Interdependence Between the Curing, Structure, and the Mechanical Properties of Phenolic Resins

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ABSTRACT: The interdependence between the curing conditions, structure, and the mechanical properties of tow neat phenolic resin systems was investigated. Changes of the distribution of the void diameters were characterized by light- an scanning electron microscope analyses. Tensile tests and dynamic mechanical thermo analysis were performed to determine the influence of the hardener concentration and the curing temperature on the mechanical and the thermomechanical properties. The study reveals that the hardener concentration predominately influenced the microscopic structure, and thus the mechanical properties of the phenolic resin systems. By varying the postcuring times, it can be shown that independent from the microstructure of the phenolic resin system, the degree of cure has a strong influence on the mechanical properties. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 3173–3185, 1999

Key words: phenolic resins; voids; mechanical properties; thermomechanical properties; glass transition temperature

INTRODUCTION

Phenolic resins are some of the oldest technical plastics still in use today and remain fundamental materials for many important technical and economical components. Besides the traditional applications—for example, molding powders, surface coatings, adhesives for plywood, and abrasives used in grinding wheels, and a binder for sand castings. Phenolic resins are also used as a matrix system for composites used in the travel, construction, and sport industries that are capable of withstanding highly corrosive environments and also as a carbon basis for carbon–fiber reinforced carbon. They exhibit excellent thermal and chemical resistance with a low flammability and a low smoke density at a low toxicity.[1–2]

Phenolic resins used to be processed via a press or an injection molding machine as a molding powder.[3–7] During the processing of phenolic resins, the by-product of the polycondensation reaction is mostly water. The by-products produced can lead to voids in the component. During the processing of molding powders, these voids can be inhibited by various means:

- By fillers—for example, cotton or wood flour to absorb the condensation by-product.
- By opening the mold to evaporate the condensation by-product.
- By increasing the mold pressure to inhibit the formation of the condensation by-product.
- By preheating so as to precure the molding powder.

Long fiber reinforced components with a phenolic resin matrix are predominately cured at ambient

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pressure—for example, by hand lamination, filament winding, and prepreg manufacturing. In this application, the formation of voids by the polycondensation reaction can not be prevented by standard processing techniques. The formation of the voids, however, are influenced by the resin and the cure cycle.[8–12] For structural components—for example, for aviation technology—phenolic resin prepregs are predominately processed via autoclave procedures. With these procedures, it is imperative that the pregpregs have an advanced degree of cure before lamination to prevent void formation.[13]

Despite the fact that phenolic resins are the oldest technological resins, limited research has been conducted on the interdependence between the curing conditions, structure, and the mechanical properties of the neat resin system. This fundamental knowledge is required for the application of these resin matrix systems in fiber reinforced plastics.

REACTION MECHANISMS

The crosslinking of phenolic and formaldehyde is a polycondensation reaction. During the reaction the by-product, mostly water, is produced and expelled. Depending on the reaction conditions (acidic or basic) during condensation of the phenolic resin and formaldehyde, novolak or resol is produced. During the crosslinking, the phenolic resin undergo changes in morphological stages.

Stage A: Beginning stage, resol or novolak, liquid, meltable and/or solvable.

Stage B: Middle stage, unmeltable, unsolvable, but can be shaped after subjected to heat with relatively low mechanical properties.

Stage C: End stage, unmeltable, unsolvable, good mechanical properties and chemical resistance.

The most liquid and castable resol contain methylene and ether bonds. They have reactive methyl end groups and thus can be cured via acid or the application of heat. In practical applications, the most frequent method for conversion is via heat activated curing. At higher temperatures, over 160°C, the ether bonds between the resol links shift to methylene bonds by producing formaldehyde. This formaldehyde can react once again
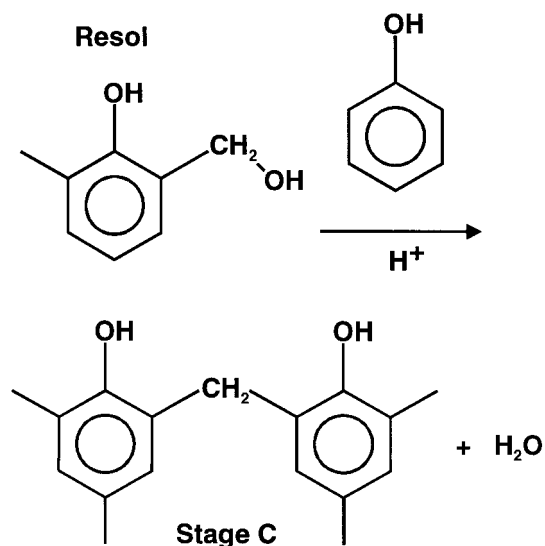

Figure 1 Illustration of the curing of resol with strong acids.

with the phenol. By the addition of H^+ ions from strong acids, it is possible to cure the phenolic resin without additional heat. Common acids used for practical applications are hydrochloric acid, phosphoric acid, *p*-toluolsulfonic acid, and phenolsulfonic acid.[14,15] The curing with the use of acids leads to crosslinking by methylene bonds.[7,14] The bond formation of the H^+ ion and the acid curing mechanism is shown in Figure 1. The relatively short branched connections via methylene bonds in phenolic resins result in brittle mechanical properties that can be slightly improved by adding fillers—for example, wood, or stone flour, or glass fibers.

MATERIALS

The examinations were conducted with two liquid resols predominately used in filament winding and resin impregnation. The phenolic resin, DW 247 from the Bakelite AG, is a low-viscosity, water-based resol with a water content of 16.6%, and contains 7.6% unreacted phenol. The hardener is *p*-toluolsulfuric acid, 0982 H from Bakelite AG, added to the resin in different ratios by mass. The phenolic resin *N* is also a low-viscosity, water-based resol with a water content of 15%, and contains 6.7% unreacted phenol. The same hardener was used for both resin systems.

Table I Processing Conditions of the Produced Neat Resin Plates

Hardener Concentration (%)	Resin System	Curing Temperature (°C)		
		40	60	80
2	DW247	No cure	—	—
2	N	24 h	—	—
3	DW247	No cure	—	—
3	N	24 h	—	—
4	DW247	No cure	—	—
4	N	24 h	—	—
5	DW247	No cure	—	—
5	N	24 h	—	—
7	DW247	24 h	24 h	24 h
7	N	24 h	24 h	24 h
9	DW247	24 h	—	—
9	N	24 h	—	—
11	DW247	24 h	—	—
11	N	24 h	—	—
13	DW247	24 h	—	—
13	N	24 h	—	—
15	DW247	24 h	—	—
15	N	24 h	—	—
17	DW247	24 h	—	—
17	N	Too fast	—	—

MANUFACTURING OF TEST SPECIMEN AND CONDUCTED EXPERIMENTATION

With the phenolic resin, approximately 4 mm thick neat resin plates were cast. The casting form consists of two verticle glass plates with a silicon profile as a seal. After casting the plates, the resin was cured at different temperatures between the plates. The curing at higher temperatures was conducted in a convection heating oven. Out of the neat resin plates, specimens were cut out with the use of a liquid cooled diamond saw. A portion of the specimens were postcured. After postcuring the specimens were cooled to ambient temperature and tested.

