

# Effect of heating time below the melting temperature on polyphenylene sulfide adhesive joint development

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## Abstract

A long heating time below the melting temperature ( $T_m$ ) was found to be detrimental to subsequent polyphenylene sulfide (PPS) adhesive joint development above  $T_m$ . This was found to be due to curing reactions below  $T_m$  and consequent reduced mass flow response above  $T_m$ . A high heating rate (small heating time) enhanced the bonding more than a high pressure. The study was conducted by measurement of the contact electrical resistance of the joint, and was supported by calorimetry. © 2000 Elsevier Science Ltd. All rights reserved.

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## 1. Introduction

Adhesive joint formation between thermoplastic adherends typically involves heating to temperatures above the melting temperature ( $T_m$ ) of the thermoplastic. During heating to the desired elevated temperature, time is spent in the range between the glass transition temperature ( $T_g$ ) and the  $T_m$ . This paper reports the detrimental effect of a long exposure to the temperature range between  $T_g$  and  $T_m$  on development of adhesive joint strength of polyphenylene sulfide (PPS).

PPS is a high-temperature thermoplastic having a thermosetting/thermoplastic character [1–10]. Although it is a linear thermoplastic polymer under normal processing conditions, PPS is known to form a crosslinked network structure on exposure to high temperatures in the presence of oxygen. PPS can be cured by two different processes, namely the melt process and the solid-state process [1]. Curing by the melt process involves thermal treatment of PPS above its melting point (315–425°C); in the solid-state process, PPS is subjected to temperatures below its melting point [2,3]. The structural changes during curing have been reported to in-

volve chain extension, crosslinking, and branching through oxidative linkages [4,5], and have been found to occur below as well as above  $T_m$  [3,6–8]. Therefore, these changes are not only relevant to adhesive bond development above  $T_m$ , but also to the effect of the time spent below  $T_m$  as the joint is heated to the final bonding temperature.

Adhesive bond development in real time was monitored in this work by measurement of the DC contact electrical resistance between the adherends in an adhesive joint during heating and subsequent cooling. Both adherends were carbon fiber-reinforced PPS; they were placed in contact in a crossply configuration. The greater is the extent of direct contact between fibers of adjacent laminae, the lower is the contact electrical resistance. The extent of direct contact is controlled by the displacement of the PPS material between or around the carbon fibers. In turn, changes in the contact resistance indicate displacement of the PPS material at the microscopic level. In addition, thermal-stress-induced debonding during cooling lowers the extent of fiber–fiber contact across the interface, thereby increasing the contact resistance. This means that the quality of the bond can be monitored by contact resistance measurement as well.

The dependence of the bond quality on the heating rate, heating time, and pressure was investigated in this work through measurement of contact resistance. This

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electrical technique is useful not only for fundamental scientific studies, but is expected to be useful as a real-time, nondestructive method for monitoring and controlling the bonding process in a manufacturing setting.

## 2. Experimental methods

The thermoplastic material used was polyphenylene sulfide (PPS), which had a glass transition temperature ( $T_g$ ) of  $90^\circ\text{C}$  and a melting temperature ( $T_m$ ) of  $280^\circ\text{C}$ . The material was in the form of continuous unidirectional carbon fiber prepreg, supplied by Quadrax Corp. (Portsmouth, Rhode Island; Product QLC4164). The thickness of the prepreg was  $250\ \mu\text{m}$ . The carbon fiber was AS-4C, from Hercules Advanced Materials and Systems Company (Magna, Utah), with a diameter of  $8\ \mu\text{m}$ . The fiber weight fraction in the prepreg was 64%.

The prepreg was used after annealing. Annealing (to flatten the coiled prepreg) was carried out in air at  $180^\circ\text{C}$  for 25 h, while pressure (1000 Pa) was applied by the weight of steel plates. After annealing, the prepreg was furnace-cooled to room temperature under pressure.

Prepreg strips 5 cm in length and 1 cm in width were placed on one another at an angle of  $90^\circ$  in a cross-shaped steel mold cavity lined with a PTFE film for electrical insulation, so that the overlap area was  $1\ \text{cm} \times 1\ \text{cm}$ , as shown in Fig. 1. Pressure was applied through a 3-cm long cross-shaped steel plate, which was electrically insulated from the prepreg strips by a PTFE film. An electrical contact in the form of silver paint in conjunction with copper wire was applied to each of the four legs of the crossed prepreg strips (Fig. 1). In the four-probe method of DC electrical resistance measurement, two of the electrical contacts (A and D in Fig. 1) were for passing current; the remaining two contacts (B and C) were for measuring voltage. The voltage divided by the current gave the contact resistance of the joint. A Keithley 2001 multimeter was used.

