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Short communication

Kinetics of autohesion of thermoplastic carbon-fiber prepregs

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Abstract

The kinetics of autohesion of continuous carbon-fiber thermoplastic-matrix prepregs above the glass transition temperature was studied by the measurement of the DC electrical contact resistance of the joint between two plies in real time during autohesion at various constant temperatures. The resistance decreased as autohesion progressed. The rate of decrease in resistance was used as an indicator of the rate of autohesion. The activation energy was 21.2 kJ/mol for both Nylon-6 and polyphenylenesulfide carbon-fiber prepregs. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Diffusion bonding; Thermoplastic; Kinetics; Activation energy; Electrical resistance; Nylon; Carbon-fiber prepregs; Phenylenesulfide

1. Introduction

The joining of materials is important for manufacturing and repair of composite material products. Joining methods for polymers and polymer-matrix composites include fusion bonding, diffusion bonding (or autohesion), use of adhesives, and fastening. In particular, autohesion is relevant to the self-healing of polymers. Diffusion bonding (or autohesion) involves interdiffusion between the adjoining materials in the solid state. In contrast, fusion bonding involves melting. Due to the relatively low temperatures of diffusion bonding compared to fusion bonding, diffusion bonding does not suffer from the undesirable side effects that typically occur in fusion bonding, such as degradation and cross-linking of the polymer matrix. Although the diffusion bonding of metals has been widely studied [1–5], relatively little study has been conducted on the autohesion of polymers [6–21]. Because of the increased segment mobility above the glass transition temperature (T_g), thermoplastics are able to undergo interdiffusion above T_g.

Diffusion, as a thermally activated process, takes time. In other words, how long diffusion takes depends on the temperature. In order for diffusion bonding or autohesion to be conducted properly, the kinetics of the process needs to be known. This paper reports a method for real-time study of the kinetics of autohesion of thermoplastic carbon-fiber prepregs.

The study of the kinetics requires monitoring the process as it occurs. A real-time monitoring technique is obviously preferable to a traditional method that requires periodic interruption and cooling of the specimen. However, real-time monitoring is experimentally difficult compared with interrupted monitoring. The method we describe is ideal for thermoplastic prepregs containing continuous carbon fibers, since the carbon fibers are conductive. Two carbon-fiber thermoplastic prepreg plies are placed together to form a joint. The electrical contact resistance of this joint is measured during autohesion. As autohesion occurs, the fibers in the plies undergoing joining come closer together, thus resulting in a decrease in the contact resistance. Hence, with the measurement of this resistance in real time, the autohesion process can be monitored as a function of time at different selected bonding temperatures. Arrhenius plots of a characteristic resistance decrease versus temperature allows determination of the activation energy for the process. The use of resistance measurement to evaluate diffusion bond quality has been previously suggested [22]. This method can possibly be used for monitoring of bonding of unfilled thermoplastics if a few carbon-fibers are strategically placed.

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Table 1
Material properties of PPS/CF and Nylon-6/CF prepregs

	Prepreg designation	Fiber type	Fiber Diameter (μm)	Fiber weight fraction(%)	Matrix T_g (°C)	Matrix T_m (°C)	Prepreg thickness (μm)
PPS/CF	QLC 4164	AS-4C[a]	8	64	90	280	250
Nylon-6/CF	QNC 4162	34-700[b]	6.9	62	40–60	220	250

[a]Hercules Advanced Materials and Systems Company, Magna, Utah.
[b]Grafil, Inc., Sacramento, California.

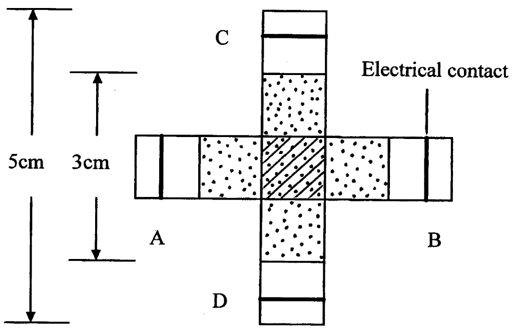

Fig. 1. Sample configuration for studying the kinetics of diffusion bonding. The dotted cross-shaped region is where pressure is applied. The square shaded region is the joint.

