Influence of Fillers on the Properties of a Phenolic Resin Cured in Acidic Medium

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ABSTRACT: The curing behavior of a phenolic resol resin in the presence of *p*-toluensulphonic acid is reported herein. The gel time of different systems has been determined by thermal scanning rheometry. Thermal and mechanical properties of the resin have been modified by the addition of varying amounts of fillers, talc, and kaolin. dynamic mechanical thermal analysis is used to determine the mechanical properties of the systems and the influence of the fillers and the post-curing. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 108: 387–392, 2008

Key words: phenolic resin; filler; gel time; glass transition; curing

INTRODUCTION

Phenolic resins belong to the broad group of the thermosetting resins and were the first technical plastics in history around 125 years ago. They are still used now a days in several applications and form the basis for a large number of materials of outstanding economical and technical importance. The demand for composite materials, combining resins with fillers and fibers, has raised an enormous interest in this type of compounds in recent years[1].

Among other properties, phenolic resins exhibit good resistance to solvents, excellent insulation capability, and good resistance to fire which, apart from being easily processable,[2] make them suitable for a wide variety of applications, such as foundry, laminates, abrasives, molding compounds, adhesives, or wood materials. In fact, phenolics are superior to all other resin systems with respect to their particularly good thermal behavior, their high level of flame resistance, low smoke density, and their use as carbon donor in pyrolitic applications.[3,4]

These properties are inherent to phenolic resins and are related to their structure[5] and their thermal degradation mechanism[6,7] which represent an addi-

tional advantage, as the use of flame retardants to improve the fire resistance of composites usually increase the release of smoke and toxic gases. The good flame-retardant properties of phenolics is used in composites intended for aircraft construction or shipbuilding industry.

After the curing process, phenolic resins are highly crosslinked materials[8,9] with good mechanical properties[10,11] (modulus and creep resistance) even at elevated temperatures. Because of the high crosslinking density after curing, phenolic resins also turn out to be relatively brittle polymers.[12] Therefore, the processing of phenolic materials requires temperature control to reduce the number of defects in the final components. The mechanical properties of phenolic resins may be improved by the addition of a rubbery phase or by blending with other polymers.[13–17] On the other hand, this handicap can be reduced by the addition of several fillers and their effect on the properties of the resin is important to develop composite materials based on phenolic resins.

Although composite materials primarily comprises a resin system plus a fibrous reinforcement, other components are frequently added to produce decorative effects, aid handling, improve molding characteristics and cured properties. These materials include fillers, pigments, thixotropic additives, and fire retardant additives.

Fillers are used to modify the properties of resin systems either during processing or in the cured state or perhaps both. Often the primary reason for adding a filler is to reduce the cost of the system;

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however, invariably, other properties are modified as well. To maximize the benefits of using a filler, it must be chosen with care, taking into account the curing process and the final use of the composite. The main factors to be considered for filler selection are cost, density, resin absorption by the filler, filler loading and particle size distribution. Additional factors which need to be taken into account are the effect of the filler on the liquid and cured systems. So, almost any powdered material may be used as filler; however, the most common fillers are those obtained from natural deposits such as chalk, slate, quartz, or clays.

The aim of this study is the curing behavior of a phenolic resol and the final properties of the cured resin when an acid is added to carry out polymerization and talc or kaolin are employed as fillers. Talc consists of hydrated magnesium silicate. When used as a filler in thermosetting resin systems it improves their electrical insulation, heat, and moisture resistance. Moreover, talc filled systems exhibit good processability. The basic composition of kaolin is an aluminium silicate with traces of other metal atoms present. Normally the kaolins used as fillers are fine white powders, and can act as flow control agents and to improve electrical properties.

