Effect of Organic Acids on the Mechanical Properties of Phenolic Resin Composites

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ABSTRACT: The effect of salicylic acid and its derivatives on the properties of phenolic resin composites was evaluated. The composites were reinforced with aluminum oxide particles in both solid and hollow forms. Differential scanning calorimetry studies have shown that the reaction rate of phenolic resin was accelerated by salicylic acid, but was not affected by the other compounds. Salicylic acid also reduced the flexural strengths of the phenolic resin composites. The strength was decreased by more than 30% in comparison to that with no acid added. In contrast, two derivatives of this acid—sodium salicylate and 4-hydroxybenzoic acid—have minimal impact on the flexural strengths of the composites. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 642–647, 2000

Key words: salicylic acid (2-hydroxybenzoic acid); sodium salicylate; 4-hydroxybenzoic acid; phenolic resin composites; flexural strength

INTRODUCTION

Phenolic resin has been used in numerous industrial applications for many decades. The widespread usage of this resin is primarily due to its unique combination of several attributes, including high thermal resistance, excellent mechanical properties, and relatively low cost. In many cases, phenolic resin is used as the binding matrix of a composite material with various types of reinforcements and fillers. The reinforcement could be continuous fibers, discrete particulate, or honeycomb structures. Organic, inorganic, and mineral fillers, either inert or functional, are commonly added to the phenolic composite to impart a specific property, or simply to reduce cost or weight. In the past decade, there have been many published articles documenting the acceleration of phenolic resin chemistry in the presence of certain classes of compounds, such as lignocellulosic,[1–4] carboxylic acid esters,[5,6] or anhydrides.[7]

Most of these reports have focused on the chemistry and mechanistic aspects of the reactions, but rarely on the material properties.

Previously, salicylic acid (2-hydroxybenzoic acid), 4-toluenesulfonic acid, and other carboxylic acids have been reported to accelerate the crosslinking reactions of epoxy resins.[8] In this study, salicylic acid and its derivatives are selected to evaluate their effect on the reaction rate of phenolic resin in a particulate-reinforced composite material. The particulate of interest is aluminum oxide in both solid and hollow forms, with a typical average particle size of 0.1–0.5 mm. In addition, the impact of these additives on the mechanical property, mainly flexural strength, of the composites will be determined.

EXPERIMENTAL

The novolac and resole phenolic resins used in this study were commercial-grade products supplied by the Durez Division of Occidental Chemical Corporation. The novolac resin was synthesized with an acid catalyst, and had a nominal

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weight-average molecular weight of 6000 g/mol. The resole was a base catalyzed resin dissolved in furfuryl alcohol with 70% solids content and pH 8. High-purity solid and hollow aluminum oxide particles were received from Saint-Gobain Industrial Ceramics Corporation, and mineral fillers and chemicals (reagent grade) were purchased from Aldrich Chemical Company.

Composite samples of aluminum oxide, calcium metasilicate (wollastonite), organic acid or salt, and phenolic resin were mixed together in a small bowl, then pressed into $13 \times 13 \times 127$-mm sticks of the desired density (1.89 g/cc). The relative weight percentages were 90, 6, 0.5, and 4%, respectively. The molded specimens were placed in a sealed container and cured at 160°C for 24 h.

Flexural strength of the composite was determined based on the stress at maximum yield load. A three-point flexure fixture was used on Instron 4204 equipment, with $13 \times 13 \times 50.8$-mm sample size, and tested at a crosshead rate of 2.54 mm/ min under ambient conditions. For the wet strength, the samples were boiled in water for $2\frac{1}{2}$ h before they were tested. Both wet and dry samples were broken and the percent strength retention was determined.

Blends of phenolic resin and additive (salicylic acid or one of its derivatives) were analyzed by differential scanning calorimetry (DSC). The following compounds were added to the blends at 0.5 wt %: salicylic acid, sodium salicylate, or 4-hydroxybenzoic acid. Thermal history, the onset (defined here as the intersection of the baseline and the ascending line), and peak temperatures of cure exotherm were recorded with a SEIKO SSC/ 5200 differential scanning calorimeter at a scan rate of 10°C/min. Dynamic Mechanical Analysis (DMA) study was performed on the similar SEIKO system in a three-point bending mode, at 1 Hz frequency and a constant ramping rate of 10°C/min.

Fourier Transform Infrared (FTIR) spectra of the specimens were collected on a KBr window in nujol oil, using a Nicolet Magna-IR 550 Series II instrument with a DTGS detector and OMNIC 3.0 software.