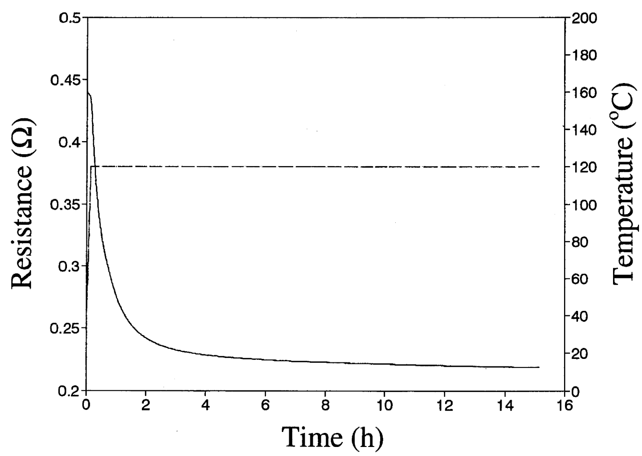

Fig. 2. Variation of the contact resistance with time during heating to 120°C and subsequent holding at 120°C for annealed Nylon-6/CF prepreg. (solid curve) resistance, (dashed curve) temperature.

2. Experimental methods

The thermoplastic matrices of the carbon-fiber prepregs in this study were Nylon-6 (PA) and polyphenylenesulfide (PPS). The unidirectional carbon-fiber prepregs were supplied by Quadrax Corp. (Portsmouth, Rhode Island). A summary of the properties of the PPS/carbon fiber (PPS/CF), and Nylon-6/CF prepregs is presented in Table 1.

Nylon-6/CF prepregs were used as received as well as after annealing. PPS/CF prepregs were used after annealing. Annealing of both Nylon-6/CF and PPS/CF prepregs was carried out in air at 140°C and 180°C, respectively for 25 h, while pressure (1000 Pa) was applied by the weight of steel plates. After heating, the prepregs were furnace-cooled to room temperature under pressure.

Identically prepared prepreg strips of length 5 cm and width 1 cm were stacked at an angle of 90° in a cross-shaped steel mold cavity lined with a PTFE film for electrical insulation, so that the overlap area was 1 cm × 1 cm, as shown in Fig. 1. A pressure of 4450 Pa was applied by the weight of a 3-cm long, cross-shaped steel plate, which was electrically insulated from the prepregs by a PTFE film. An electrical contact in the form of silver paint in conjunction with copper wire was applied at each of the four legs of the crossed prepreg strips (Fig. 1). 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. This constituted the four-probe method of DC electrical resistance measurement. A Keithley 2002 multimeter was used.

Samples as illustrated in Fig. 1 were heated from 30°C to different temperatures (80, 100, …, 200°C) at a heating rate of 10°C/min and then held at the temperature for 15 h for autohesion to occur. During heating and temperature holding, the contact resistance was continuously measured.

3. Results and discussion

Fig. 2 shows the decrease in contact resistance with time during heating and subsequent holding at 120°C for the annealed Nylon-6/CF prepreg. Since the holding temperature was reached almost immediately, almost all of the resistance drop occurred in the isothermal portion of the applied temperature profile. The resistance leveled off at a relatively low value after several hours of isothermal holding. Similar results were obtained at other temperatures. The only difference was that the rate of resistance drop increased with the isothermal holding temperature. For the sake of analysis, the rate of resistance drop was taken as the absolute value of the slope of

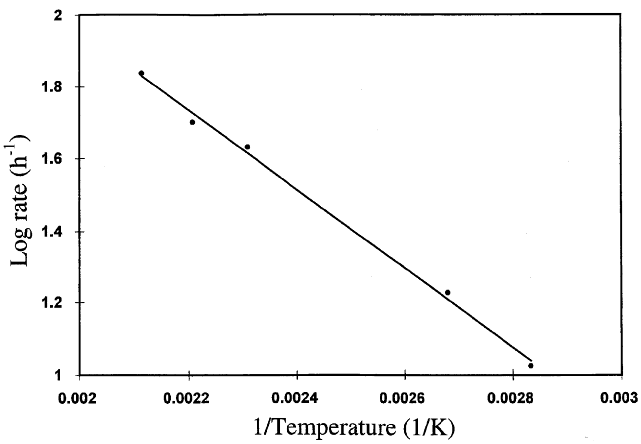

Fig. 3. Arrhenius plot of log rate vs. reciprocal absolute temperature for annealed Nylon-6/CF prepreg.