EXPERIMENTAL

Materials

The resin used was a commercial liquid resol resin (pH = 9.1) supplied by Fers Resins (Barcelona, Spain) as TH-215 and containing 3 wt % of free phenol and 13 wt % of water. The phenolic resin was stored at 4°C under nitrogen to avoid water condensation. As catalyst p-toluensulphonic acid was used in aqueous solution. The p-toluensulphonic acid monohydrate was purchased from Merck and the solution was prepared prior to use. Potentiometric acidimetry was used to determine the molarity of this solution (3.7M).

Talc ($Mg_3Si_4O_{10}(OH)_2$) and kaolin ($Al_2Si_2O_5(OH)_4$) were used as fillers and were supplied by Lorda and Roig, S.A. (Barcelona, Spain).

Rheological measurements

The rheological measurements were carried out by thermal scanning rheometry (TSR) using a Rheometric Scientific TSR (Epsom, Surrey, UK). All the measurements were performed at a constant oscillation frequency of 2 Hz. The rheological parameters, i.e., storage modulus (G'), loss modulus (G'') and loss tangent (tan δ) were measured and recorded every 10 s during the curing process.[18,19]

TABLE I
Preparation of Samples for DMTA

T (°C)	Catalyst (wt %)	Filler (wt %)
80	12, 13, 14, 15, 16	0
80	14	5, 10, 15, 20, 25, 30
	16	5, 10, 15, 20, 25, 30

Dynamic mechanical thermal analysis

Samples for DMTA measurements were prepared by mixing the components (resol resin, acid catalyst, and filler) in different proportions as shown in Table I. The mixture was then molded into a bar shaped sample of dimensions 10 × 35 × 2 mm and compressed at 80°C under a pressure of 250 kg/cm^2 for 2 h.[20] After curing, the samples were stored in the freezer to avoid further polymerization.

Some of the samples were postcured in an oven at 80°C for 7 days to determine the effect of postcuring.

DMTA measurements were carried out on a Polymer Laboratories Model Mk II equipment, from −100 to 280°C at a heating rate of 2°C/min and frequencies of 1, 3, and 10 Hz.[20–22] All the experiments were performed in the bending mode and dual cantilever geometry with a displacement of 64 μm (strain level 4×).

RESULTS AND DISCUSSION

The isothermal curing of phenolic resins results in a polymer network structure. Two stages, which are divided by the gel point, are distinguished in the process. The gel time (t_g) is commonly used to characterize the gel point and is a very important parameter from the point of view of the resin processability since after the gel point is reached the resin is no longer able to be molded.

The curing process can be monitored by means of the TSR technique through the change in the rheological parameters as the curing reaction takes place. The determination of the t_g can be carried out according to several criteria.[23–26] The criterion of the tangent line to G' curve was selected as the most representative and was used in this study. The t_g is measured at the crossover between the base line ($G' = 0$) and the tangent drawn at G' when G' reached a value close to 100 kPa.

Table II shows the t_g values obtained for the curing process of the pure resin, under isothermal conditions at several temperatures, with different amounts of catalyst. As expected, the magnitude of the t_g decreases as the catalyst weight percent is increased at a fixed temperature because of the increasing number of functional groups capable of reacting. It can be noted as well the great effect of

TABLE II
TSR Measurements Without Filler and
Calculated Gel Times (t_g)

T (°C)	Catalyst (wt %)	t_g (min)
40	12	360
	13	157
	14	102
	15	69.6
	16	61.1
50	12	109
	13	43.3
	14	33.2
	15	31.3
	16	26.8
60	12	32.5
	13	17.1
	14	14.5
	15	9.00
	16	8.15
70	12	9.75
	13	7.00
	14	4.90
	15	4.26
	16	3.43
80	12	4.94
	13	4.00
	14	3.33
	15	2.90
	16	2.12

the temperature on the gel time for a fixed wt % of catalyst which reflects the larger mobility of the active chains at higher temperatures, leading to a faster curing reaction.

