22,31</sup>

In this research, we performed DMTA on cured pristine allylester polymers and composites filled with various contents of alumina. DSC, gel permeation chromatography (GPC), and viscometry were also carried out to make up for the results of DMTA.

The ultimate goals of this study are to determine the glass transition temperatures and the values of the storage moduli in both the glassy and rubbery states in each system and to compare the mechanical-thermal behavior of pristine allylester polymers

**Table II Chemical Structures of Curing Agent (DCP) and Catalyst (MBO) Used in This Study**

Nomenclature (Abbreviation)	Chemical Structure
Dicumyl peroxide (DCP)	
Monobutyltin oxide (MBO)	

with that of composites filled with alumina using DMTA.

## EXPERIMENTAL

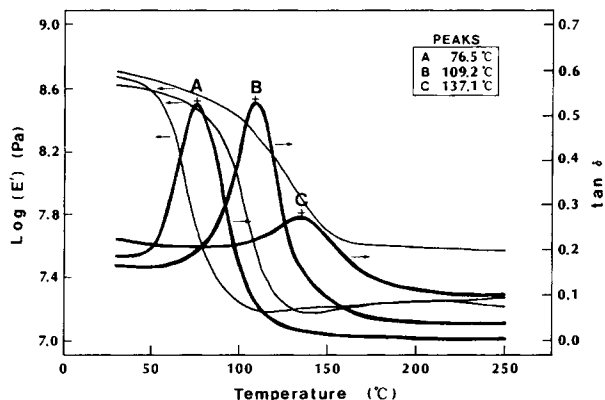
### Materials

Diallyl monomers used in this study were diallyl terephthalate (DAT) and diallyl isophthalate (DAIP) supplied by Daiso in Japan. 1,3-Butylene glycol (1,3-BG) and diethylene glycol (DEG) were used as diols for transesterification. Monobutyltin oxide was used as catalyst and dicumyl peroxide (DCP) as a curing agent in this study. Alumina purchased from Showa Denko, Co. was used as the filler.

Tables I and II show the chemical structures of the materials for this study.

### Synthesis and Curing

The preparation method of prepolymers was identical with previous articles.<sup>13-15</sup> The samples are divided into two classes: curing of pristine prepolymers, DAT+1,3-BG (PR-1), DAIP+1,3-BG (PR-2), and DAIP+DEG (PR-3), and change in the content of alumina, 10 (AL-10), 20 (AL-20), 30 (AL-30), and 40 (AL-40) phr based on prepolymer in DAT+1,3-BG system.

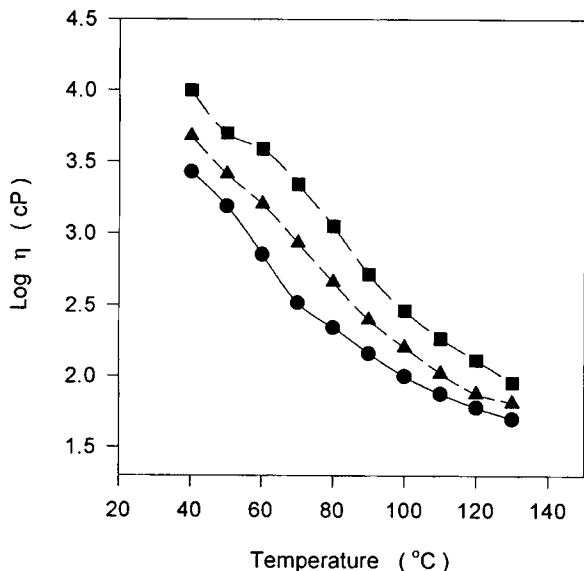


**Figure 1** DMTA thermograms of three allylester polymers with 2 phr DCP at heating rate, 3 $^{\circ}\text{C}/\text{min}$ ; DAIP+DEG (A), DAIP+1,3-BG (B), and DAT+1,3-BG (C).

