

Effects of Physical Confinement (< 125 nm) on the Curing Behavior of Phenolic Resin

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ABSTRACT: How the physical confinement of phenolic resin in nano porous silica ($8 \text{ nm} \leq \text{pore diameter } (D_p) \leq 125 \text{ nm}$) affected the polymer's curing behavior was examined by conducting differential scanning calorimetry experiments at $320 \text{ K} \leq T \leq 500 \text{ K}$. Our results suggested that upon incorporating the phenolic resin into the silica, its curing temperature was lowered. However, what was interesting was that there was an inverse linear dependence between

the pore size and the curing temperature, i.e., the smaller the pore diameter the higher the curing temperature. There was evidence that phenolic resin was unable to penetrate into 8 nm-sized pores. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 3183–3186, 2006

Key words: nanolayers; thermosets; thermal properties; differential scanning calorimetry (DSC); voids

INTRODUCTION

It is argued that one of the advantages of nanocomposites over conventional composites is that the overall mechanical properties can be better tailored.^{1–4} Various fillers are incorporated into neat resin in an effort to control the tensile strength, modulus, and heat distortion temperature, etc., of the composite. The motivation of adding fillers is not only driven by a desire for a technically-superior product but also by the economics of the manufactured product. Recently, it has been reported that the addition of ceramic nanoparticles into thermoset polymer improved the yield stress values of the composites as well as the modulus of the material.^{3,4} Micron-sized ceramic particle filled composites generally show a decrease in strength.^{3–5} Moreover, the toughness of the composite rapidly decreases with the increasing micron-sized particle content. Therefore, intense research is underway to develop new nanoparticle filled composites, and also to understand the complex interactions between the polymer and large surface area nano ceramic particles.

In the development of nanocomposites, different techniques are being explored, e.g., sol–gel technique, exfoliating clay particles and their subsequent dispersion in polymer, and the dispersion of preformed nano particles in polymer. Along the same line, controlled polymerization can lead to the development of self healing materials.^{6,7} If nano-sized porous ceramic

particles are dispersed in polymer, then there is a potential to form self-healing nanocomposite materials. Because it is known that geometrical confinement of fluid substantially modifies its dynamic and thermodynamic properties,⁷ it will be important to investigate how the confinement of polymer in controlled nano-sized porous ceramics modifies its curing behavior. It has been reported that the melting, freezing, evaporation, and glass transition of fluids confined in nano channels are different from their corresponding bulk values.^{8–10} In this communication, we report for the first time that geometrical confinement in porous silica ($7.9 \text{ nm} < \text{pore diameter } (D_p) < 125 \text{ nm}$) of a commercial phenolic polymer modifies its curing behavior. This effect can modify the conditions under which nanocomposites are formulated using thermoset polymers, which are physically restricted in nano-channels.

EXPERIMENTAL

Porous silica was obtained from Phase Separation Inc., and powder phenolic (GP 5548) resin was received as a gift from Georgia Pacific. More details on the porous silica samples used in the present study can be found elsewhere.^{8,9} The particle size along with the surface area of the porous silica samples are listed in Table I. To study the curing behavior of the polymer physically confined in nano-sized pores, the resin was first dissolved in methanol in a 1 : 1 ratio. The solution was divided and transferred into six separate vials. To five of these vials, we added different pore size silica particles. All six vials were transferred to a vacuum chamber and were evacuated at 32 kPa for 30 min. A few

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TABLE I
Physical Characteristics of Porous Silica Used and the Observed Curing Behavior of Phenolic Resin Confined in These Pores

Pore diameter [D_p] (nm)	Particle size range (μm)	Surface area (m^2/g)	Peak temperature (K)	ΔH (J/g)
8	75–150	400	413	–29
15	106–125	200	416	–35
30	106–125	100	411	–60
60	106–125	50	409	–59
125	75–150	25	405	–47
As-received Phenolic resin			422	–87
Phenolic resin dissolved in methanol			404	–27

minutes after suction had started, the silica particles began to sink. Bubbles could be observed under an optical microscope as the polymer solution displaced the air from the pores. Figure 1 shows the captured digital image of these bubbles. It is worthwhile to mention that we did not observe similar bubbles when spherical, but nonporous, fly ash particles were added to the polymer solution. In an effort to further remove air from the pores and the methanol, the vials were transferred to a vacuum desiccator chamber. The phenolic impregnated silica samples were aged for 24 h before undertaking thermal measurements.