Specimens, as illustrated in Fig. 1, were ramp-heated from 30 to  $315^\circ\text{C}$  ( $T_m = 280^\circ\text{C}$ ) at different heating rates (1, 5 and  $10^\circ\text{C}/\text{min}$ ) and were then held at  $315^\circ\text{C}$  for 5 h. After that, they were cooled to  $140^\circ\text{C}$  at a rate of  $2^\circ\text{C}/\text{min}$  and then were held at  $140^\circ\text{C}$  for 15 h. During the temperature variation, the contact resistance was continuously measured. For investigation of the effect of pressure for the heating rate of  $10^\circ\text{C}/\text{min}$ , the pressure during heating and cooling was varied by use of steel plates of different weights. The pressures were  $4.4 \times 10^3$ ,  $2.1 \times 10^5$  and  $6.8 \times 10^5$  Pa.

For investigation of the effect of heating time, as opposed to heating rate, stepped heating was conducted by (i) heating from 30 to  $230^\circ\text{C}$  at a rate of  $10^\circ\text{C}/\text{min}$ , (ii) holding at  $230^\circ\text{C}$  for 2 h, (iii) heating to  $315^\circ\text{C}$  at  $10^\circ\text{C}/\text{min}$ , (iv) holding at  $315^\circ\text{C}$  for 5 h, (v) cooling to  $140^\circ\text{C}$  at a rate of  $2^\circ\text{C}/\text{min}$  and (vi) holding at  $140^\circ\text{C}$  for

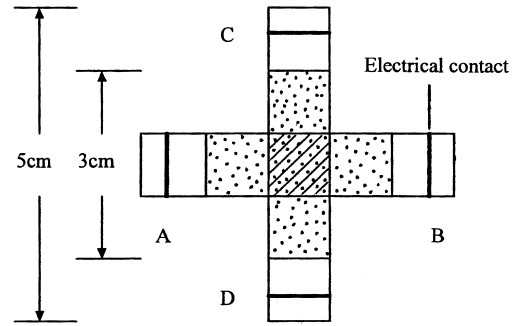


Fig. 1. Sample configuration. The dotted cross-shaped region is where pressure is applied. The square shaded region is the joint.

15 h. The stepped heating meant that more time was spent below  $T_m$  than in the case of the ramp heating.

Testing for each combination of conditions (heating rate, heating time and pressure) was conducted on at least two specimens in order to ascertain that the results were reproducible.

The melting and cold-crystallization (crystallization of an amorphous polymer during heating below  $T_m$ ) behaviors were studied using a Perkin-Elmer Corp. (Norwalk, CT) DSC-7 differential scanning calorimeter. The amorphous specimens were prepared by melting and then quenching, as described below. About 10 mg of prepreg which had been annealed at  $180^\circ\text{C}$  for 25 h was weighed and placed in a standard aluminum DSC pan. Such specimens were then subjected to one of two heating procedures carried out outside the DSC instrument. In heating procedure A, individual specimens were heated from 30 to  $315^\circ\text{C}$  (above  $T_m$ ) at various fixed heating rates (1, 5 and  $10^\circ\text{C}/\text{min}$ ), held at  $315^\circ\text{C}$  for 3 min, and then quenched in ice water. In heating procedure B, stepped heating was carried out by (i) heating from 30 to  $230^\circ\text{C}$  at a rate of  $10^\circ\text{C}/\text{min}$ , (ii) holding at  $230^\circ\text{C}$  for 2 h, (iii) heating to  $315^\circ\text{C}$  at  $10^\circ\text{C}/\text{min}$ , (iv) holding at  $315^\circ\text{C}$  for 3 min, and (v) quenching in ice water. After either heating procedure, the specimens were placed in the DSC instrument, and DSC scans were conducted in air at a heating rate of  $10^\circ\text{C}/\text{min}$ .

## 3. Results and discussion

Fig. 2 shows the effect of heating rate and stepped heating on the cold-crystallization DSC peak and melting DSC peak. The DSC results are summarized in Table 1. The DSC thermogram of the amorphous specimen prepared by using heating procedure A at a heating rate of  $10^\circ\text{C}/\text{min}$  shows three transitions, namely, in order of increasing temperature, the glass transition, the exothermic cold-crystallization, and the endothermic melting (Fig. 2(a)). The glass transition ( $T_g$ ) was around  $86^\circ\text{C}$ ; the cold-crystallization exothermic peak