RESULTS AND DISCUSSION

Differential scanning calorimetry (DSC) was used to explore the effect of salicylic acid and other additives on the curing reaction rate of phenolic resin. In this case, the reaction onset tempera-
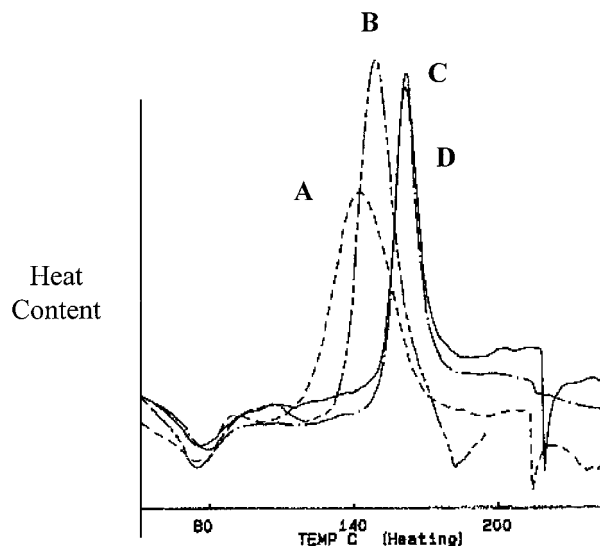

Figure 1 DSC curves of various additives. A: Salicylic Acid; B: 4-Hydroxybenzoic Acid; C: Sodium Salicylate; D: No additive.

tures of various phenolic mixtures were the major focus. Figure 1 superimposes the DSC thermograms of the salicylic acid–phenolic system with those from neat phenolic, sodium salt–phenolic, and 4-hydroxybenzoic acid–phenolic resins. These curves showed that the addition of salicylic acid resulted in a low reaction onset temperature of 130°C, which was 10–20°C below those of the other systems. This early onset with salicylic acid indicated that the phenolic polymerization reactions were close to completion before the entire composite even had a chance to reach the final cure temperature of 160°C. Consequently, the resin in the salicylic acid–phenolic system would gel and solidify prematurely before it had an opportunity to fully wet the surfaces of aluminum oxide and other fillers.

To determine the mechanical properties of phenolic composites, a three-point bending test was utilized in this study. In particular, the flexural or bending strength was of primary interest. Although it has been argued that this test may not generate the "true" strength values, it nevertheless, was a very valuable tool for comparing the strengths of various systems. The effect of different acid or salt on the dry and wet flexural strengths of the composites is graphically shown in Figure 2. The results are also tabulated in Table I. The general trend was that the strengths were lower with additives, but the reductions differed, depending on the additive type. When salicylic acid was added to the formula, the strengths
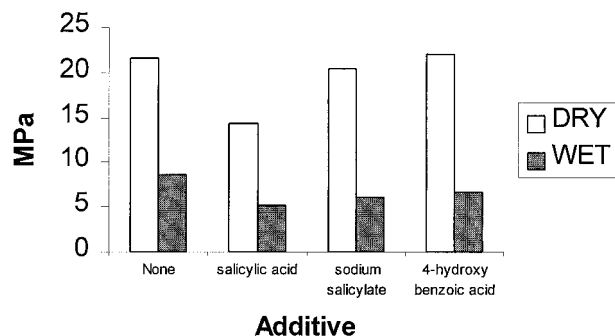
Figure 2 Dry and wet flexural strength vs. additives.

decreased substantially. The dry strength suffered a 33% reduction, while the wet strength registered a 40% reduction, all in comparison to those with no additive. However, when 4-hydroxybenzoic acid or sodium salicylate was used in place of salicylic acid, there was practically no change in the dry strength, and the reduction in wet strength was less (around 25%).

The large strength reduction with salicylic acid is undesirable because it would dramatically limit the use of phenolic composites in humid or wet conditions. One possible reason for this loss of strength could be a lower crosslinking density in the salicylic acid–phenolic system. Therefore, a DMA study was used to measure the glass transition temperatures of two composites—one with the acid, and the other only neat resin. Based on the peak temperatures of the tanδ curves displayed in Figure 3, both systems had T_g values of around 230°C. Despite the fact that the shape of the curve for the salicylic acid–phenolic system was not identical to that of the neat phenolic, the difference was not sufficient to justify for the large reduction in strength. Instead, it suggested the presence of a loose crosslinked network system that affected the cohesive strength of the resin.[9]