Table I shows the processing conditions of the produced neat resin plates. With the phenolic resin N, curing at 40°C with a 2% acid content within 24 h was not possible. With the phenolic resin, DW 247, the lower processing limit of acid was 7%. Adding more than 15% of acid to the phenolic resin N, the curing reaction was too fast for practical processing times. This upper processing limit with the DW 247 was 17%.

Tensile Tests

The tensile tests were conducted according to DIN 29971 using a Zwick 1465 mechanical testing machine with standard tensile test specimen geometry ($150 \times 15 \times d$ mm) at a constant test velocity of 2 mm/min. The distance of the strain gauges was 50 mm.

Determination of the Glass Transition Temperature by Dynamic Mechanical Thermal Analyzer

The storage modulus and the mechanical dampening were characterized with a torsional rheometer by Polymer Laboratories with a temperature range from -20 to 200°C at a heating rate of 5°C/min. The dimensions of the test specimen was $60 \times 10 \times 4$ mm. The glass transition temperature T_g, is characterized the point of intersection between the first tangent with a second tangent drawn at the inflection point of the storage modulus as shown in Figure 2.

Microscopic Investigations

To determine the average void diameter in the phenolic resins, light and scanning electron microscopic investigations were performed. The specimens were polished and analyzed with a

Table II Postcuring Conditions

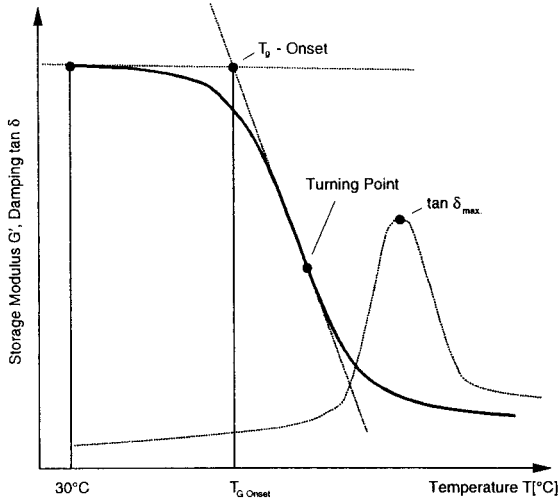| Hardener Concentration (%)	Resin System	Postcuring Condition
7	DW247	At 90° for 0, 3, 6, 12, 24, 48, 168 h
7	N	At 90° for 0, 3, 6, 12, 24, 48, 168 h
15	DW247	At 90° for 0, 3, 6, 12, 24, 48, 168 h
15	N	At 90° for 0, 3, 6, 12, 24, 48, 168 h
17	DW247	At 90° for 0, 3, 6, 12, 24, 48, 168 h
17	N	At 90° for 0, 3, 6, 12, 24, 48, 168 h

Figure 2 Graphical determination of the onset T_g.

light microscope Axiophot by Zeiss. The fracture surface of the tensile test specimen were analyzed with a scanning electron microscope. The specimens were adhered to test stands with an electroconductive adhesive and were ionozied with a thin layer of gold.

Determination of the Distribution of the Void Diameters

Since microscopically only the surfaces can be characterized, an exact determination of the distribution of the void diameters is not possible. As shown in Figure 3, only the intersection between the spheroid and the cutting plane can be microscopically evaluated. In addition, the void depth cannot be microscopically determined. For this reason, the exact distribution of the void diameters cannot be determined by simple mathematical relations from the intersection between the spheroid and the cutting plane. For this reason, the real distribution must be determined by statistical methods.

The determination of the intersection between a void and a cutting plane by light microscopic analysis were supported by a computer image processor. For the mathematical evaluation of the real void diameter distribution, one basic assumption was that the shape of the voids were spherical. If a sphere with a radius r will be cut at a distance h from the center of the sphere, the radius t of the intersection can be determined by

$$t = \sqrt{r^2 - h^2} \tag{1}$$

Assuming that H is a normal randomly distributed value within the interval from $-r$ to r, the distribution P of the radii T can be determined with

$$T = \sqrt{r^2 - H^2} \tag{2}$$

by

$$P(T > t) = \sqrt{1 - \left(\frac{t}{r}\right)^2} \tag{3}$$

The distribution function $F(t, r) = P(T \leq t)$ of the intersection radii with a fixed spherical radius r such that $0 < t < r$ is

$$F(t, r) = 1 - \sqrt{1 - \left(\frac{t}{r}\right)^2} \tag{4}$$

The probability density is simply the first derivative of eq. (4):

$$f(t, r) = \frac{t}{r \sqrt{1 - \left(\frac{t}{r}\right)^2}} \tag{5}$$

Equation (4) is the probability density for a fixed spherical radius. In addition to the distribution of the intersection radii, the radii of the voids also have an unknown distribution. If $f(t)$ is the probability density of the radii of intersection for a fixed spherical radius, then $g(t)$ is the probability density of the combination of random intersec-
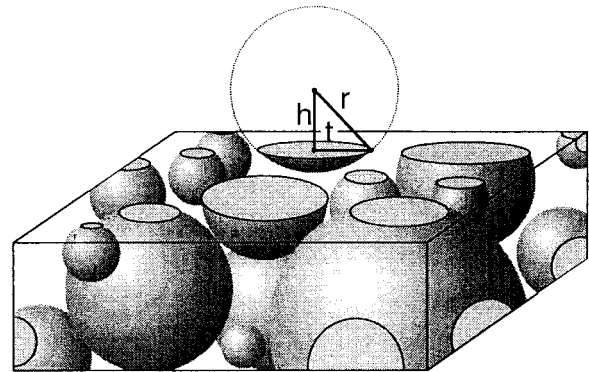

Figure 3 Random determination of the intersection between a void and a cutting plane by light microscopic analysis.

tions and random void radii. Both probability densities are related by eq. (5).

$$g(t) = \int_t^\infty f(t, r) f(r) \, dr \qquad (6)$$

If $g(t)$ is known by the microscopically evaluated intersection radii, than the unknown probability density of the real spherical radii of the voids $f(r)$ can be determined by solving the integral eq. (6).[16]

RESULTS AND DISCUSSION

Results of the Tensile Tests

Influence of the Hardener and the Curing Temperature

The results of the tensile test of the neat resin specimens are shown in the stress–strain diagram for six trials in Figure 4. The stress–strain behavior at the beginning is approximately linear and becomes only slightly digressive at higher strains. For both the phenolic resin systems, the fracture strain increases with a higher concentration of hardener. The fracture stress for both phenolic resin systems is reduced with a hardener concentration greater than 9%. The fracture strain and the fracture stress for both phenolic resin systems for all of the hardener concentrations investigated are shown in Figure 5.