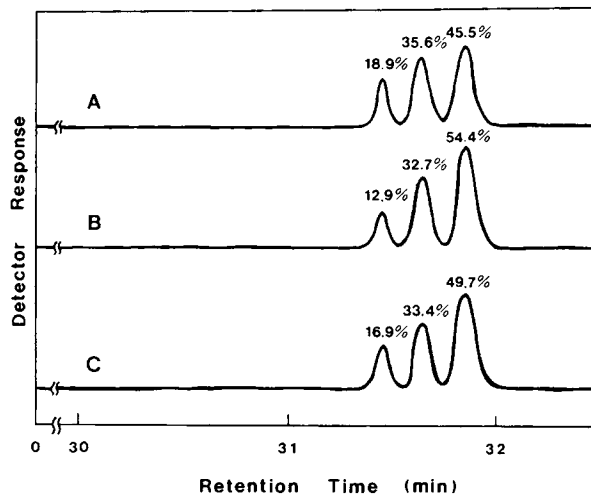
All samples contained 2 phr DCP and were cured in 130 $^{\circ}\text{C}$  for 18 hr.

**DMTA**

A dynamic mechanical thermal analyzer (Polymer Laboratories, Ltd.) was used in this research. Scanning of bending type was performed from 30 to 250 $^{\circ}\text{C}$  and the heating rate was 3 $^{\circ}\text{C}/\text{min}$ . The frequency was 1 Hz. Dual catilever and C flat faced clamp were used. The geometry of specimen was 35  $\times$  6  $\times$  3 mm.



**Figure 2** Plot of viscosities as a function of temperature on each prepolymer; PR-1 ( $\bullet$ ), PR-2 ( $\blacksquare$ ), and PR-3 ( $\blacktriangle$ ).



**Figure 3** Chromatograms of each prepolymer; PR-1 (A), PR-2 (B), and PR-3 (C).

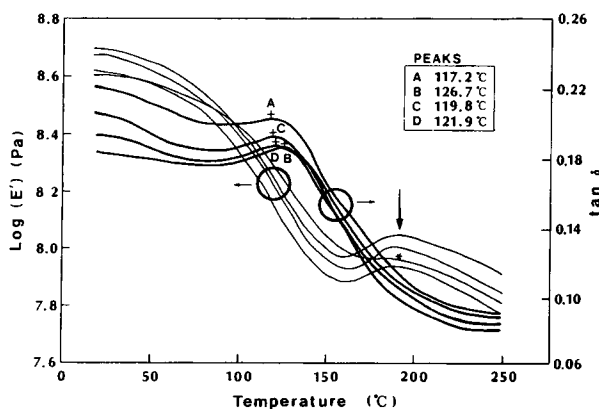
**DSC**

To verify the result of DMTA, another dynamic experiment was performed with DSC (Rigaku 8230) for all the same samples used in DMTA. The heating rate was 3 $^{\circ}\text{C}/\text{min}$ , and the temperature range was 30–250 $^{\circ}\text{C}$ . The instrument was calibrated for scanning temperature and enthalpy with high-purity titanium.

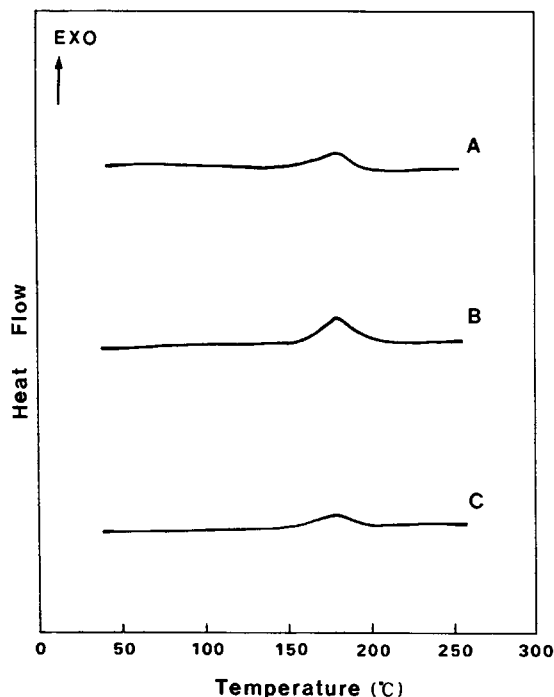
Some 10–15 mg of each sample in a crimped aluminum cell was recured under dynamic conditions at nitrogen atmosphere. An empty cell was used as the reference.<sup>32</sup>