The aluminum oxide particulate used in this study was of high purity, with greater than 99% oxide. It contained, nevertheless, typically 0.2 wt % of sodium oxide (Na_2O) as an impurity. In the presence of moisture, sodium oxide on the particulate surfaces could change into sodium hydroxide, and the surfaces would become mildly alkaline. For a phenolic composite, water was readily available, starting around 80°C, as a byproduct of the condensation reactions at the early stage of polymerization. Therefore, it was reasonable to expect that sodium hydroxide would readily form on the surfaces. The FTIR technique was subsequently employed to evaluate whether the sodium hydroxide would react with an acid, when present. The FTIR spectrum of salicylic acid in nujol oil, shown in Figure 4, possesses the characteristic absorption bands of an aromatic carboxylic acid with a hydroxyl group attached to the phenyl ring (in the 1000 to 2000 cm^{-1} range only). The top part of Figure 5 displays an FTIR spectrum of salicylic acid after it was exposed to sodium oxide. The FTIR spectrum of pure sodium salicylate is included in the bottom half of the same figure for comparison purposes. In the top graph, the relative intensity of the peak at 1660 cm^{-1} has decreased substantially (from that in Fig. 4), and two new strong peaks at 1530 and 1380 cm^{-1} have appeared. The former peak corresponds to the asymmetrical carbonyl stretching absorption of salicylic acid, and the latter two are the respective asymmetrical and symmetrical stretching bands of salicylate anion. These changes indicated that much of the salicylic acid has been transformed into a salt-type entity similar to sodium salicylate. It was also reasonable to expect that this newly formed salicylate anion would reside around the particulate surfaces because of the strong ionic interactions with its counter sodium cation.

Table I Strength Data of Various Systems

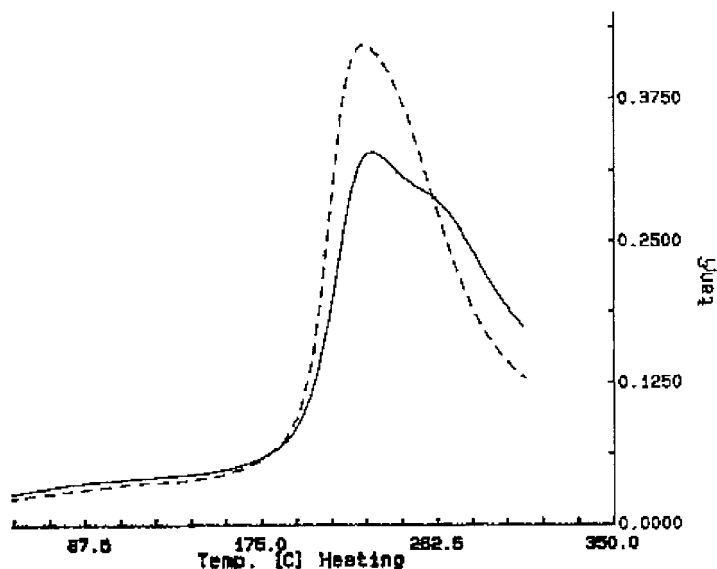| Additive	Dry Flexural Strength MPa ± 8%	% Reduction[a]	Wet Flexural Strength MPa ± 6%	% Reduction[a]
None	21.6	—	8.6	—
Salicylic acid	14.4	33	5.2	40
Sodium salicylate	20.4	5.5	6.1	29
4-Hydroxybenzoic acid	22.0	1.8	6.6	23

[a] Relative to no additive.

Figure 3 DMA tanδ curves of neat phenolic (solid line) and salicylic acid–phenolic (dash line) systems.