The influence of the curing temperature on the stress–strain response is shown in Figure 6. An increase in the curing temperature from 40 to 60°C for both phenolic resin systems result in a significant increase in the mechanical properties. Increasing the curing temperature to 80°C decreases the fracture strain and fracture stress of both phenolic resin systems.

Influence of Postcuring

To determine the influence of the curing alone on the mechanical properties of the phenolic resin system, it is necessary to ensure that the same microstructure of the resin systems is maintained. Thus the size and the distribution of the size of the voids must be similar for each curing cycle. Hence, the phenolic resin N with a hardener concentration of 7 and 15% and for the phenolic resin DW 247 with a hardener concentration
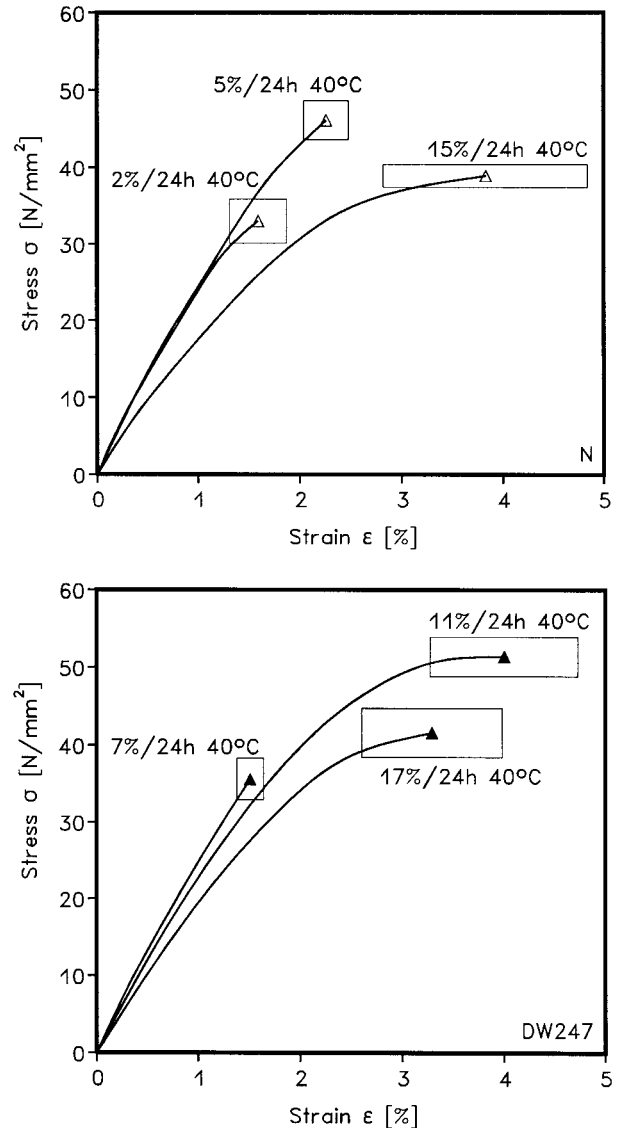

Figure 4 Stress–strain diagram of the phenolic resin systems N (top) and DW 247 (bottom) with the different hardener concentrations, curing conditions at 40°C for 24 h.

of 7 and 17% cured at 40°C for 24 h and then postcured at 90°C for various time durations. Figure 7 illustrates that for the phenolic resin N, the fracture strain for all the specimens with a hardener concentration of 15% decrease significantly with an increase in the postcuring time, whereas the 7% concentration shows less of an influence.

The fracture stress of these specimens show hardly any influence on the postcuring time and thus the E-modulus of the specimen increases with postcuring time. A similar behavior can be
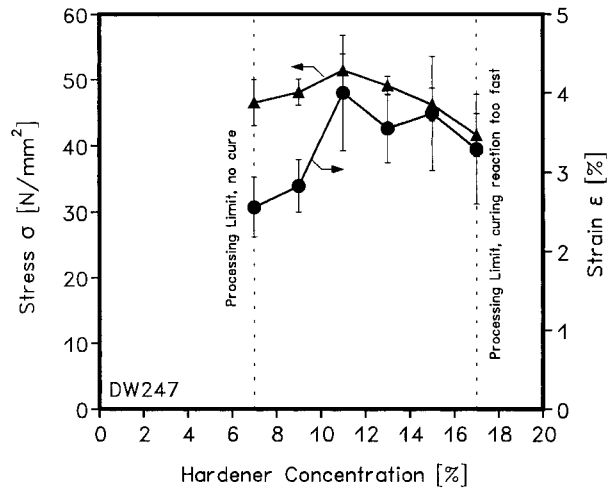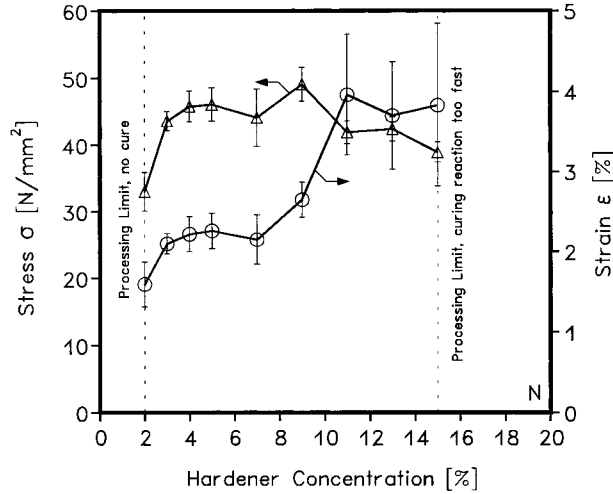
Figure 5 Fracture strain and fracture stress of the phenolic resin systems N (top) and the DW 247 (bottom) as a function of the hardener concentration, curing conditions at 40°C for 24 h.

observed for the phenolic resin system DW247. With an increasing in the postcuring time for both the 7 and 17% hardener concentrations, the fracture strain decreases and the fracture stress remains almost constant.

Results of the Structural Investigation

Figures 9 and 10 illustrate the scanning electron microscope photographs of the fracture surface of both phenolic resin systems at the two processing limits, both 2 and 15% for the resin N and both 7 and 17% for the resin DW 247, respectively. The photographs illustrate that the void diameter decrease with an increase in the amount of hardener.

The hardener percentage influences both the void size and also the void diameter distribution in the resin system. Thus the structure influence on the mechanical properties due to the voids must be taken into account. For this reason, no direct interrelation between the hardener concentration and the mechanical properties can be declared.