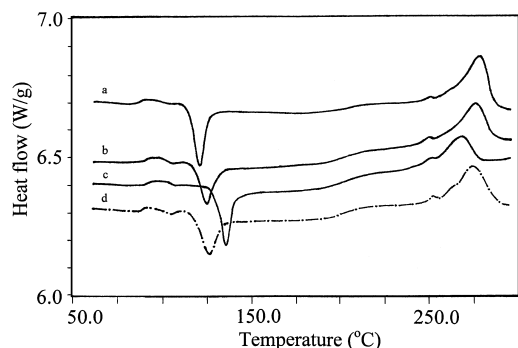


Fig. 2. DSC curves of amorphous PPS composite obtained by heating procedure A at heating rate (a) 10°C/min, (b) 5°C/min and (c) 1°C/min, and (d) obtained by heating procedure B (stepped heating).

temperature ( $T_c$ ) was 120°C; the melting endothermic peak temperature ( $T_m$ ) was 278°C and the heat of fusion ( $\Delta H_f$ ) was 20.0 J/g. As the heating rate used in heating procedure A decreased, the cold-crystallization exothermic peak shifted to a higher temperature, while the melting endothermic peak shifted to lower temperature (Fig. 2(a)–(c) for heating rates of 10, 5 and 1°C/min, respectively). From Table 1, it is also clear that, as the heating rate decreased,  $T_g$  and  $\Delta H_f$  decreased. These observations indicate that the heating rate used in heating procedure A had a significant influence on the chemical structure, the crystalline perfection, and the degree of crystallinity of the polymer matrix.

Heating of amorphous PPS in the presence of oxygen is known to cause chain extension, branching through oxidative linkages, and crosslinking [4,5]. All these changes in the chemical structure of PPS could provide more chain entanglement in the amorphous state before crystallization, thus hindering molecular motion and molecular chain packing in the crystalline state and resulting in higher  $T_g$ , lower degree of crystallinity and less crystalline perfection. The lower the heating rate, the greater is the time spent below  $T_m$ , and the more extensive are

these changes in the chemical structure, thus leading to a lower degree of crystallinity and less crystalline perfection. The decrease of  $T_m$  and  $\Delta H_f$  and increase of  $T_g$  and  $T_c$  of PPS as the heating rate decreases (Table 1) are attributed to the chemical changes that take place during heating in heating procedure A. The step (interrupted heating) in heating procedure B lengthens the time spent at temperatures below  $T_m$  compared to heating without the step, so it has a similar influence on  $T_g$ ,  $T_m$ ,  $\Delta H_f$  and  $T_c$  as a lower heating rate in heating procedure A (Fig. 2(d)).

Fig. 3 shows the effect of the heating rate in heating procedure A on the joint development for a pressure of  $4.4 \times 10^3$  Pa. The resistance decreased upon heating above  $T_g$  at all heating rates, due to the softening of the polymer and the squeezing of the fibers closer together by the applied pressure. Upon reaching 315°C (above  $T_m$ ), the resistance abruptly increased such that the increase was reduced sharply as the heating rate below 315°C in heating procedure A decreased. This abrupt resistance increase is attributed to the mass flow of the polymer matrix causing decrease in the extent of direct fiber–fiber contact across the interface. The higher is the heating rate below  $T_m$  in heating procedure A, the more is the tendency for the polymer matrix to flow above  $T_m$ , as suggested by the DSC results (Fig. 2). As explained in connection with Fig. 2, this is due to the less extensive branching and crosslinking reactions that occur below  $T_m$  during the heating at a higher heating rate. These reactions cause the molecules to be less mobile, which in turn inhibit the mass flow of the polymer matrix. The higher is the heating rate, the less is the time spent below  $T_m$ , and the less extensive are these reactions.

Fig. 3 also shows that the resistance increased upon cooling (due to thermal-stress-induced debonding), such that the increase became more significant as the heating rate in heating procedure A decreased. More debonding between the two plies upon cooling indicates poorer bonding. Hence, a larger resistance increase upon cooling indicates poor bonding. Looking at both features

Table 1  
Calorimetry data obtained after different heating procedures<sup>a</sup>

Heating procedure	$T_g$ (°C)	$T_c^o$ (°C)	$T_c$ (°C)	$T_m^o$ (°C)	$T_m$ (°C)	$\Delta H_f$ (J/g)
10°C/min	86.7	114.6	120.2	252.8	278.0	20.0
5°C/min	88.8	117.6	124.2	253.0	276.5	14.6
1°C/min	91.3	129.0	134.9	253.8	268.0	9.1
Stepped heating	90.2	118.0	124.9	253.9	275.0	16.1

<sup>a</sup>Note:  $T_g$ : Glass transition temperature.