Chemical structures of salicylic acid, 4-hydroxybenzoic acid, and sodium salicylate are displayed in Scheme 1. In salicylic acid or sodium salicylate, the hydroxyl group is adjacent to the acid group; while in 4-hydroxybenzoic acid, the relative positions of these two groups are farther apart, on the opposite end of the phenyl ring. Because the aluminum oxide surfaces in the discontinuous phase of the phenolic composites were alkaline, either acid could bind to them via the carboxylate groups, leaving the hydroxyl groups unbound. Sodium salicylate was a salt, and therefore, was not affected by the alkalinity. This molecules, therefore, would not have interacted strongly with the surfaces or have any preferred orientation. For 4-hydroxybenzoic acid, the polar hydroxyl groups would stay "outward," rendering the oxide surfaces polar or hydrophilic. However, the scenario for salicylic acid was quite different. Both polar groups, the hydroxyl and carboxylate, would orient inward toward the surfaces of aluminum oxide. The nonpolar phenyl rings, in turn,
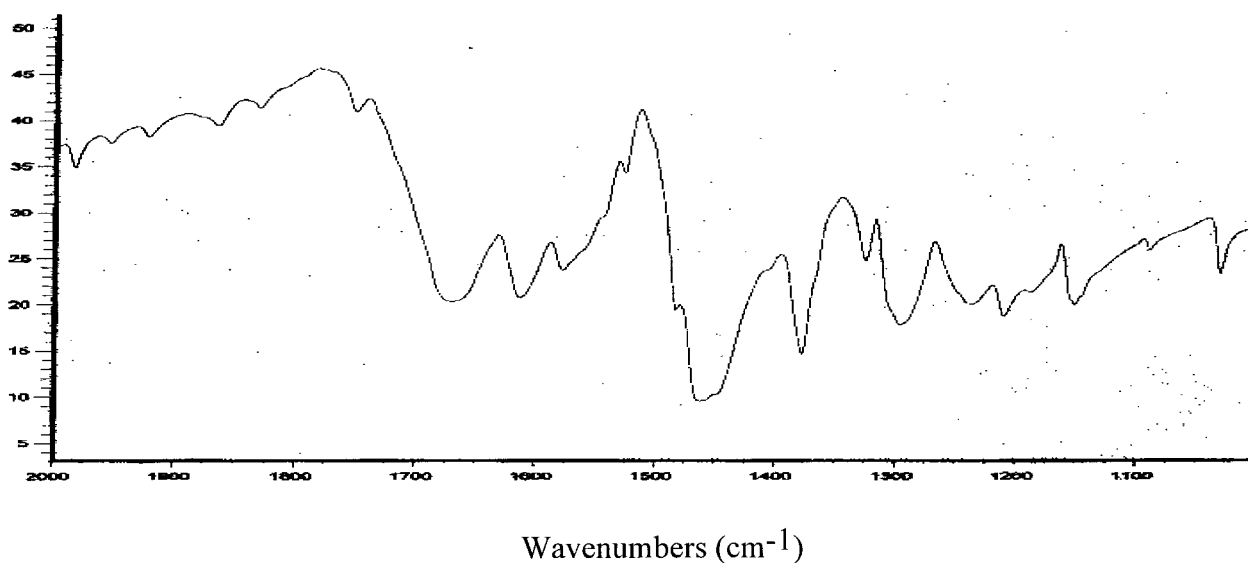

Wavenumbers (cm^{-1})

Figure 4 FTIR spectrum of salicylic acid (from 1000 to 2000 cm^{-1}).
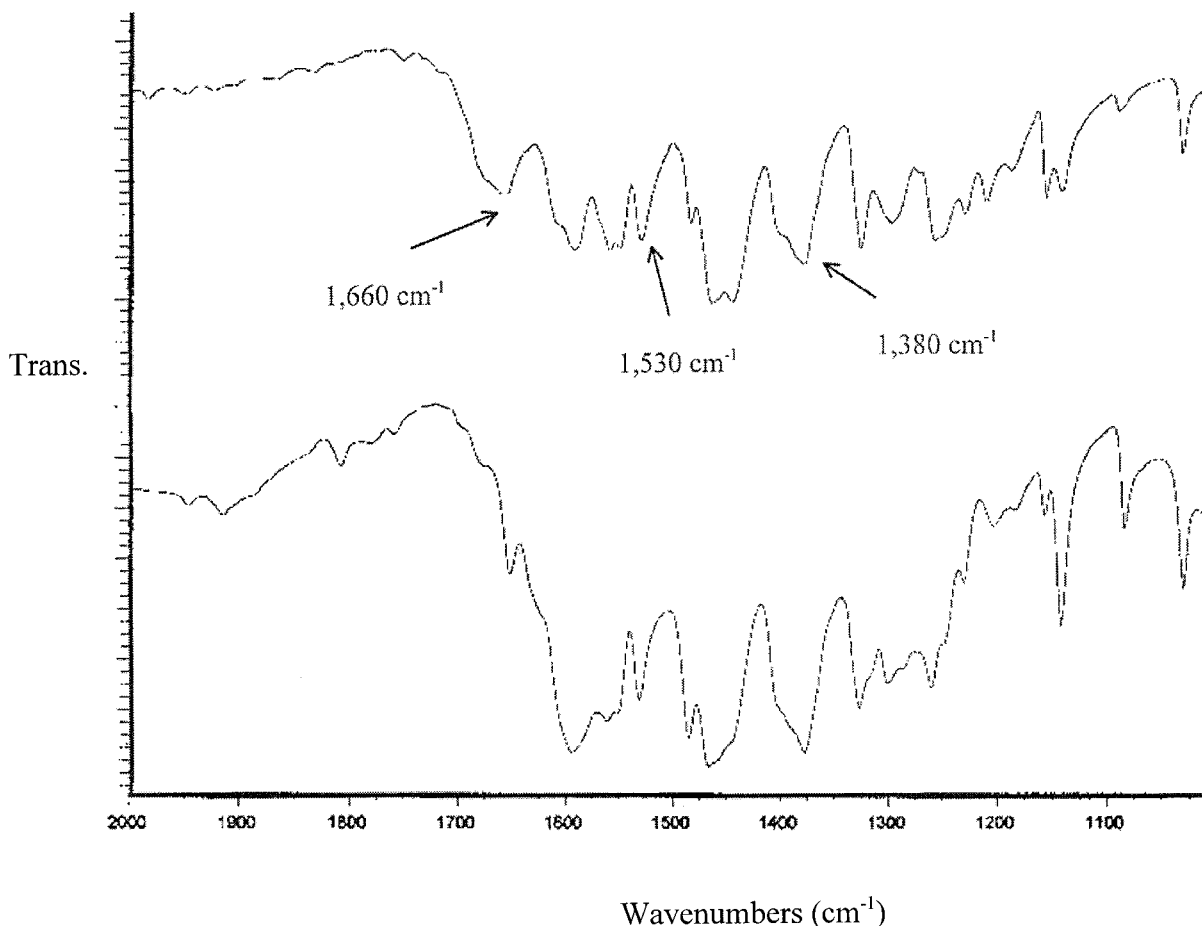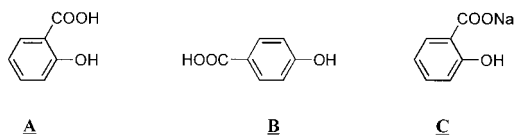
Figure 5 FTIR spectra of salicylic acid–Na₂O (top curve) and sodium salicylate (bottom curve).