The curing behavior of the phenolic polymer was monitored with the help of a differential scanning calorimeter (DSC), i.e., Perkin–Elmer DSC 7 system. The samples were loaded in preweighed aluminum pans and sealed. To avoid pressure buildup within the pans, a hole was drilled into the lid. The DSC measurements were conducted in two steps: (a) The samples were first heated under N_2 gas from 323 K to 383 K, at a rate of 20 K/min. The samples were held at 383 K for 5 min to ensure the removal of methanol. The

samples were then cooled to 323 K and reweighed. (b) After the initial thermal treatment to remove methanol from the polymer solution, the samples were scanned from 323 K to 493 K, at a heating rate of 5 K/min.

RESULTS AND DISCUSSION

In the first set of DSC scans where we heated the samples to 383 K, we did not observe any reaction, neither endothermic nor exothermic. We expected to see the evaporation of methanol at this stage. Our earlier investigation on the evaporation of cyclohexanone, physically confined in porous silica, showed that the evaporation shifted to higher temperature relative to its bulk value when fluid was confined in pores with $D_p < 60$ nm.^{8,9} Similar observations have been reported for water's evaporation from silica gels.¹⁰ One possible explanation for a lack of an endothermic peak during the first DSC runs could be that methanol gradually evaporated as the sample's temperature was raised above 323 K.

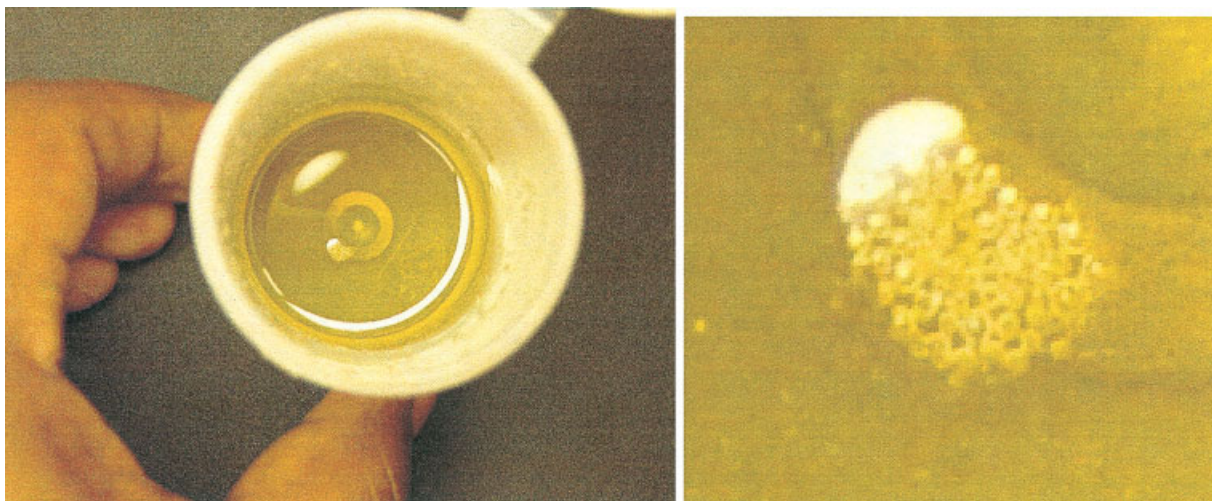


Figure 1 This picture shows that air was displaced from the pores (see the bubble formation on the right) by the phenolic–methanol solution when porous silica was added to the solution. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

