A Dynamic Mechanical Thermal Analysis on Surface-Modified Alumina Filled Allylester Composites

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SYNOPSIS

A dynamic mechanical thermal analysis was performed on allylester composites filled with alumina. Alumina was treated with various concentrations of four silane coupling agents. 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 unmodified or modified alumina. At optimum concentrations of silane coupling agents in each system, the maximum crosslinking reaction occurred and the maximum glass transition temperature appeared at the same concentrations by their effective surface coverage. Differential scanning calorimetry experiments proved this fact. The order of the glass transition temperatures was 3-aminopropyltriethoxysilane (APS) $\cong$ vinyltrimethoxysilane (VTS) > 3-methacryloxypropyltrimethoxysilane (MPS) $\cong$ (3-glycidoxypropyl)trimethoxysilane (GPS) modified systems because MPS and GPS have flexible ether linkages in their structures but APS and VTS do not. The structures of each silane coupling agent influenced significantly on the glass transition temperature, the storage modulus, and tan δ. © 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.[1-4] 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.[5,6] 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 too long to cure allylester systems completely, and that is its weakness. However, the possibility of new processing applications is expected.

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, applications 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.[7-12]

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.[13-15] We have already carried out a dynamic mechanical thermal analysis (DMTA) on allylester polymers and composites filled with alumina.[16]

In an effort to achieve better end-use properties of composites, one inevitably uses reinforcements such as inorganic fibrous materials and fillers such as particulates. Unlike thermoplastic composites, the curing of thermosetting resins can be influenced by reinforcements and fillers.[14,17]

The compatibility between matrix and filler is the most important factor in the composite system. To increase compatibility between the particulates and the matrix resin, alumina was surface modified with silane coupling agents: 3-methacryloxypropyltrimethoxysilane (MPS), 3-aminopropyltriethoxysilane (APS), (3-glycidoxypropyl)trimethoxysilane (GPS), and vinyltrimethoxysilane (VTS). It is rationalized that the type of chemicals applied for surface treatment is usually proprietary.[18,19]

As a result, little information has been reported that discusses the effect of silane coupling agents on the mechanical properties of composites. However, a thorough understanding of the relationships among the fillers, the silane coupling agent, and the matrix is the key to successful fabrication of composites. We have already studied the cure kinetics on allylester composites reinforced with alumina treated with silane coupling agents.[15] Here, we study some mechanical–thermal behaviors on surface-modified alumina filled allylester composites.

There are several techniques to monitor thermal behavior, such as thermomechanical analysis, differential thermal analysis, DSC, and thermogravimetric analysis.[9,10,20–26] We used the DMTA to search for some mechanical–thermal behaviors in this study.

The dynamic methods, in which the system is cured on a 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 well as the glass transition relaxation process. Many researchers reported their successful studies using the dynamic mechanical method.[27–31] It is known that DMTA is a powerful and useful method in making out mechanical–thermal behaviors.[26,32]

In this research, we performed DMTA on cured allylester composites filled with 20 phr alumina. The surface of alumina was treated with various concentrations of four silane coupling agents.

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 with that of composites filled with unmodified or modified alumina using a dynamic mechanical thermal analyzer. This study has also been carried out to elucidate the effects in the mechanical–thermal behavior as a function of silane coupling agent concentration.

EXPERIMENTAL

Materials

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

The following silane coupling agents were applied for surface treatment of alumina: MPS, APS, GPS, and VTS. These four silanes were purchased from Petrarch Systems Inc.

Table I shows the chemical structures of the silane coupling agents used for this study.

Synthesis, Treatment of Alumina, and Curing

The preparation method of prepolymers was identical to previous articles.[13–15] The samples are treated with various silane coupling agents (MPS, APS, GPS, and VTS) and concentrations (0.1–0.5 wt %) of DAT+1,3-BG with 20 phr alumina systems.

Silane coupling agents were hydrolyzed in ethanol/water (70/30) solution with trace acetic acid at pH 3.5 for 1 h. Then alumina was immersed in the silane solution and dried at room temperature for 7 days.

All samples contained 2 phr DCP and were cured at 130°C for 18 h.