became the *de facto* outer layers residing on the surfaces. This orientation becomes even more predominant because of the strong ionic interaction of the acid with the oxide surfaces, as demonstrated by the FTIR results in the previous paragraph. These nonpolar hydrophobic groups, in conjunction with the rapid gelation of phenolic resin alluded to earlier, hindered the resin from properly and completely wetting the particulate oxide surfaces. Con-

Scheme 1 : Chemical Structures of the Acids and Salt

A : Salicylic Acid ; B : 4-Hydroxybenzoic Acid ; C : Sodium Salicylate

Scheme 1 Chemical structures of the acids and salt.

sequently, the phenolic composite had a weak interface, which would lead to lower adhesive strengths.

CONCLUSION

In conclusion, we have demonstrated that for phenolic resin composites, salicylic acid at a concentration as low as 0.5% by weight can accelerate the phenolic polymerization reactions by initiating the gelling process early. In addition, the transformation from an acid to a salt on the surfaces of oxide particles has a significant ramification on the mechanical strength of the composite. Flexural strengths of the composites are decreased by more than 30% in comparison to those with no acid added. The major causes were the combined effect of chemical reactivity and molecular configuration. In addition to the lower cohesion strength of the phenolic resin as a consequence of a nonacidic pH, the reduction is attributed to an

incomplete wetting of phenolic resin on the particulate surfaces that have been rendered hydrophobic by salicylic acid. On the contrary, two derivatives of this acid, sodium salicylate and 4-hydroxybenzoic acid, have minimal impact on both the reaction rate and flexural strength of the composites.

REFERENCES

1. Simitzis, J.; Karagiannis, K.; Zoumpoulakis, L. Polym Int 1995, 38, 183.
2. Borman, S. Chem Eng News 1990, 10 September, 19.
3. Muller, P. C.; Kelley, S. S.; Glasser, W. G. J Adhesion 1984, 17, 185.
4. Pizzi, A.; Mtsweni, B.; Parsons, W. J Appl Polym Sci 1994, 52, 1847.
5. Pizzi, A.; Garcia, R.; Wang, S. J Appl Polym Sci 1997, 66, 255.
6. Tohmura, S.; Higuchi, M. Mokuzai Gakkaishi 1995, 41, 1109.
7. Pizzi, A.; Stephanou, A. J Appl Polym Sci 1994, 51, 1351.
8. Partansky, A. M. Epoxy Resins; Lee, H., Ed.; Adv Chem Series 92; American Chemical Series: Washington, DC, 1970, pp. 29–47.
9. Pizzi, A.; Lu, X.; Garcia, R. J Appl Polym Sci 1999, 71, 915.