$T_c^o$ : Onset temperature of the cold-crystallization peak.

$T_c$ : Peak temperature of the cold-crystallization peak.

$T_m^o$ : Onset temperature of the melting peak.

$T_m$ : Peak temperature of the melting peak.

$\Delta H_f$ : Heat of fusion.

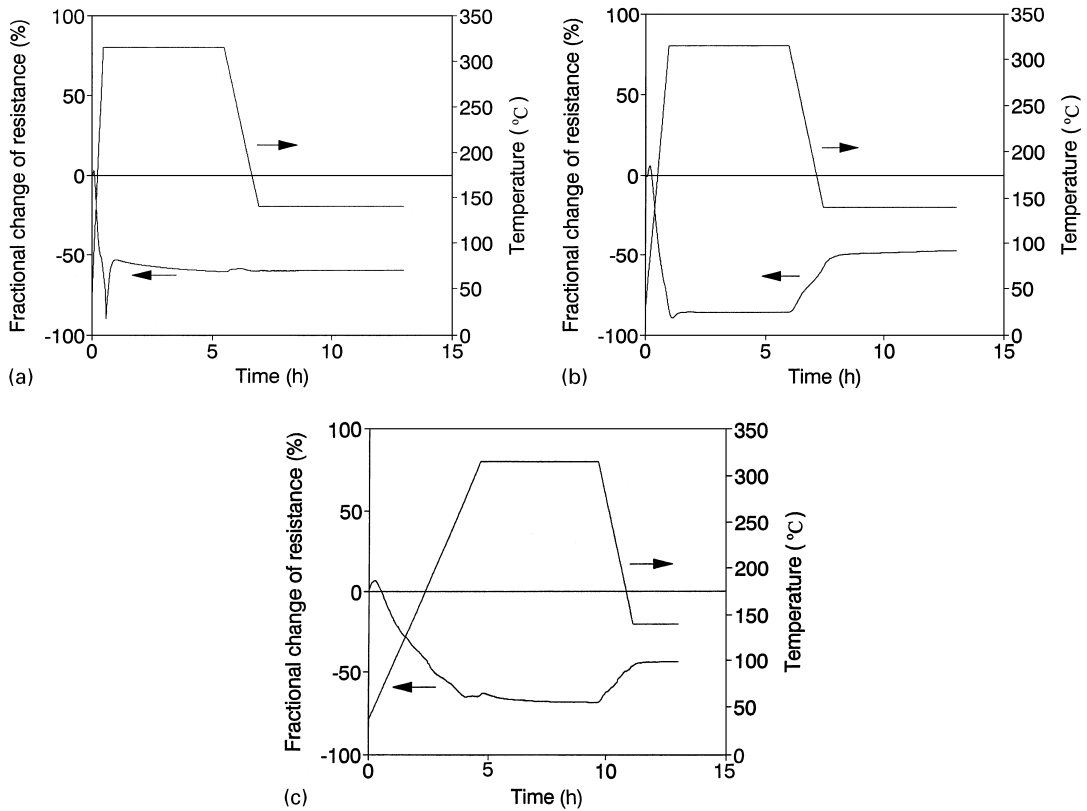


Fig. 3. Effect of heating rate below 315°C in heating procedure A on subsequent adhesive joint development. (a) 10°C/min. (b) 5°C/min. (c) 1°C/min. The pressure was  $4.4 \times 10^3$  Pa.