The analysis of the void diameter distribution using eq. (5) shows that the hardener concentration influences the structure of both phenolic resin systems. With an increase in the hardener concentration, the average void diameter will decrease. Figure 11 shows the histogram of the void
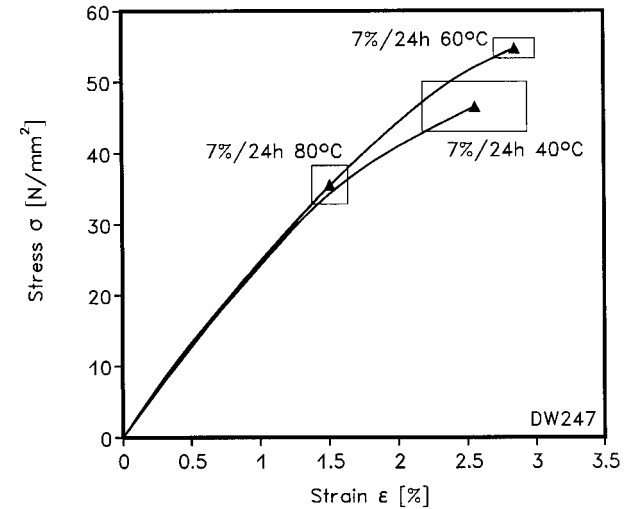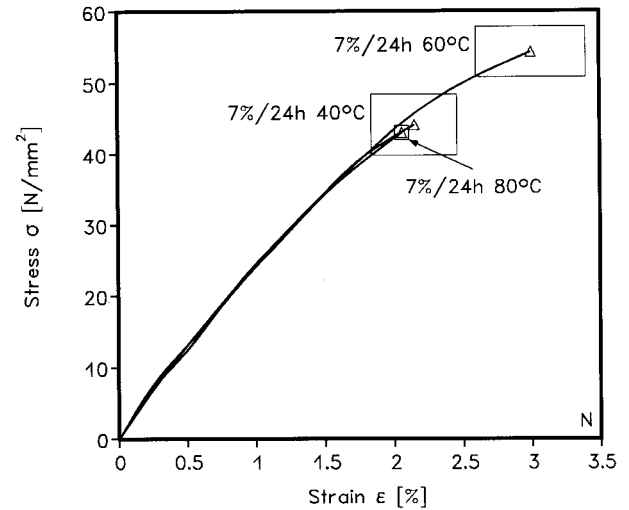

Figure 6 Stress–strain diagram of the phenolic resin systems N (top) and DW 247 (bottom) as a function of the cure temperature 40, 60, and 80°C, curing conditions at 7% hardener for 24 h.
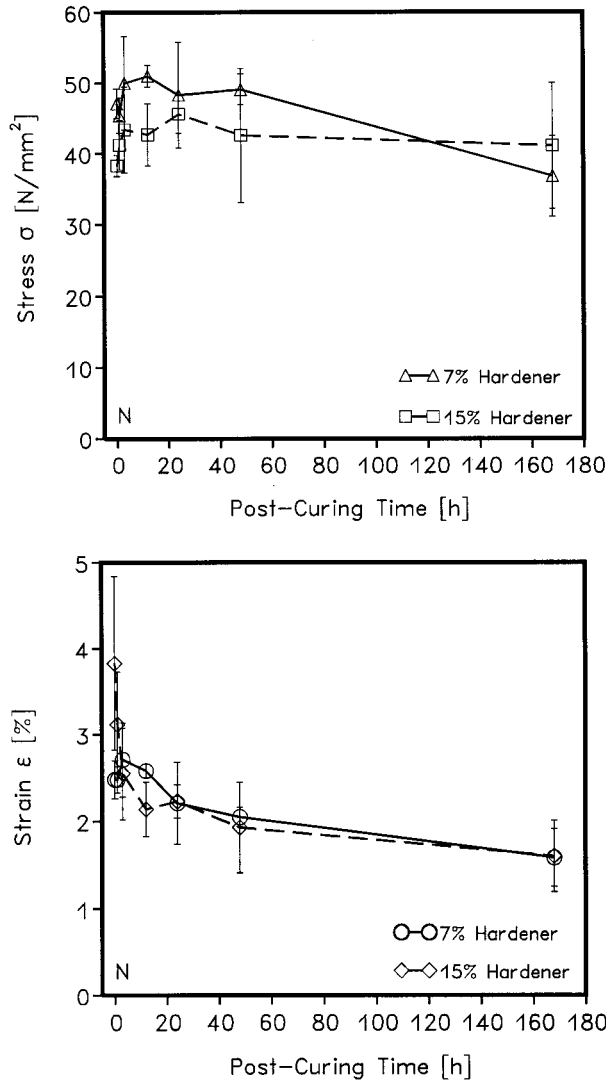
mated by a linear relationship as shown in Figure 12.

The average void diameter for the curing temperatures of 40, 60, and 80°C for both phenolic resin systems with a hardener concentration of 7% is shown in Figure 13. Similar to the increase in the hardener concentration, a decrease of the average void diameter can be observed with an increase in the curing temperature. The average void diameter of the phenolic resin system N decreases from 2.4 μm at a curing temperature of 40°C to 1.6 μm at 80°C. Likewise, the average void diameter of the phenolic resin system DW
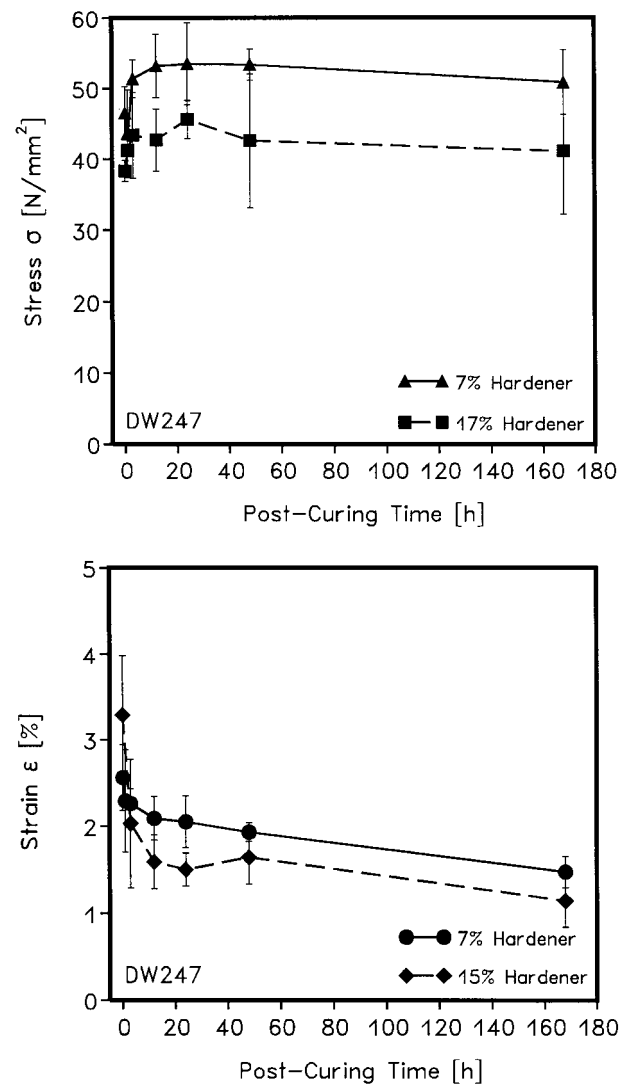