**Viscometry**

To determine the viscosities of three neat prepolymers and alumina-filled prepolymers, a Brookfield



**Figure 4** DMTA thermograms of DAT+1,3-BG with 2 phr DCP and different contents of alumina; 10 phr (A), 20 phr (B), 30 phr (C), and 40 phr (D) at heating rate, 3 $^{\circ}\text{C}/\text{min}$ .



**Figure 5** DSC dynamic thermograms of three allylester polymers with 2 phr DCP at heating rate, 3°C/min; PR-1 (A), PR-2 (B), and PR-3 (C).

Viscometer LVTDV-II (Brookfield Engineering Laboratories, Co.) was used. The number of spindles used in this study was 34. Motor speed was 6 rpm. The measuring was performed from 40 to 130°C at an interval of 10°C.

### GPC

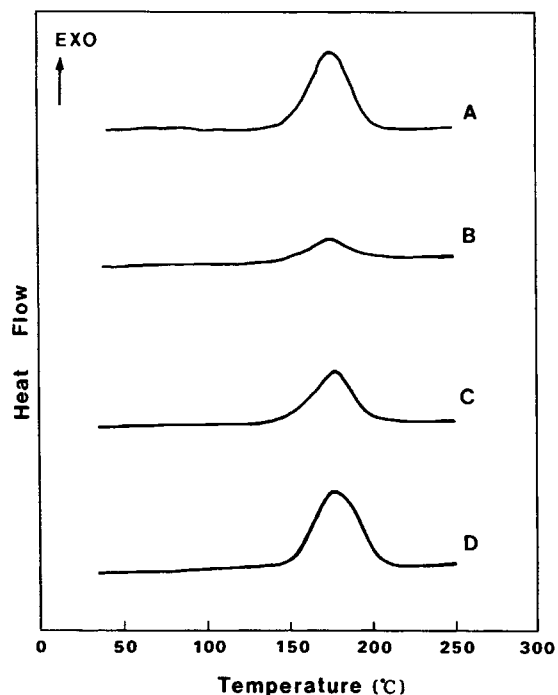
To estimate molecular weights of synthetic prepolymers, GPC was carried out with a Waters model 440. The solvent was tetrahydrofuran. Polystyrene was used as the packing material and the pore sizes were about  $5 \times 10^2$ ,  $10^3$ ,  $10^4$ , and  $10^5$  Å. The concentration of injected solution was 0.25%. Injection rate was 1.5 mL/min. The experiment was achieved at room temperature.

## RESULTS AND DISCUSSION

Figure 1 shows the DMTA thermograms of three kinds of cured prepolymers. Each sample had similar values of storage moduli in glassy state,  $\sim 10^{8.7}$  Pa. In the rubbery state, however, PR-1 indicated a higher value ( $10^{7.7}$  Pa) than PR-2 and PR-3 ( $10^{7.2}$  Pa). The order of the glass transition temperatures was PR-1 > PR-2 > PR-3. It means that DAT and

1,3-BG have more stiffness than DAIP and DEG, respectively. It is reasonable that DAT and 1,3-BG should be more rigid than DAIP and DEG because DAT is a para-substituted aromatic ring structure but DAIP is meta one, and DEG has flexible ether linkage in the structure but 1,3-BG does not. In addition, it can be said that diallyl has more influence on the glass transition temperature than diol because PR-1 showed the highest glass transition temperature. The fact that PR-1 was more rigid than PR-2 and PR-3 resulted in the difference of the moduli between PR-1 and PR-2 or PR-3 in the rubbery state. PR-1 was less softened than PR-2 and PR-3.