DMTA

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

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°C/min and the temperature range was 30–250°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.[33]

RESULTS AND DISCUSSION

Figure 1 shows the DMTA thermograms of composites treated with MPS at various concentrations. The values of the storage moduli were higher at the concentrations of 0.1–0.3 wt % than untreated system, AL-20, but lower at 0.4–0.5 wt %. The decrease of the storage moduli after 0.4 wt % comes from the effect as a diluent or lubricant when the coupling agent is introduced in excess.[12] The differences between E'_g and E'_r in treated systems were less than those in untreated systems because the cure inhibition effect of alumina decreases when the surface of alumina is modified with a silane coupling agent. The glass transition temperatures were shifted to the higher region as the concentration of MPS increased. At the concentration of 0.3 wt %, the glass transition temperature was maximum. After this, the glass transition temperature lowered as the concentration of MPS increased. It is also due to the effect as a diluent.

Figure 2 and Table II show, respectively, the DSC dynamic thermograms and the peak temperatures and heat of exotherms of composites treated with
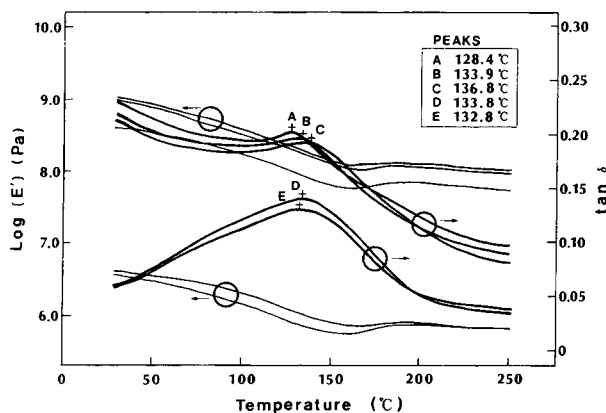

Figure 1 DMTA thermograms of DAT+1,3-BG with 20 phr alumina treated with MPS as a function of the concentration; 0.1 wt % (A), 0.2 wt % (B), 0.3 wt % (C), 0.4 wt % (D), and 0.5 wt % (E) at heating rate, 3°C/min.

MPS. The maximum peak temperature and the minimum heat of exotherm appeared at the concentration of 0.3 wt % MPS. The trend of the glass transition temperatures coincided with that of the peak temperatures. Exactly, the higher the glass transition temperature, the higher the peak exotherm temperature, and the lower heat of exotherm in DSC. However, the peak exotherm temperatures were nearly similar values.

Figure 3 is the DMTA thermograms of composites modified with APS at various concentrations. The values of the storage moduli were higher at the concentrations of 0.1–0.2 wt % than untreated system, AL-20, but lower at 0.3–0.5 wt %. The trends of the differences between E'_g and E'_r and shift of the glass transition temperatures were similar to the MPS system. The differences between E'_g and E'_r in treated systems were less than those in untreated systems. The maximum glass transition temperature in the case of the APS system, however, was higher

Table I   Chemical Structures of Silane Coupling Agents Used for Treatment of Alumina in This Study