Figure 7 Fracture stress (top) and fracture strain (bottom) of the phenolic resin system N as a function of the postcuring at 90°C, curing conditions of 7 and 15% hardener, 40°C for 24 h.

diameter distribution for the phenolic resin system N with a 2% hardener concentration.[16]

The void diameter of the phenolic resin system N decreases from an average of 4.6 μm with a 2% hardener concentration to an average of 0.25 μm with a 15% hardener concentration. Likewise, the void diameter of the phenolic resin system DW 247 decreases from an average of 1.8 μm with a 7% hardener concentration to an average of 0.25 μm with a 17% hardener concentration. In summary, it is clear that the average void diameter for both phenolic resin systems is dependent on the hardener concentration and can be approxi-

Figure 8 Fracture stress (top) and fracture strain (bottom) of the phenolic resin system DW 247 as a function of the postcuring at 90°C, curing conditions of 7 and 17% hardener, 40°C for 24 h.
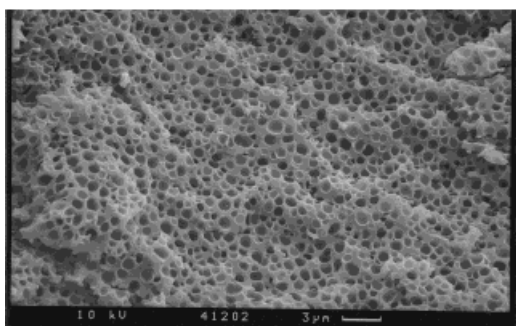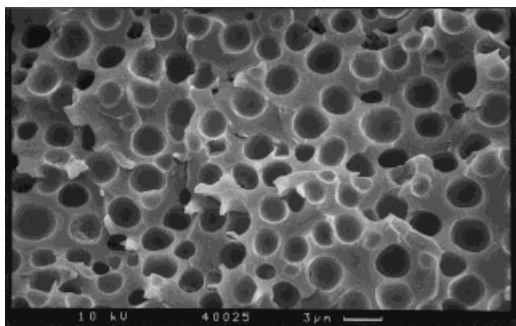
Figure 9   Scanning electron microscope photograph of the fracture surface of the phenolic resin N, 7% hardener concentration (top) and at the processing limit 15% hardener concentration (bottom), curing conditions at 40°C for 24 h.
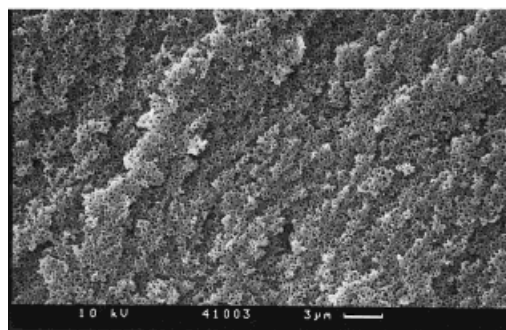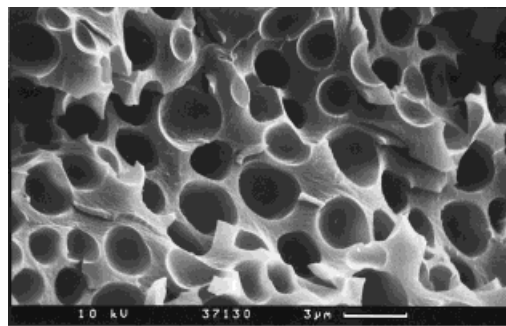
Figure 10   Scanning electron microscope photograph of the fracture surface of the phenolic resin DW 247 for both processing limits, 7% hardener concentration (top) and 17% hardener concentration (bottom), curing conditions at 40°C for 24 h.

247 decreases from 1.8 μm at a curing temperature of 40°C to 1.5 μm at 80°C.[16] However, the curing temperature does not influence the average void diameter as much as the hardener concentration.

Characterization of the Curing and the Thermomechanical Behavior

Influence of the Hardener Concentration and the Curing Temperature

The dynamic mechanical analyzer (DMA) analysis of the phenolic resin systems show that the torsional modulus and the mechanical damping are influenced by the hardener concentration and also the curing temperature. It can be seen that the mechanical dampening is not as strongly affected by the hardener concentration and curing temperature as the slope in the torsional modulus. For instance, the phenolic resin system *N* with a hardener concentration of 2% exhibits almost no residual stiffness at 100°C. On the other

hand, the same resin system with a hardener concentration of 15% shows approximately a 50% reduction in its residual stiffness at room temper-
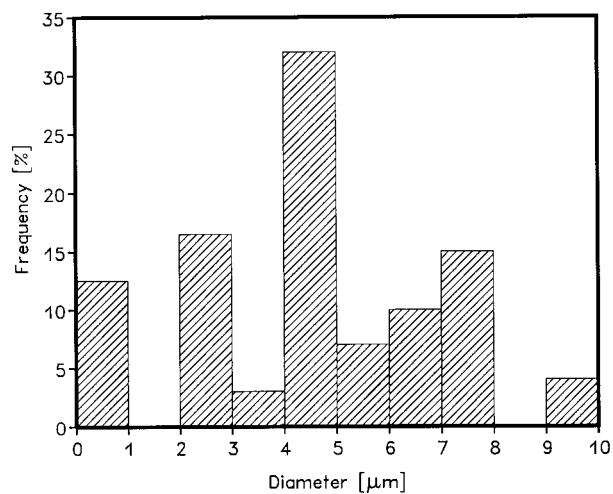