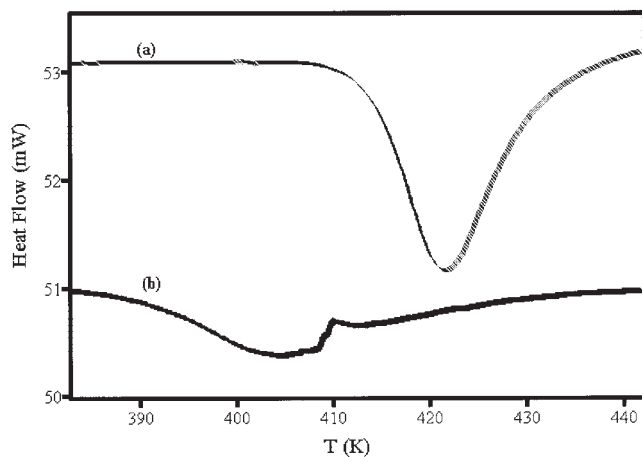


Figure 2 This figure depicts the curing behavior of (a) as-received phenolic polymer and (b) phenolic dissolved in methanol. The DSC curves were obtained under nitrogen gas at a heating rate of 5 K/min.

Figure 2 reproduces the observed DSC curves for as-received phenolic resin and resin dissolved in methanol. As expected, the as-received phenolic resin showed a strong exothermic peak because of condensation and curing reaction at 422 K.¹¹ Besides suppressed curing reaction at 405 K, the methanol dissolved phenolic showed a superimposed exothermic peak and a sharp endothermic peak. Because this sample had already been subjected to first DSC run in which it was held at 383 K for 5 min, the presence of a sharp endothermic peak did suggest that some of the methanol was perhaps trapped within the resin.

It is interesting to note that on dissolving the phenolic resin in methanol and then subsequently drying it at 383 K, not only was the polymer's curing temperature affected but also the enthalpy (see Table I). It could be argued that the observed reduced ΔH value for methanol dissolved phenolic resin was due to some methanol still being present in the polymer when the sample was dried at 383 K, thus, contributing to the weight of the sample when measured after drying at 383 K. The other possible explanation can be that solvent resulted in a larger spatial distribution of monomers, thus, hindering the condensation reaction. We believe that both these mechanisms might have contributed to the observed reduced enthalpy for the methanol dissolved phenolic resin because higher enthalpies were observed when the same solution was confined in porous silica.

Figure 3 depicts how the exothermic curing reaction of phenolic resin changed when it was confined in porous silica. The observed peak temperatures of the exothermic reaction along with their observed enthalpy (ΔH) are listed in Table I. Even though efforts were made to have the same amount of phenolic resin in each sample relative to silica, it was difficult to

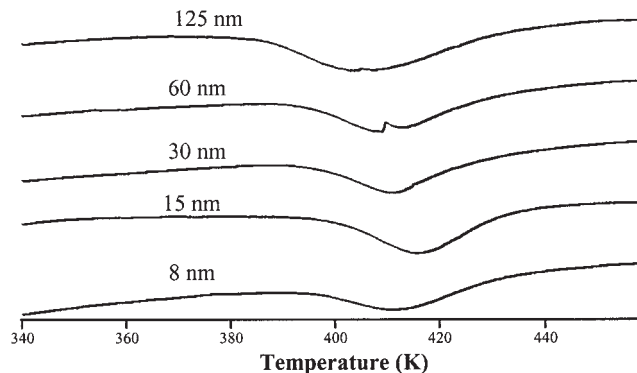


Figure 3 This figure shows the observed exothermic reaction of phenolic resin when it was confined in porous silica of various diameters. The y-scale is heat flow in mW. The observed ΔH values are listed in Table I.

ascertain the exact weight of the polymer in the sample. Therefore, the ΔH values listed in Table I may or may not reflect whether physical confinement affected the enthalpy of the curing reaction. Figure 4 graphs the dependence of the curing temperature as a function of pore diameter. It should be noticed that as the pore size decreased the peak temperature of the curing reaction shifted upward, except for the 8 nm-sized porous silica. The curing reaction was much weaker for phenolic resin confined in 8 nm-sized porous silica, and the peak temperature for the reaction was between the one observed for 15 and 30 nm-sized porous silica. For 125 nm-sized porous silica, the peak tem-