Meanwhile, Figure 2 is the plot of temperature versus viscosity in logarithmic scale on three prepolymers. All prepolymers nearly showed linearity. The order of the viscosities was PR-1 < PR-3 < PR-2 in the temperature range of 40–130°C. It can be assumed that the order of the molecular weights of prepolymers should be PR-1 < PR-3 < PR-2 only by the results of viscosity. Therefore, we performed GPC to estimate molecular weights of synthetic prepolymers. Figure 3 represents the interesting result. Each weight-averaged molecular weight ( $M_w$ ) is  $1.01 \times 10^3$  (PR-1),  $9.93 \times 10^2$  (PR-2), and  $1.00 \times 10^3$  (PR-3). Each number-averaged molecular weight



**Figure 6** DSC dynamic thermograms of DAT+1,3-BG with 2 phr DCP and different contents of alumina; 10 phr (A), 20 phr (B), 30 phr (C), and 40 phr (D) at heating rate, 3°C/min.

**Table III The Peak Temperatures and Heat of Exotherms for Three Allylester Polymers From DSC Dynamic Experiments**

Allylester Polymers	Peak Temperature (°C)	Heat of Exotherm (cal/g)
PR-1	180.6	0.918
PR-2	180.1	1.92
PR-3	177.4	0.516

( $M_n$ ) is  $1.00 \times 10^3$  (PR-1),  $9.87 \times 10^2$  (PR-2), and  $9.96 \times 10^2$  (PR-3). Thus, the average degree of prepolymerization is about 4–5. Molecular weights of three prepolymers are nearly the same values. According to the results of viscosity and GPC, it seems that the degree of prepolymerization of three prepolymers are similar; however, viscosities are different because meta-substituted DAIP, flexible-ether-linkaged DEG, and 1,3-substituted 1,3-BG lead to the various configurations and raise entanglement.

Figure 4 is the DMTA thermograms as a function of alumina content. The alumina had little effect on the values of the storage moduli in glassy state ( $E'_g$ ) but much in rubbery state ( $E'_r$ ) by the order of 0.2–0.4 in comparison with pristine polymer system. The differences between  $E'_g$  and  $E'_r$  in composites were smaller than the difference in the pristine polymer system, PR-1. This result comes from the fact that inorganic filler, alumina, is not in the same state at the temperature where the polymer is in the rubbery state. Consequently, in the rubbery state, the values of storage moduli in composites are higher than that of polymer. Meanwhile, the greater the content of alumina, the higher the glass transition temperature. But the glass transition temperature at 20 phr (126.7°C) was higher than at 40 phr (121.9°C). Besides, AL-10, AL-30, and AL-40 showed some increase in the storage moduli at about 180°C but AL-20 did not. Thus, we practiced another dynamic experiment, DSC, to verify the data in DMTA.