Figure 11   Histogram of the void diameter distribution of the phenolic resin system N with a 2% hardener concentration.
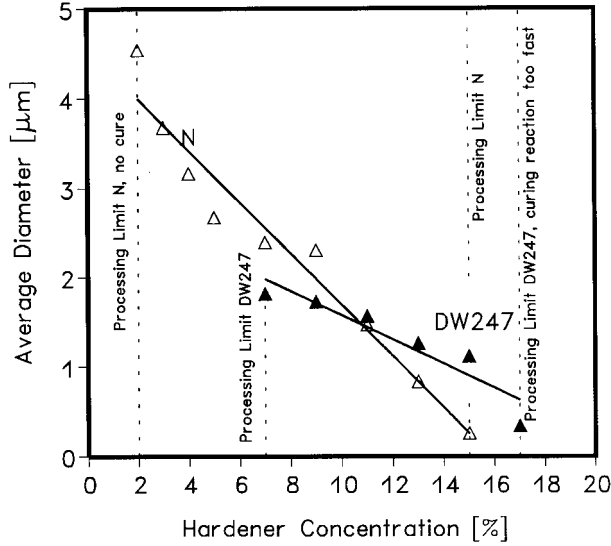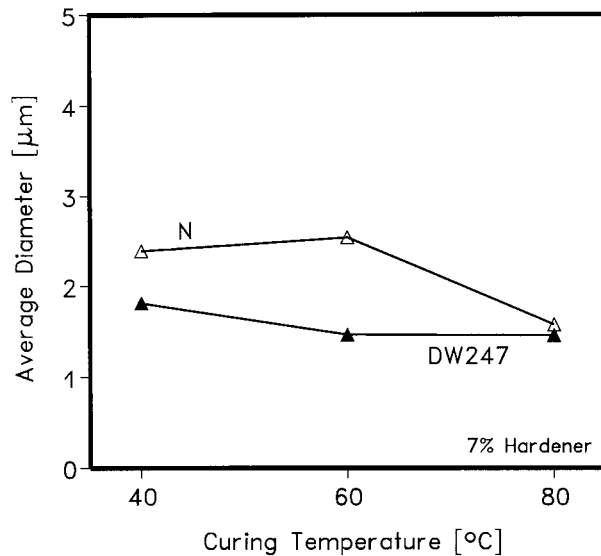
Figure 12 The average void diameter determined eq. (6) for the phenolic resin system N and DW 247 dependent on the hardener concentration, curing conditions at 40°C for 24 h.

Figure 14 The torsional modulus and the mechanical dampening of the phenolic resin system N at both 2 and 15% hardener concentrations, curing conditions at 40°C for 24 h.

ature, as shown in Figure 14. The phenolic resin system DW 247 shows little influence of the hardener concentration on the slope of the torsional modulus. Differences in the torsional modulii between the specimens with 7 and 17% hardener concentration become apparent only when the

glass transition temperature is approached, as shown in Figure 15. At temperatures greater than the glass transition temperature, a postcuring reaction can be observed in each DMA measurement.

The postcuring reaction becomes evident by an increase in the torsional modulus. At a temperature of 300°C, all the phenolic resin systems still have 25% of its residual stiffness at room temperature; this illustrates the excellent thermal stability of the phenolic resin systems.

The difference in the onset and δ_{max} glass transition temperature between the specimens with different hardener concentrations are hardly perceptible for both resin systems, as shown in Figure 16. Only a slight increase in the T_g tan δ_{max} of

Figure 13 The average void diameter determined eq. (5) for the phenolic resin system N and DW 247 dependent on the curing temperature at 40, 60, and 80°C with a hardener concentration of 7%.
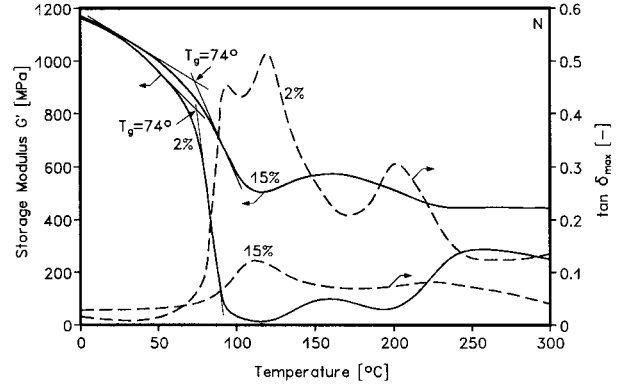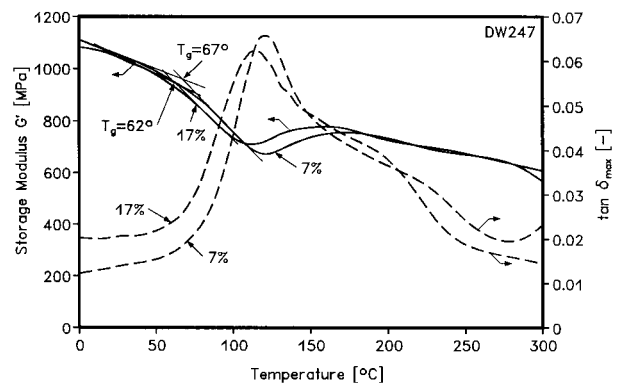

Figure 15 The torsional modulus and the mechanical damping of the phenolic resin system DW 247 at both 7 and 17% hardener concentrations, curing conditions at 40°C for 24 h.
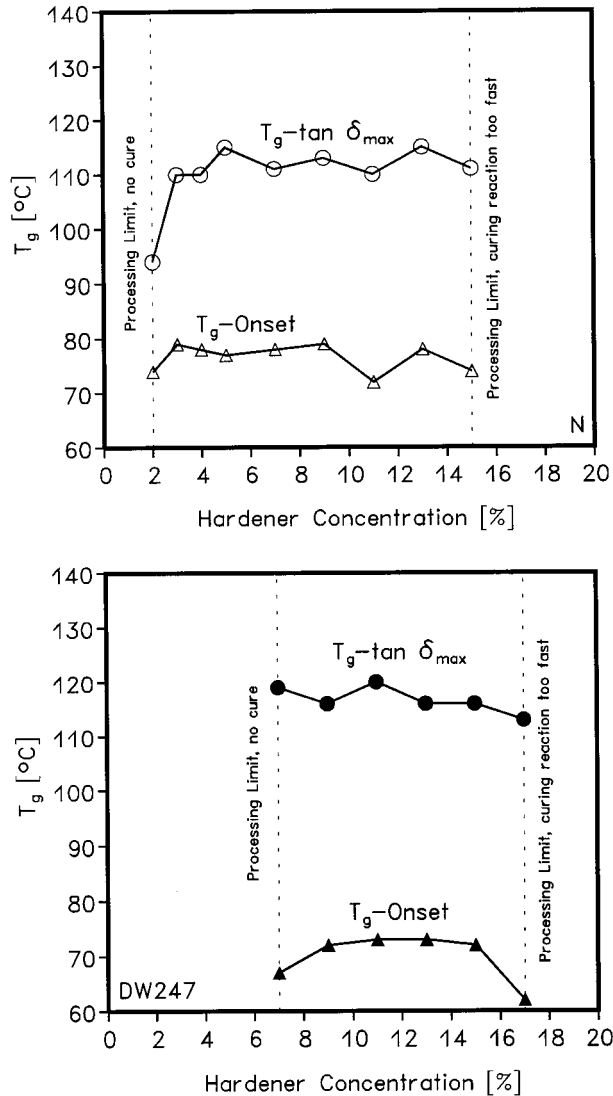
Figure 16 T_g onset and T_g tan δ_{max} of the phenolic resin system N (top) and DW 247 (bottom) as a function of the hardener concentration, curing conditions at 40°C for 24 h.

the phenolic resin system N when the hardener concentration is increased from 2 to 3%.