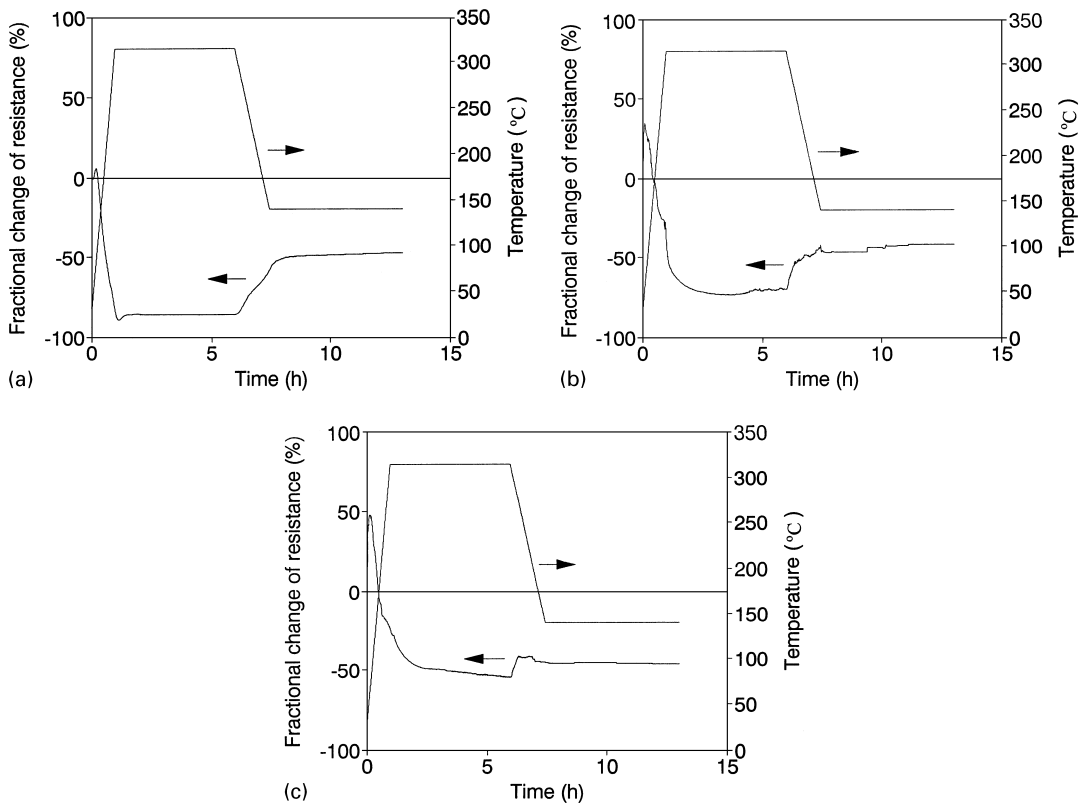


Fig. 4. Effect of pressure on adhesive joint development. The heating rate was 5°C/min. (a)  $4.4 \times 10^3$  Pa. (b)  $2.1 \times 10^5$  Pa. (c)  $6.8 \times 10^5$  Pa.

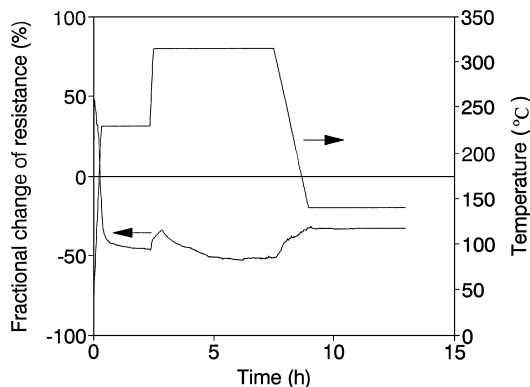


Fig. 5. Effect of stepped heating below 315°C on subsequent adhesive joint development. The heating rate was 10°C/min. The pressure was  $6.8 \times 10^5$  Pa.

together (i.e. resistance increase upon reaching 315°C and resistance increase upon cooling), one sees that a high heating rate (below 315°C) is associated with more mass flow at 315°C and better bond formation.

Fig. 4 shows the effect of pressure on the bond development for a heating rate of 5°C/min in heating procedure A. The higher was the pressure, the slightly smaller was the resistance increase upon reaching 315°C and the smaller was the resistance increase upon cooling. Hence, pressure reduced the mass flow slightly, but still improved the bond due to its squeezing effect. Comparison of Figs. 4 and 3 shows that a high pressure is less influential than a high heating rate in affecting molecular mobility or bond quality.

Fig. 5 shows the result for stepped heating (heating procedure B) at a pressure of  $6.8 \times 10^5$  Pa. The resistance decreased upon heating, as in Fig. 3. However, upon heating above 230°C (after the step), the resistance increased abruptly, presumably due to limited molecular

movement that was possible at a temperature that approached  $T_m$ . As the specimens cooled, their resistances increased, as in Fig. 3. Comparison of Figs. 5 and 3(c) indicates that stepped heating gave effects similar to those of a low heating rate. This is also consistent with DSC results (Fig. 2). In spite of the higher pressure on the specimens of Fig. 5 compared with those of Fig. 3(c), the bond quality indicated by Fig. 5 is similar to that indicated by Fig. 3(c). Thus, it is the heating time rather than heating rate that most affects the bond development. The longer is the time spent below  $T_m$ , the less is the flow response of the polymer and the poorer is the resulting bond.

#### 4. Conclusion

A long heating time below  $T_m$  was found to be detrimental to subsequent PPS adhesive bond formation above  $T_m$  due to reduced mass flow of the polymer above  $T_m$ . The reduced mass flow of the polymer is caused by curing reactions below  $T_m$ . Pressure enhanced the bonding, although less so than a high heating rate.

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