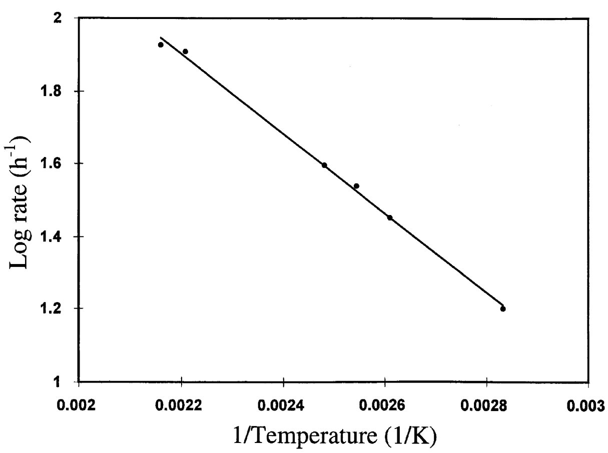

Fig. 4. Arrhenius plot of log rate vs. reciprocal absolute temperature for annealed PPS/CF prepreg.

the curve of the fractional change in resistance vs. time at the point at which the resistance had dropped by half of the way toward the leveled-off resistance. The rate of resistance drop can be used to describe the rate of autohesion. Fig. 3 shows the Arrhenius plot: log rate vs. reciprocal temperature (in K), where temperature is the isothermal holding temperature. From the slope of this plot, the activation energy was found to be 20.9 ± 0.7 kJ/mol.

Similar results were obtained for annealed PPS/CF prepreg. The data gave the Arrhenius plot of Fig. 4, from which an activation energy of 21.7 ± 0.8 kJ/mol could be extracted. Similar results for as-received Nylon-6/CF prepreg gave an activation energy of 20.4 ± 0.6 kJ/mol. Hence, the activation energy for autohesion is similar for Nylon-6/CF prepreg and PPS/CF prepreg, and also is similar for annealed and as-received Nylon-6/CF prepregs.

4. Conclusion

The kinetics of autohesion of thermoplastic prepregs above T_g was studied in real-time by the measurement of the DC electrical contact resistance of the joint between two plies. The contact resistance decreased as bonding progressed and then leveled off. Resistance measurement was made as a function of time for different autohesion temperatures. The activation energy of autohesion was thus found to be around 21.2 kJ/mol for both Nylon-6/CF and PPS/CF prepregs. Prior annealing of the prepregs had no effect on the activation energy for Nylon-6/CF prepregs.

References

[1] Wu H-Y, Lee S, Wang J-Y. J Mater Proc Tech 1998;75(1-3):173–9.
[2] Church S, Day J, Wild B. Mater World 1996;4(7):385–6.
[3] Godfrey SP, Threadgill PL, Strangwood M. High-temperature ordered intermetallic alloys VI, Materials Research Society Symp Proc 364(2). Pittsburgh, PA, USA;Materials Research Society, 1995. p. 793–8.
[4] Hwang HR, Lee RY. J Mater Sci 1996;31(9):2429–35.
[5] Wang ZC, Ridley N, Lorimer GW, Knauss D, Briggs GAD. J Mater Sci 1996;31(19):5199–206.
[6] Vallat MF, Stachnik M, Schultz J. J Adhesion 1996;58(3–4):183–90.
[7] Pitchumani R, Ranganathan S, Don RC, Gillespie Jr. JW, Lamontia MA. Int J Heat Mass Transfer 1996;39(9):1883–97.
[8] Loos AC, Li M. J Thermoplastic Composite Mater 1994;7(4):280–310.
[9] Jun EJ, Kim TW, Lee WI. High Temperatures — High Pressures 1990;22(6):655–61.
[10] Jou J, Liu C, Liu J, King J. J Appl Polym Sci 1993;47(7):1219–32.
[11] Raghava RS, Smith RW. J Polym Sci, Part B — Polym Phys 1989;27(12):2525–51.
[12] Mikos AG. Polymer 1989;30(1):84–91.
[13] Hamed GR. Rubber Chem Tech 1988;61(3):548–53.
[14] Howes JC, Loos AC. Proc American Soc Composites. Second Technical Conf. Lancaster, PA, USA: Technomic Publ Co, 1987. p. 110–9.
[15] Hamed GR, Shieh C-H. J Polym Sci, Part B — Polym Phys 1983;21(8):1415–25.
[16] Bothe L, Rehage G. Rubber Chem Tech 1982;55(5):1308–27.
[17] Hamed GR. Rubber Chem Tech 1981;54(3):576–95.
[18] Rhee CK, Andries JC. Rubber Chem Tech 1981;54(1):101–14.
[19] de Gennes PG. J Chem Phys 1971;55(2):572–9.
[20] Kim YH, Wool RP. Macromolecules 1983;16(7):1115–20.
[21] Wool RP. Rubber Chem Tech 1984;57(2):307–19.
[22] Lodge KW, Briggs GAD. J Mater Sci 1983;18(8):2354–60.