

Some Filler Effects on Cross-Linking of Unsaturated Polyesters

M. PAAUW and A. PIZZI*

Department of Chemistry, University of the Witwatersrand, Johannesburg, South Africa

SYNOPSIS

The effect of five fillers on the cross-linking macro- and microcharacteristics of simple unsaturated polyester resins was investigated by differential scanning calorimetry (DSC), reactivity tests, and gel time tests. Glass beads and silica flour appeared to have little influence on the cross-linking reaction of the resin itself, their effect being comparable to mere dilution of the resin. Kaolin presented some interaction with the resin due to its absorption characteristics and acid groups. Reground polyester/glass fiber powder and especially wood flour appeared to present clear chemical interactions with the curing behavior of the resin. Wood flour, in particular, was shown by DSC analysis to strongly co-react with the resin during cross-linking and altered markedly the resin enthalpy change and energy of activation during curing. The wood flour component causing the altered behavior of the resin appears to be lignin. DSC analysis of resins filled with three different types of isolated lignins indicated that this wood flour component reacts in a heterogeneous phase reaction with the resin during cross-linking. It appears that it is the lignin unsaturated carbon-carbon double bonds at the polyester/wood flour and at the polyester/lignin interphases that are likely to co-react by heterogeneous phase radical cross-linking with the polyester resin and styrene unsaturation, markedly changing the resin curing behavior.

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INTRODUCTION

The resins commonly referred to as unsaturated polyesters are mixtures of linear polymers that result from the esterification of difunctional unsaturated acids or their anhydrides with a glycol, dissolved in a polymerizable monomer, most commonly styrene, which provides cross-linking units to network chains tridimensionally. The two components co-react and the resin sets, upon introduction of a peroxide catalyst and an accelerator, to form a rigid, infusible network. Thus, the cross-linking mechanism of simple unsaturated polyesters is based on the addition of peroxides to introduce a radical induced carbon-carbon double-bond opening and a radical cross-linking of the resin. The carbon-to-carbon double bond introduced into the resin skeleton by the most commonly used maleic or fumaric residues

is the unsaturation through which radical-induced cross-linking occurs.

Cured unsaturated polyesters exhibit brittleness in their unfilled state. Fillers are generally used with polyester resins to help reduce costs. They permit the use of higher curing temperatures as well as reducing the tendency of the resin to craze or crack during cure and improving resin shrinkage. The characteristics, physical and chemical, of the filler can then influence extensively not only the properties of the cured resin¹ but also its processability. Although, often, the selection of a filler is dictated mainly by its chemical constitution, price, availability, and physical characteristics, its influence on resin flow and particularly on the rate of free-radical polymerization are important factors that must also be taken into account.

The curing kinetics of unsaturated polyesters and the kinetic modeling of their cross-linking reactions have already been studied in detail by several investigators.²⁻¹³ However, notwithstanding that reinforced thermosetting polyesters of commercial

* To whom correspondence should be addressed.

interest contain a large quantity of particulate fillers, little information is available in the literature on their effect on the curing behavior of the resin. Important works by Kubota¹⁴ and Lem and Han¹⁵ on the rheology, rate of cure, viscosity, and radical termination centered on particulate inorganic fillers. Fillers, however, can be both inorganic and organic, fibrous and nonfibrous, and reinforcing and non-reinforcing. In short, they appear to have vastly different characteristics. Consequently, it also appears that there is a real need to investigate in much more depth the role of different filler types. In this study, two common fibrous organic fillers—wood flour and reground polyester—and three equally common nonfibrous inorganic fillers—kaolin, silica flour, and glass beads—were examined and compared. As a result of the initial unexpected finding on the influence on polyester curing of one of these fillers and of the study with pure model compounds of the reaction kinetics between resin and filler when applied to a specific industrial problem,^{16,17} the study was extended to the use of one of the filler components in order to better explain its co-reaction with the resin.

EXPERIMENTAL

Resin Synthesis, Curing, and Fillers

The resin was prepared according to the following procedure, in the following molar proportions: 1.3 mol propylene glycol, 0.5 mol maleic anhydride, 0.5 mol phthalic anhydride, and 0.0002 mol hydroquinone were charged into a flat-bottom glass reactor equipped with a distillation condenser, a thermometer, heating and cooling facilities, and a mechanical stirrer. The apparatus was flushed with nitrogen and then gradually heated, under continuous mechanical stirring and a slow stream of nitrogen, up to 80°C. Xylene, 0.11 mol, was then added to aid azeotropic distillation of the water produced in the reaction. The reaction mixture was then heated to 180°C and the temperature maintained between 180 and 190°C for a required reaction time of 8 h, under nitrogen atmosphere and continuous mechanical stirring. Water and xylene were distilled as the reaction proceeded. The reaction was then cooled to 140°C and 0.96 mol of distilled styrene containing 0.0001 mol hydroquinone added over a period of 1 min while stirring. The mixture was then rapidly cooled to room temperature to prevent premature cross-linking. A viscous, clear solution of unsaturated polyester of a very pale yellow color (due to hydroquinone addition) was obtained.