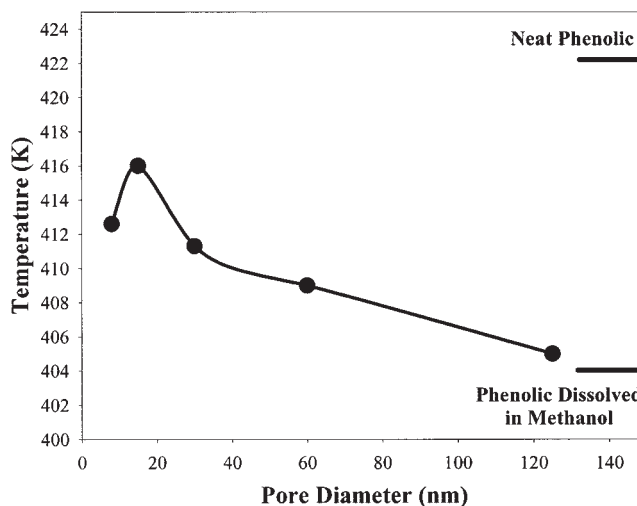


Figure 4 This graph shows how the curing reaction temperature was affected when the phenolic resin was confined in porous silica. The solid horizontal line signifies the curing temperature of neat phenolic resin, while the dashed horizontal line indicates the curing temperature of phenolic when it was dissolved in methanol. The maximum error in the curing temperature of geometrically confined phenolic was ± 2 K.

perature was lower than that observed for phenolic resin, which was not physically confined.

It has been reported that inorganic additives have catalytic effects on the polymers,^{12,13} resulting in lowering the curing reaction temperature. Because on physically confining phenolic-methanol solution in 125 nm sized pores, we did not observe any experimentally significant shift in curing temperature, it is unlikely that porous silica manifests any catalytic effects. If it is argued that the curing reaction of phenolic resin was modified by 125 nm-sized porous silica particles, then it is difficult to explain the observed upward shift in temperature for other pore sizes. Moreover, the particle size for 15, 30, and 60 nm-sized porous silica was the same. Though the total surface area increased as the pore diameter decreased, one would have expected a shift to lower temperatures if the effect was purely catalytic in nature. We believe that the variation in curing temperature observed as a function of pore size was due to the physical confinement at nano scale effect of the polymer.

The driving force during the curing reaction is the change in Gibbs' free energy, ΔG , i.e.,

$$\Delta G = \Delta H - T\Delta S \quad (1)$$

where T is the temperature, ΔH is the enthalpy associated with the reaction, and ΔS is the entropy of the reaction. The contribution for the entropy comes from two parts, i.e., from the rotational degree of freedom, ΔS_{rot} , and the translational degree of freedom, ΔS_{tran} . Therefore, eq. (1) can be written as,

$$\Delta G = \Delta H - T(\Delta S_{\text{rot}} + \Delta S_{\text{tran}}) \quad (2)$$

As the phenolic resin is physically restricted in porous silica, some of the degrees of the freedom are lost. Therefore, the temperature must be raised to compensate for the loss of degrees of freedom. This should shift the curing temperature higher for phenolic resin that was physically restricted in porous silica. As the pore size decreased, more and more degrees of freedom of the polymer would be lost, forcing the curing to occur at higher temperatures. An inverse relation was observed between the curing temperature and pore diameter. However, the observed curing temperature for 8 nm-sized porous silica did not fit this trend. It is possible that large molecules, like phenolic resin, could not fill the 8 nm-sized pores because of higher

radius of curvature. Even if some phenolic resin penetrated the pores, these large molecules may be pinned in place, thus, not capable of crosslinking. It has been reported that silver nitrate failed to fill 4 nm-sized porous carbon nanotubes.¹⁴ The 8 nm-sized porous silica samples used in the present study had a distribution in pore sizes, with the dominant contribution coming from 8 nm pores. Therefore, the weak curing reaction observed for 8 nm-sized porous silica came from those phenolic resin molecules that were confined in pores larger than 8 nm.

CONCLUSIONS

From DSC experiments on phenolic resin geometrically confined in nano scales pores of size $8 \text{ nm} \leq \text{pore diameter} \leq 125 \text{ nm}$, it is suggested that the curing reaction temperature is modified. There appears to be an inverse relationship between pore diameter and curing temperature though this relationship may not be linear. This could have a bearing on the formulation of polymer nanocomposites where geometrical confinement of the polymer is a possibility.

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