Table III shows the gel time values obtained in the presence of different amounts of kaolin, at 80°C and 14 wt % of catalyst. This temperature was chosen because the gel times obtained for any catalyst wt % are fast enough for an efficient cure of the phenolic resin without thermal cure taking place. The values of the gel times are higher than without filler and, as it can be observed, there is an increase in the gel time up to 10 wt % kaolin after that the values tend to be constant. The use of talc as filler (in the same proportions as for kaolin) gives rise to curing reac-

TABLE III
TSR Measurements with Kaolin at 80°C and
Calculated Gel Times (t_g)

Kaolin (wt %)	t_g (min)
0	3.33
5	10.9
10	14.2
15	12.8
20	11.7
25	10.4
30	10.5

tions slower than kaolin and the values of the gel times reached several hours.

This behavior can be explained because the polymerization process of the phenolic resins is acid controlled and changes in pH affect kinetics; the fillers used are slightly soluble in acidic medium, so an interaction is established with the catalyst which is partially neutralized.

Thermomechanical properties of phenolic resins are closely related to the high crosslinking density reached after curing.[27] Plots of the storage modulus (E') and tan δ versus temperature (T) are shown in Figure 1 for the resol resin cured with a 14 wt % of acid catalyst in absence of filler. The value of E' decreases quickly right from the start of the experiment indicating a low quality of the crosslinked network, that is to say, a low degree of curing during molding. This fall is sharper between –100 and 0°C. At the same time there is a maximum in tan δ at −30°C; both the decrease in E' and the maximum in tan δ indicate a transition in the resin, which is related to β transition. Then, there is a slow decrease in the modulus until ∼ 120°C; after that the progress of the curing reaction at higher temperature causes an increase in the modulus[28] being observed several peaks in tan δ, corresponding to α transitions (T_g).

This behavior can be explained considering that the extent of the initial crosslinking reaction is low[29,30] and the material has its own glass transition temperature (T_{g1}). When running the sample in DMTA, the glass transition region is reached, thermal energy provides enough molecular mobility so that the chemical reaction can continue, leading to an increase in the crosslinking degree and therefore in T_g. Then, the material shows several maxima in tan δ, depending on the growing rate of T_g with respect to the heating rate in DMTA experiment.[31] From the last maximum[32] ($T_{g\infty}$), it is possible to determine the glass transition temperature of the
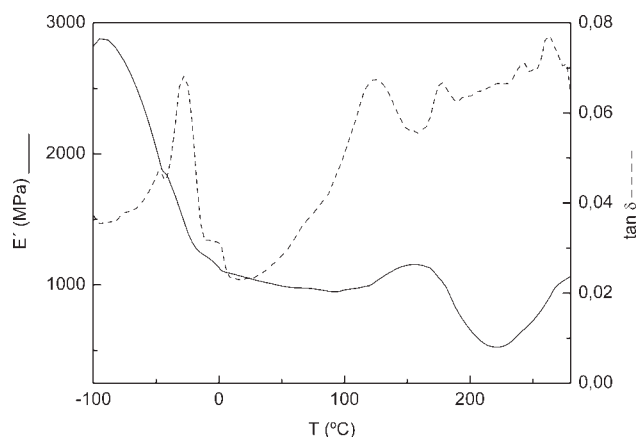

Figure 1 E' and tan δ in absence of filler (14 wt % catalyst).

TABLE IV
T_g Values (°C) for Samples Cured Without Filler (3 Hz)

Catalyst (wt %)	Tg_1	Tg_2	Tg_∞
12	119.3	194.1	258.1
13	121.5	204.6	263.0
14	121.9	177.0	261.8
15	106.7	159.5	234.9
16	124.6	197.3	262.5

fully cured material. Table IV shows the T_g values obtained for samples cured without filler.

Influence of fillers

Figures 2 and 3 show the variation of E' and tan δ during DMTA measurements of samples with the same content in acid (14 catalyst wt %) and 10 wt % of talc and kaolin, respectively. The behavior is basically the same as with nonfilled samples, with a fast initial decrease in the modulus, and several maxima in tan δ (α and β transitions). The main difference with respect to nonfilled samples is the magnitude of E' indicating that the mechanical response of phenolic resins are improved with the addition of both fillers.