The influence of the curing temperature on the glass transition temperature is significantly stronger than on the hardener concentration. Both the phenolic resin system N and DW 247 show an increase in the onset and tan δ_{max} T_g with an increase in the curing temperature, as shown in Figure 17.

Influence of Postcuring

The influence of the postcuring at 90°C on the onset and tan δ_{max} glass transition temperature is

shown in Figures 18 and 19. It can be seen that both resin systems exhibit a strong increase in the T_g values within the first 24 h of postcuring. The increase is almost independent from the hardener concentration.

Interdependence Between the Curing Conditions and the Mechanical Properties

Via statistical analysis of the measured average void diameters, it was shown that higher hardener concentrations significantly reduce the average void diameter in the phenolic resin systems investigated. Likewise, thermoanalytical analysis via DMA reveals that the glass transition temperature of the investigated phenolic resin systems is almost independent from the hardener concentration. Thus the increase in the mechanical behavior of the phenolic resin system shown in Figure 5 must be predominately dependent on the structural state or average void diameter within the resin.

For the postcured test specimens, structural influences on the mechanical properties can be excluded. Thus the changes in the mechanical properties must be related to the changes in the degree of cure of the phenolic resin system.

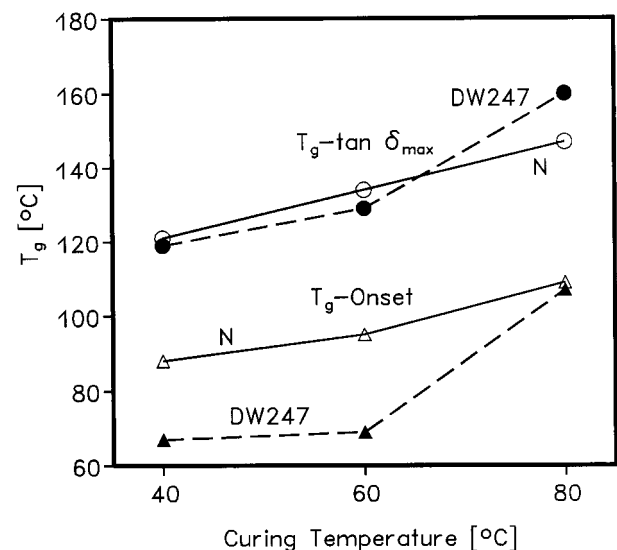Figure 20 shows the fracture strain determined by tensile tests of the phenolic resin system N as a function of the onset and tan δ_{max}

Figure 17 T_g onset and T_g tan δ_{max} of the phenolic resin system N and DW 247 as a function of the curing temperature at 40, 60, and 80°C with a hardener concentration of 7%.
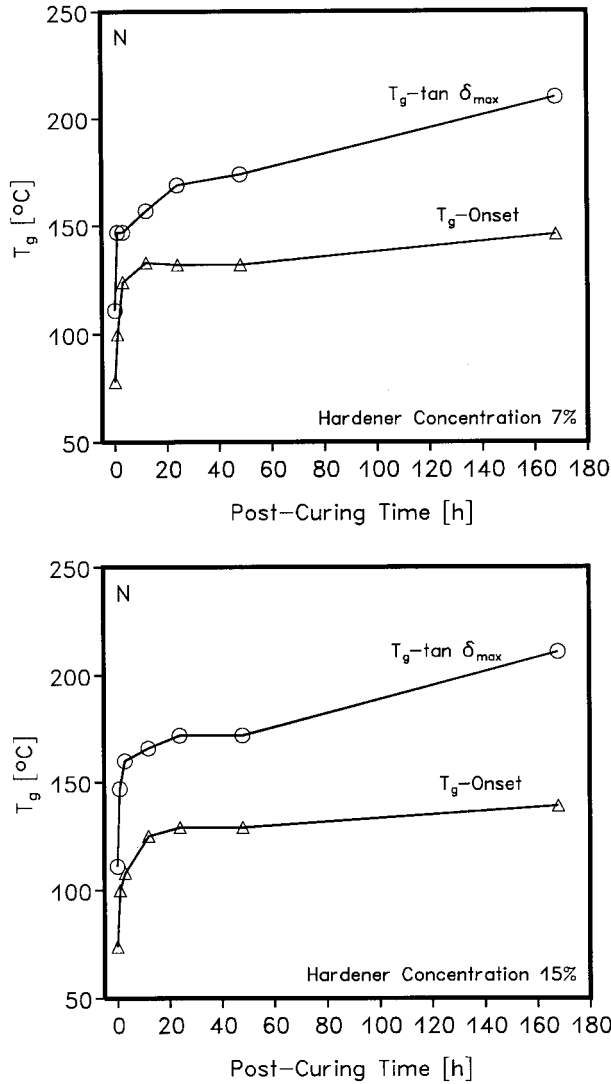
Figure 18 T_g onset and T_g tan δ_{max} of the phenolic resin system N with 7% (top) and 15% (bottom) hardener concentration as a function of the postcuring time at 90°C, curing conditions at 40°C for 24 h.

glass transition temperature determined via DMA. With a hardener concentration of 7%, no changes in the fracture strain up to an onset T_g of 120°C and a δ_{max} glass transition temperature of 150°C can be observed. With higher T_g values, the fracture strain decreases significantly. With a hardener concentration of 15%, almost a linear decrease in the fracture strain as well as an increase in glass transition temperature is evident. A similar behavior is observed with the phenolic resin system DW 247 as shown in Figure 21.

CONCLUSION

The interdependence between the structure and both the mechanical and thermal mechanical properties of two phenolic resin systems was investigated. It was shown that the hardener concentration predominately influenced the microscopic structure, and thus the mechanical properties of the resin system. A significant decrease in the average void diameter as a result of the polycondensation reaction with an increasing hardener concentration was detected. However, the
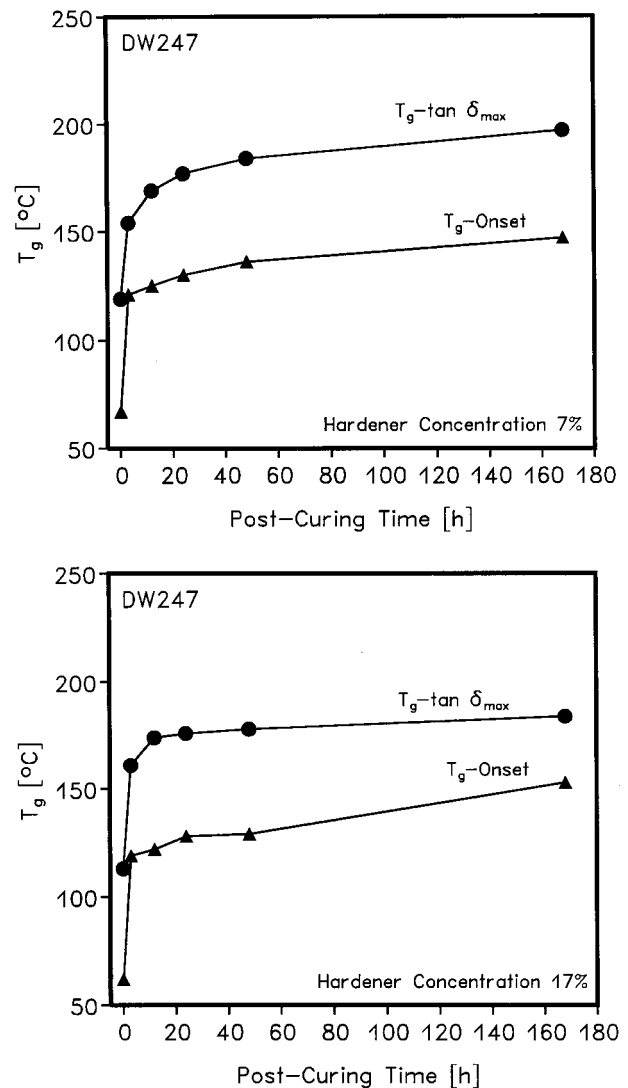