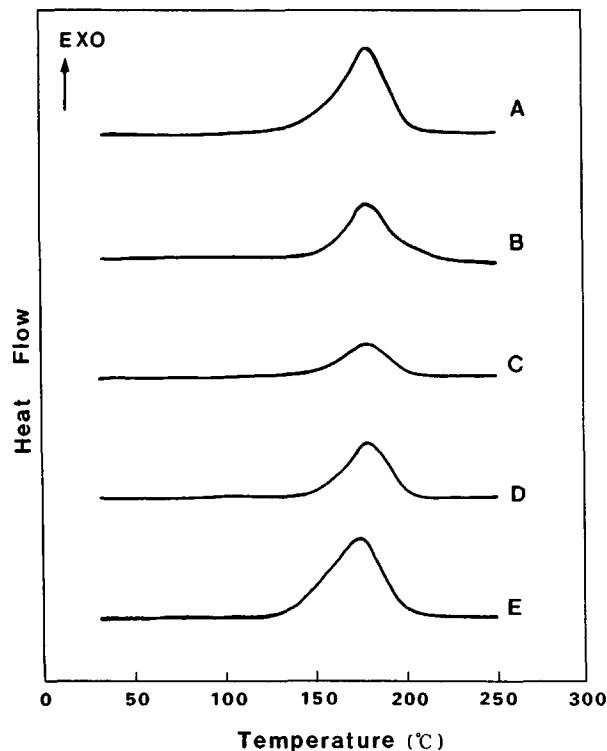| Nomenclature (Abbreviation)	Chemical Structure
3-Methacryloxypropyltrimethoxysilane (MPS)	$CH_2{=}C\overset{\displaystyle CH_3}{\underset{\displaystyle O}{\overset{\displaystyle \vert}{\underset{\displaystyle \parallel}{C}}}O(CH_2)_3Si(OCH_3)_3$
3-Aminopropyltriethoxysilane (APS)	$H_2NCH_2CH_2CH_2Si(OC_2H_5)_3$
(3-Glycidoxypropyl)trimethoxysilane (GPS)	$\overset{O}{\triangle}CH_2{-}O{-}(CH_2)_3Si(OCH_3)_3$
Vinyltrimethoxysilane (VTS)	$CH_2{=}CH{-}Si(OCH_3)_3$

Figure 2   DSC dynamic thermograms of DAT+1,3-BG with 20 phr alumina treated with MPS as a function of the concentration; 0.1 wt % (A), 0.2 wt % (B), 0.3 wt % (C), 0.4 wt % (D), and 0.5 wt % (E) at heating rate, 3°C/min.

Figure 3   DMTA thermograms of DAT+1,3-BG with 20 phr alumina treated with APS as a function of the concentration; 0.1 wt % (A), 0.2 wt % (B), 0.3 wt % (C), 0.4 wt % (D), and 0.5 wt % (E) at heating rate, 3°C/min.

than that in the MPS system by 0.9°C. After 0.3 wt %, the glass transition temperature lowered as the concentration of APS increased. Figure 4 is the DSC dynamic thermograms of composites treated with APS, and Table III shows the peak temperatures and heat of exotherms of composites treated with APS as a function of the concentration. The minimum value of heat of exotherm in the APS system was lower than that in the MPS system. Take notice of the structures of MPS and APS. MPS has double bonds but APS does not. Thus, the double bonds of
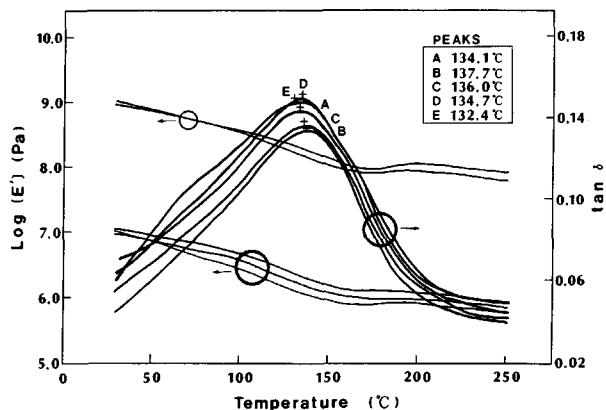
MPS can take part in curing. That is the reason the minimum value of heat of exotherm in the MPS system was higher than that in the APS system.

Figure 5 is the DMTA thermograms of composites treated with GPS at various concentrations. The values of the storage moduli were higher at the concentrations of 0.1–0.2 wt % than untreated system, AL-20, but lower at 0.3–0.5 wt %. The differences between E'_g and E'_r in treated systems were less than those in untreated systems. The glass transition temperatures were higher as the concentration of GPS increased. At the concentration of 0.2 wt % GPS, the glass transition temperature was maximum. After this, glass transition temperature lowered as the concentration of GPS increased. The maximum glass transition temperature in the case of the GPS system was lower than that in the APS system by 1.0°C. The flexible ether linkages that MPS and GPS have can contribute to the lower shifts of the glass transition temperatures. Figure 6 and Table IV show the DSC dynamic thermograms and the peak temperatures and heat of exotherms