The influence of the amount of filler (kaolin) can be observed in Figures 4 and 5. Although the behavior during the experiment is similar, samples containing a greater amount of kaolin show a larger modulus at high temperatures, indicating that an increase in the filler content improves the mechanical response of the material, because of the intrinsic hardness brought by the filler. Moreover, tan δ plot shows several maxima, corresponding to β and α transitions, their position changing slightly depending on the filler amount as shown in Figure 5. Table V shows the $T_{g\infty}$ values for all samples cured using
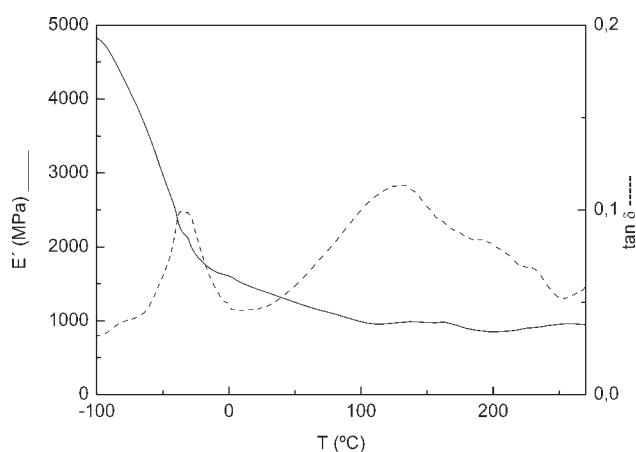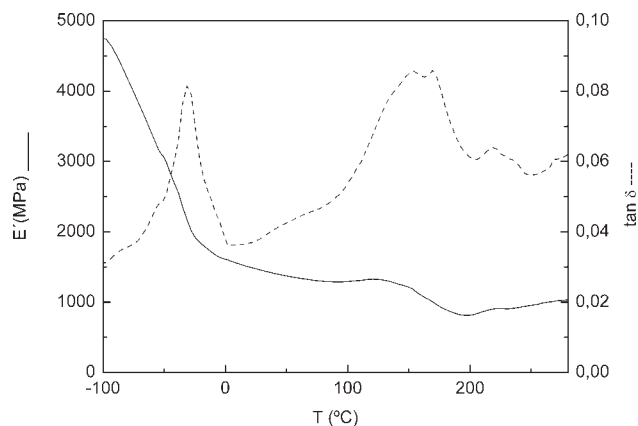

Figure 3 E' and tan δ for a kaolin (10 wt %) filled sample (14 catalyst wt %).

both fillers. As it can be seen, the values for the filled samples are lower than for the neat samples indicating a lower crosslinking density, the lowest values being obtained when talc is used as filler. This behavior can be explained, as already has been mentioned, because the polymerization process of the phenolic resins is acid controlled. As indicated earlier, the catalyst is partially neutralized by the filler which gives rise to changes in pH and so in the crosslinking density.

The final value of E' is different for each sample indicating that the crosslinking density, and so the structure of the material, are different depending on the amount of filler.

Influence of postcuring

Figures 6 and 7 show the variation in the E' modulus and tan δ, respectively, after a period of poscur-

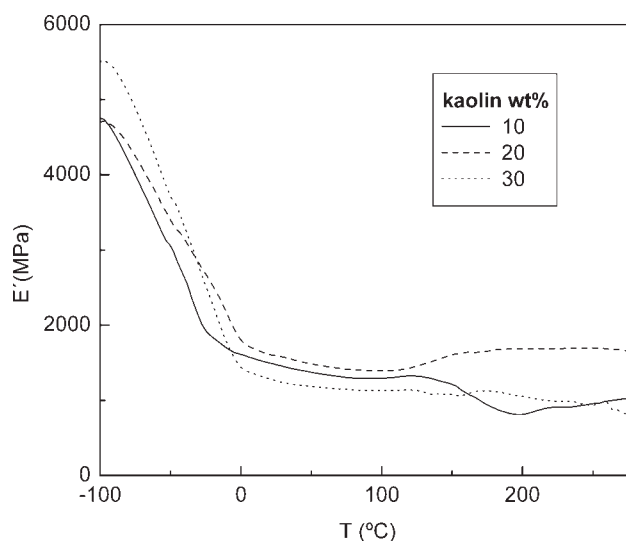**Figure 2** E' and tan δ for a talc (10 wt %) filled sample (14 wt % catalyst).