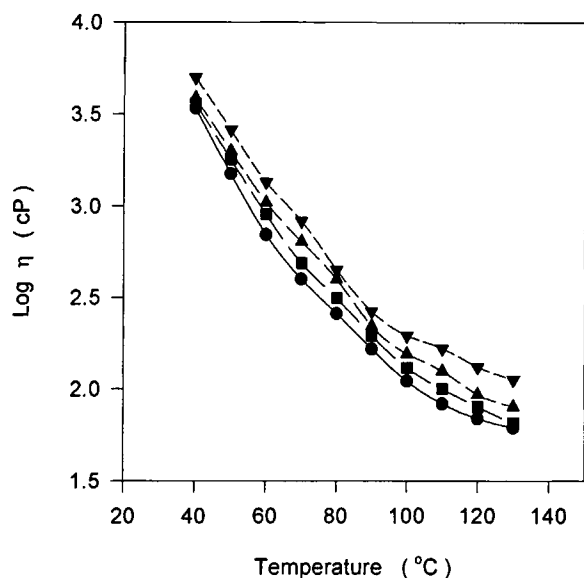
Figures 5 and 6 are DSC dynamic thermograms of recuring of pristine polymers and composites filled with various content of alumina, respectively. When recuring pristine polymers, a little heat of exotherms appeared. PR-2, which has the highest viscosity, shows the largest heat of exotherm of the three polymers in the secondary curing. High viscosity disturbs the motion of molecules so the diffusion is restricted. Thus, PR-2 is less crosslinked in the primary curing.

When recuring of composites, there was considerable heat of exotherms resulting from the chemical cure inhibition of alumina in the previous cure.<sup>33,34</sup> It means that the previous curing was not complete so the crosslinking was less dense in the composites than in the polymers. This fact can explain why the glass transition temperatures of composites were lower than that of pristine polymer, PR-1. Tables III and IV show the peak temperatures and heat of exotherms in each case. The higher the glass transition temperature in DMTA, the higher the peak exotherm temperature and the lower the heat of exotherm in DSC.

The AL-20 system shows the lowest heat of exotherm in composites. In our previous article, the values of the activation energy in curing at different content of alumina were obtained.<sup>14</sup> Thus, we already know that the value of the activation energy in AL-20 system is lower than other content of filled systems. Low activation energy helps the AL-20 system cure more easily. The minimum value of heat of exotherm in DSC and the highest glass transition

**Table IV The Peak Temperatures and Heat of Exotherms for DAT+1,3-BG with Different Content of Alumina From DSC Dynamic Experiments**

Content of Alumina (phr)	Peak Temperature (°C)	Heat of Exotherm (cal/g)
10	177.6	7.49
20	178.8	2.96
30	178.6	8.09
40	178.5	10.72



**Figure 7** Plot of viscosities as a function of temperature on each prepolymer filled with various content of alumina; 10 phr (●), 20 phr (■), 30 phr (▲), and 40 phr (▼).

temperature in DMTA of AL-20 are due to the maximum cure in the previous cure caused by the lowest value of the activation energy.

Figure 7 is the plot of temperature versus viscosity in logarithmic scale as a function of the content of alumina. It is proper the higher the content of alumina, the higher the viscosity. The differences of viscosities at the lower temperature region is smaller than those at the higher region. At the experimental temperature, 130°C, the viscosities of AL-10 and AL-20 are similar and those of AL-30 and AL-40 are much higher. So the freedom of molecular motion of AL-10 and AL-20 is alike. This fact also promotes the crosslinking of AL-20. The higher viscosities of composites also give another effect to the lower crosslinking.

## CONCLUSION

From the DMTA on allylester polymers and alumina filled composites, the following is concluded:

1. The order of the glass transition temperature was PR-1 > PR-2 > PR-3 in allylester polymers and the difference between  $E'_g$  and  $E'_r$  of PR-1 was smaller than that of PR-2 or PR-3.
2. The degree of prepolymerization of three prepolymers are similar; however, viscosities

are different owing to the matter of entanglement.

3. The more content of alumina, the higher the glass transition temperature. However, the glass transition temperature at 20 phr alumina was higher than at 40 phr, owing to the matter on the activation energy.
4. Compared with the pristine polymers, there was considerable heat of exotherms resulting from the chemical cure inhibition of alumina in the previous cure when the composites are recured.
5. The higher the glass transition temperature in DMTA, the higher the peak exotherm temperature and the lower the heat of exotherm in DSC.
6. The higher the content of alumina, the higher the viscosity. Compared with the AL-10, the similar viscosity of AL-20 helps the maximum crosslinking of AL-20.

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