Table II   The Peak Temperatures and Heat of Exotherms for DAT+1,3-BG Filled with 20 phr Alumina Treated with MPS as a Function of the Concentration From DSC Dynamic Experiments

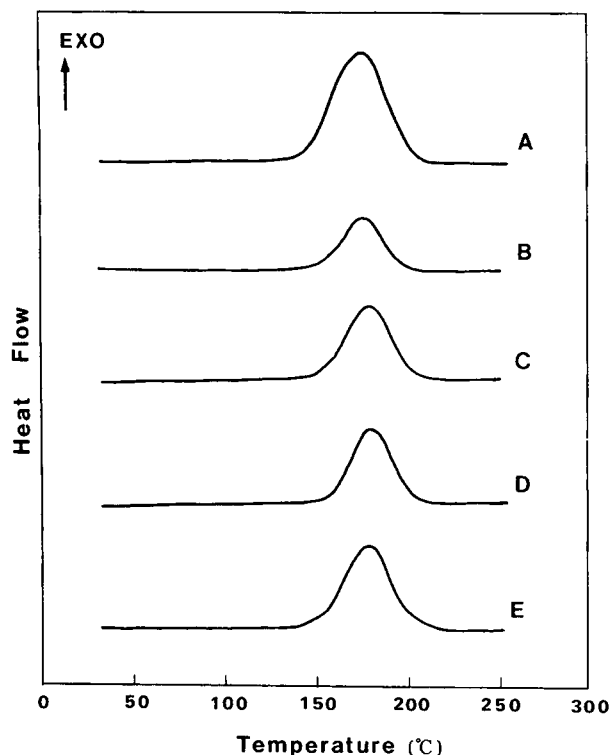| Concentration of MPS (%)	Peak Temperature (°C)	Heat of Exotherm (cal/g)
0.1	175.4	9.90
0.2	178.0	5.46
0.3	178.5	5.26
0.4	178.2	6.78
0.5	177.0	8.60

Figure 4   DSC dynamic thermograms of DAT+1,3-BG with 20 phr alumina treated with APS as a function of the concentration; 0.1 wt % (A), 0.2 wt % (B), 0.3 wt % (C), 0.4 wt % (D), and 0.5 wt % (E) at heating rate, 3°C/min.
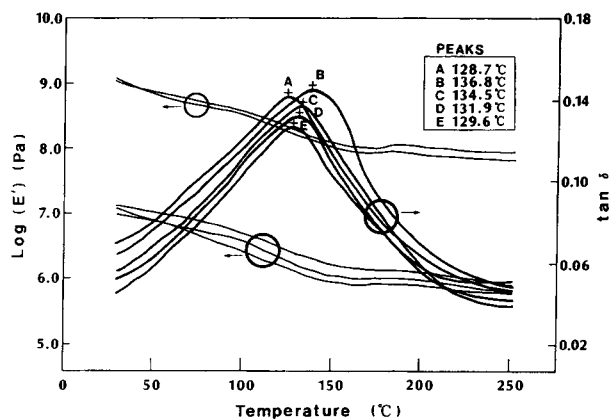

Figure 5   DMTA thermograms of DAT+1,3-BG with 20 phr alumina treated with GPS as a function of the concentration; 0.1 wt % (A), 0.2 wt % (B), 0.3 wt % (C), 0.4 wt % (D), and 0.5 wt % (E) at heating rate, 3°C/min.

of composites treated with GPS, respectively. The minimum value of heat of exotherm in the GPS system was higher than that in the APS system owing to the epoxy ring being able to join in cure reaction.

Figure 7 is the DMTA thermograms of composites treated with VTS at various concentrations. The values of the storage moduli were higher at the concentrations of 0.1–0.3 wt % than untreated systems but lower at 0.4–0.5 wt %. The glass transition temperatures shifted to the higher temperature region as the concentration of VTS increased up to 0.3 wt

%. The maximum glass transition temperature in the case of the VTS system was higher than that in the MPS or GPS systems because MPS and GPS have flexible ether linkages but VTS does not. Figure 8 shows the DSC dynamic thermograms of composites modified with VTS, and Table V represents the peak temperatures and heat of exotherms as a function of the concentration. The maximum value of heat of exotherm in VTS was higher than those in other silane coupling agents.