Figure 4 E' versus temperature for samples containing different kaolin wt % (14 wt % catalyst).
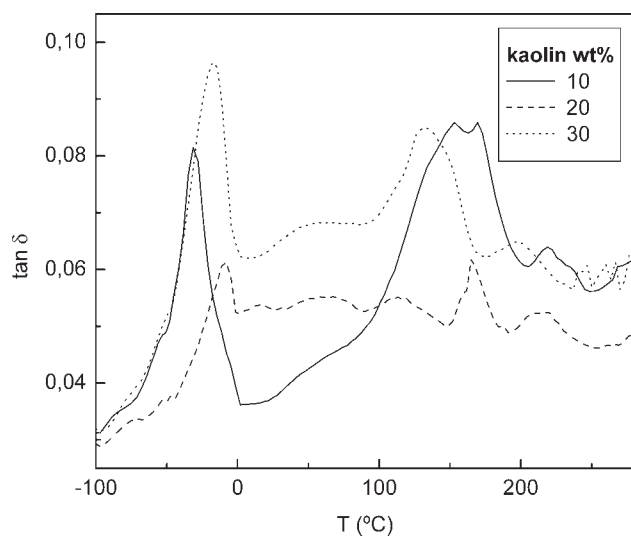
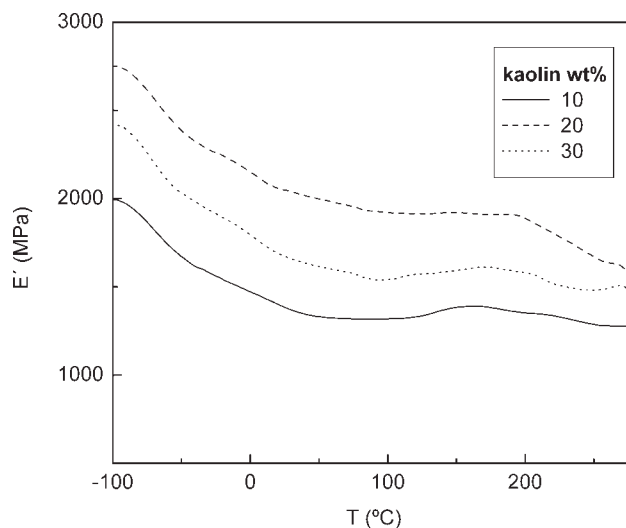**Figure 5** Tan δ versus temperature for samples containing different kaolin wt % (14 wt % catalyst).

Figure 6 E' versus temperature for postcured samples (14 wt % catalyst).

ing of 7 days at 80°C. When comparing Figures 4 and 6 several effects are observed:

- At temperatures below 0°C the values of E' for the postcured samples are lower than for non-postcured ones whereas above 0°C the postcured samples have higher values of E'.
- A sharp decreasing in the value of the modulus is observed between –100 and 0°C for nonpost-cured samples whereas for postcured samples the modulus decreases gradually during the experiment remaining almost unchanged from 100°C.

These results can be explained if we consider that water is generated in the curing process as a conden-sation product (20–30%) remaining inside the poly-mer structure. When the sample is postcured this water is going out, so the nonpostcured samples will show all the effects caused by the remainder water; at low temperatures (−100 and 0°C) water solid will contribute to enhance the polymer rigidity and it can be noted a sharp tan δ peak at low temperature in Figure 5. On the other hand, from Figures 4 and 6 it

can be observed that the initial modulus is clearly higher for the non postcured samples being reversed this behavior at high temperatures as a consequence of the water elimination and the postcuring effect.