Figure 19 T_g onset and T_g tan δ_{max} of the phenolic resin system DW 247 with 7% (top) and 17% (bottom) hardener concentration as a function of the postcuring time at 90°C, curing conditions at 40°C for 24 h.
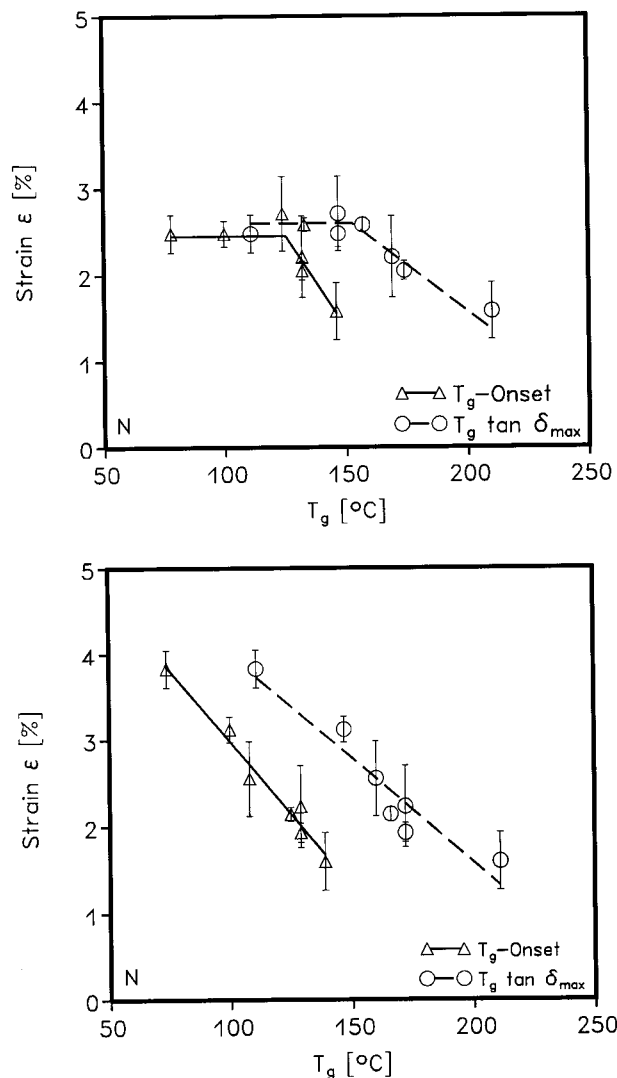
of the phenolic resin system, the degree of cure has a strong influence on the mechanical properties. Thus a significant decrease in the fracture strain of the neat phenolic resin systems with an increase in the glass transition temperature was detected.

Figure 20 Progression of the fracture strain of the phenolic resin system N with a hardener concentration of 7% (top) and 15% (bottom) as a function of the onset and δ_{max} glass transition temperature measured via DMA.

hardener concentration shows almost no influence on the glass transition temperature determined via DMA.

The curing temperature has been shown not to influence the average void diameter as much as the hardener concentration. However, it was determined that the curing and the postcuring temperatures have a strong influence on the glass transition temperatures measured via DMA independent of the hardener concentrations.

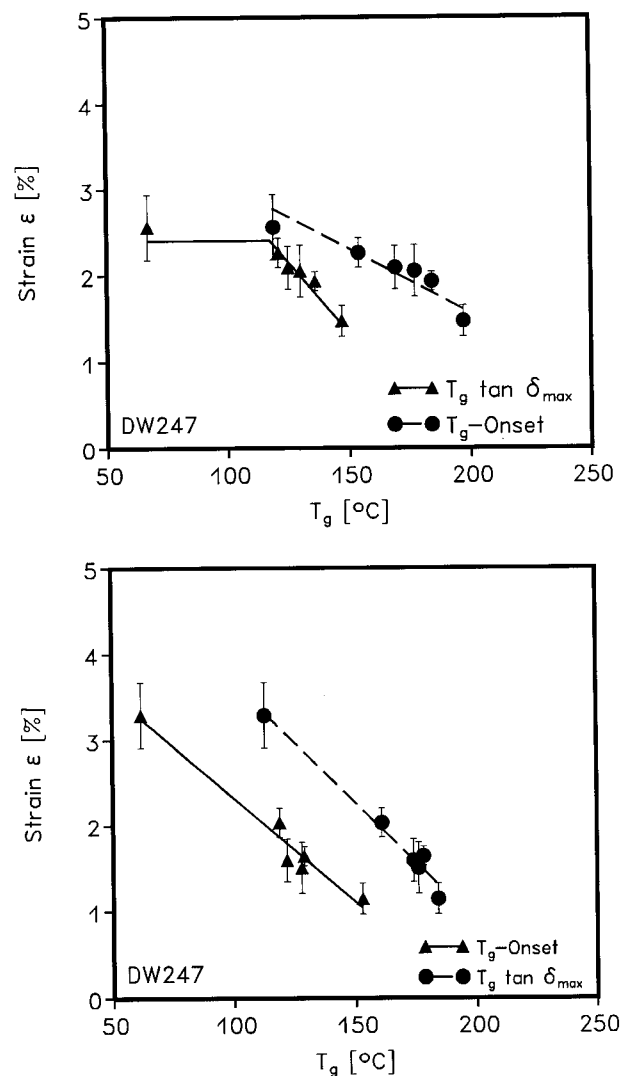By varying the postcuring times, it can be shown that independent from the microstructure

Figure 21 Progression of the fracture strain of the phenolic resin system DW 247 with a hardener concentration of 7% (top) and 17% (bottom) as a function of the onset and δ_{max} glass transition temperature measured via DMA.

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