At optimum concentrations of silane coupling agents in each system, the maximum crosslinking reaction occurred in primary curing and the maximum glass transition temperature appeared at the same concentrations.

The order of the glass transition temperatures was APS ≅ VTS > MPS ≅ GPS because MPS and GPS have flexible ether linkages in their structures but APS and VTS do not.

The values tan δ of MPS and VTS systems in the rubbery state showed differences between 0.1 and 0.3 wt % and 0.4 and 0.5 wt % by 0.06. However,

Table III   The Peak Temperatures and Heat of Exotherms for DAT+1,3-BG Filled with 20 phr Alumina Treated with APS as a Function of the Concentration From DSC Dynamic Experiments

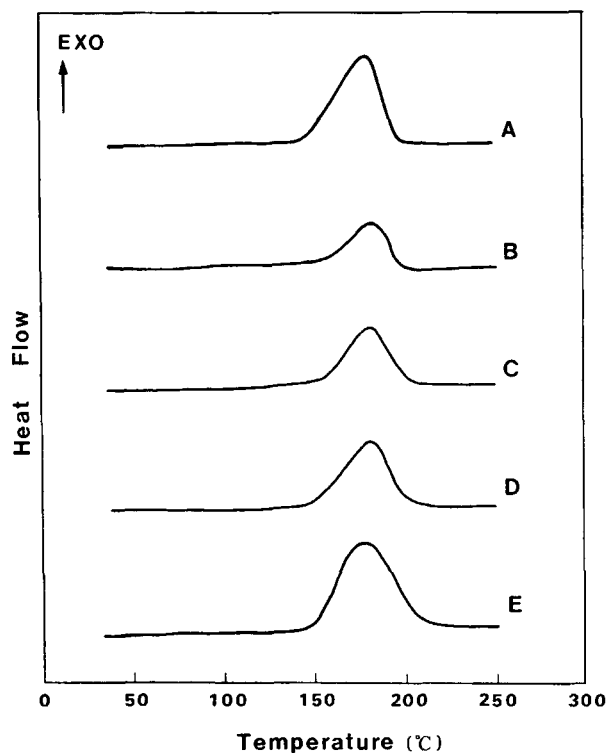| Concentration of APS (%)	Peak Temperature (°C)	Heat of Exotherm (cal/g)
0.1	179.4	5.58
0.2	180.6	3.50
0.3	179.6	3.68
0.4	179.3	3.96
0.5	178.9	5.71

Figure 6 DSC dynamic thermograms of DAT+1,3-BG with 20 phr alumina treated with GPS as a function of the concentration; 0.1 wt % (A), 0.2 wt % (B), 0.3 wt % (C), 0.4 wt % (D), and 0.5 wt % (E) at heating rate, 3°C/min.

the values of tan δ of APS and GPS systems in the rubbery state were almost the same at each concentration (0.1–0.5 wt %). The tan δ is the loss modulus over the storage modulus. Therefore, loss modului in MPS and APS systems are larger than those in MPS and VTS systems. The distinction between the two cases is that MPS and VTS have double bonds but APS and GPS do not. This distinction in structure is seemingly one cause of the difference. Thus, it is necessary that we should closely examine each system.
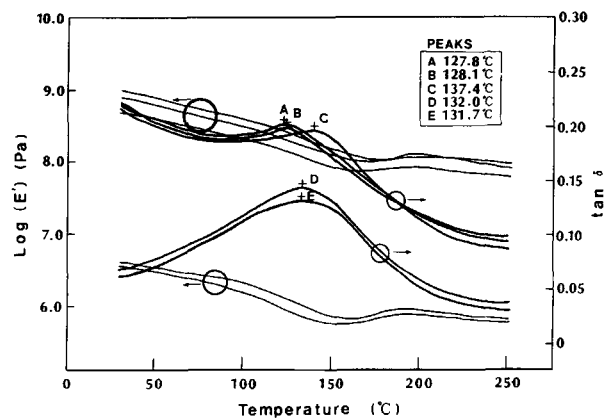

Figure 7 DMTA thermograms of DAT+1,3-BG with 20 phr alumina treated with VTS as a function of the concentration; 0.1 wt % (A), 0.2 wt % (B), 0.3 wt % (C), 0.4 wt % (D), and 0.5 wt % (E) at heating rate, 3°C/min.