Figure 7 shows the evolution of tan δ. As it can be observed, the β transition appears at –60°C and is in-dependent of the amount of filler; Table VI shows the $T_{g\infty}$ values obtained for all the postcured sam-ples. As it can be observed, the values of $T_{g\infty}$ for samples filled with kaolin are higher than those for samples filled with talc because of the higher basic character of this filler. It can be observed as well that the amount of filler does not affect significantly the $T_{g\infty}$ values. Only a small proportion of these fillers are solved in the medium, affecting the pH an in

TABLE V
$T_{g\infty}$ **Values (°C) for Samples Cured with 14 Catalyst wt % (3 Hz)**

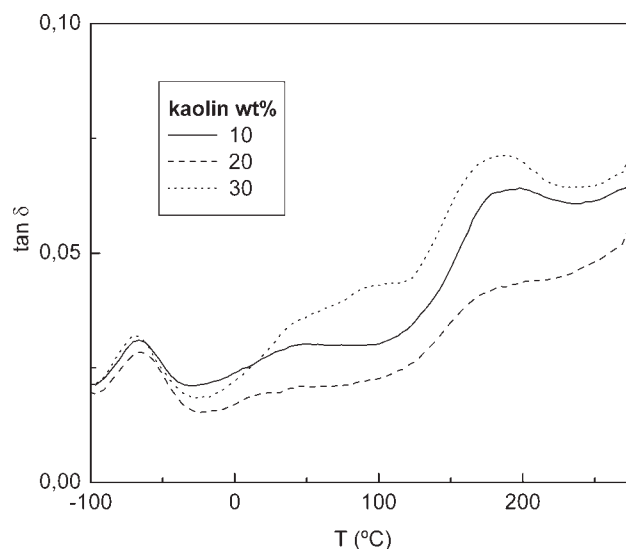| Filler (wt %)	Kaolin	Talc
5	240.3	194.4
10	219.7	191.9
15	244.1	185.5
20	216.2	219.7
25	258.5	199.1
30	242.7	232.5

Figure 7 Tan δ versus temperature for postcured samples (14 wt % catalyst).

TABLE VI
T_g **Values (°C) for Samples Postcured**
with 14 wt % Catalyst (3 Hz)

Kaolin (wt %)	T_{g1}	$T_{g\infty}$
5	208.1	269.3
10	199.1	271.9
15	210.9	252.4
20	185.4	263.4
25	173.9	262.1
30	189.3	268.8
Talc (wt %)	$T_{g\infty}$	
5	209.9	
10	193.7	
15	196.5	
20	203.1	
25	200.6	
30	201.7	

consequence the crosslinking process; the increase in the amount of filler will increase only the quantity remaining in suspension.

The $T_{g\infty}$ values for postcured samples are in general higher and more homogeneous than for non-postcured samples because of the lower distortion caused by water besides the effect of the postcuring.

CONCLUSIONS

The TSR technique has been used as an easy and fast way of determining the gel time in the curing process of a resol resin acid catalyzed. The values of the gel time show a strong dependence with curing temperature and acid catalyst weight percent and are increased when a filler is added to the resin, because of the changes in the pH of the system caused by the added filler.

The presence of fillers leads to an apparent increase in the mechanical properties. However, for the postcured samples, a decrease in the modulus is observed in all cases at temperatures lower than 0°C, because of the fact that the water contained in the resin has been evolved. With respect to the thermal behavior, a decrease in the glass transition temperature is observed in the presence of fillers as consequence of a lower crosslinking density because the interaction with the catalytic system.

We can conclude that the presence of fillers in the final formulation of the composite is a suitable method to improve the mechanical and thermal behavior, although it must be used an additional amount of catalyst to avoid the effect of the fillers on the pH.

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