CONCLUSION

From the mechanical–thermal analysis on allylester composites filled with alumina modified with various silane coupling agents, the following is concluded:

1. As alumina was treated with various silane coupling agents, the storage moduli and the glass transition temperatures shifted to the higher values up to the optimum concentrations.

2. When alumina was treated with various concentrations of silane coupling agents, the optimum silane concentrations showed up at about 0.2–0.3 wt %, which is the maximum at which the glass transition temperatures appeared.

3. The higher the glass transition temperature in DMTA, the higher the peak exotherm temperature and the lower the heat of exotherm in DSC.

Table IV The Peak Temperatures and Heat of Exotherms for DAT+1,3-BG Filled with 20 phr Alumina Treated with GPS as a Function of the Concentration From DSC Dynamic Experiments

Concentration of GPS (%)	Peak Temperature (°C)	Heat of Exotherm (cal/g)
0.1	177.1	9.28
0.2	178.3	6.84
0.3	177.8	7.93
0.4	177.6	8.20
0.5	177.3	8.40

Table V   The Peak Temperatures and Heat of Exotherms for DAT+1,3-BG
Filled with 20 phr Alumina Treated with VTS as a Function of the
Concentration From DSC Dynamic Experiments

Concentration of VTS (%)	Peak Temperature (°C)	Heat of Exotherm (cal/g)
0.1	176.2	9.79
0.2	176.9	8.95
0.3	177.6	7.34
0.4	177.2	7.51
0.5	176.5	8.43

4. In the case of silane-treated alumina filled allylester composites, heat of exotherm increased due to the double bonds or epoxy ring being able to take part in crosslinking.

5. The order of the glass transition temperatures in using various silane coupling agents was APS ≅ VTS > MPS ≅ GPS for the flexible ether linkages; MPS and GPS could have contributed to the lower shifts of the glass transition temperatures.
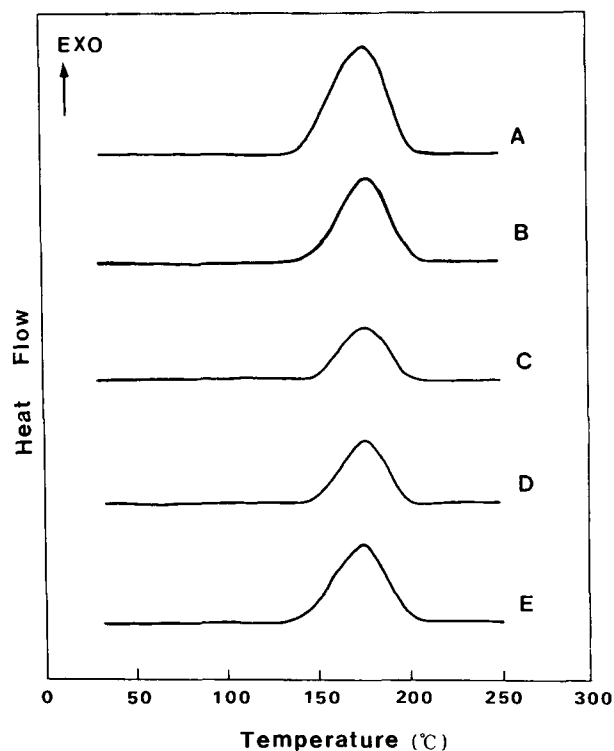

Figure 8   DSC dynamic thermograms of DAT+1,3-BG with 20 phr alumina treated with VTS as a function of the concentration; 0.1 wt % (A), 0.2 wt % (B), 0.3 wt % (C), 0.4 wt % (D), and 0.5 wt % (E) at heating rate, 3°C/min.

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