Curing for DSC purposes was carried out by adding to 100 parts by mass of the resin 1 part Co(II) naphthenate and 1 part methyl ethyl ketone peroxide.

Differential Scanning Calorimetry

A Mettler DSC 20 system was used to follow the cross-linking reactions. Both low-pressure crucibles (40 μ L, Mettler 27331) and high-pressure crucibles (120 μ L, Mettler 29990) in aluminum were used. The DSC scan was run up to 210°C, at a rate of 10 K°/min. The particulate fillers—pine wood flour 100 mesh, kaolin, silica flour, glass beads, and reground polyester/glass fiber 2/1 fine powder—were mixed with the resin at ambient temperature in the mass ratio of resin : filler = 80 : 20. The sugar cane bagasse lignin fine powder, hardwood kraft lignin, and softwood kraft lignin fine powder (all containing less than 1% residual sugars) were added to the resin at the mass ratio of resin : filler = 98 : 2. The sugar cane bagasse lignin was a commercial sample, whereas the two kraft lignins were obtained by concentrated sulfuric acid precipitation from spent pulp with kraft liquors, washing, and drying.

Gel Times and Reactivity (Catalyzed Gel Exotherm) Tests

Gel Time Test

Gelation is defined by the point at which the resin after being catalyzed ceases to be a viscous liquid and becomes a soft, elastic rubbery solid. Ten grams of liquid resin is weighed into a test tube. In the case where fillers are added, they are added at this point and thoroughly dispersed in the resin. Cobalt naphthenate, 0.1 g, followed by 0.1 g methyl ethyl ketone peroxide are then added. A spring wire is placed in the test tube containing the resin and moved up and down continuously, by hand. The test tube is placed in a boiling water bath (93°C, due to Johannesburg altitude = 2000 meters) and the time taken to gel is measured using a stopwatch. The moving spring wire is very sensitive to the onset of gelation. The test is done in duplicate.

Reactivity (Catalyzed Gel Exotherm) Test

The reactivity of the unsaturated polyester is measured as the exothermic heat when the resin is mixed with accelerator and catalyst. It is measured as a peak exotherm and temperature increase against time. A graph of temperature vs. time is plotted and the slope of the curve obtained is a measure of reac-

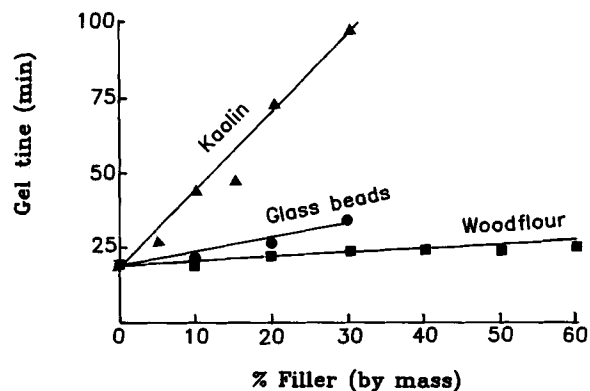


Figure 1 Effect of wood flour, glass beads, and kaolin as fillers on the gel time of an unsaturated polyester resin.

tivity. The method used was as follows: Resin and catalyst were temperature-stabilized at 20°C, in advance. One hundred grams of the resin and 1 g cobalt naphthenate were accurately weighed and mixed into a paper cup inserted in an insulated wooden box and with a thermocouple inserted in the resin, the thermocouple being protected by a small test tube sleeve (10 × 75 mm) containing ethylene glycol. The cup is covered with a plexiglass lid. One gram methyl ethyl ketone peroxide was added and mixed well with the resin mixture, using a wooden spatula, for 45 s. The temperature variation as a function of time was recorded on a flat-bed chart recorder until the temperature reached its maximum. The reactivity in °C/min is taken as the ratio change in temperature increase/time. A standard base-line point on the curve is taken at 35°C so that the calculation becomes

Reactivity (°C/min)

$$= \frac{\text{Max temperature} - 35}{\text{time to max temp} - \text{time to } 35^{\circ}\text{C}}$$

Reactivity analyses were performed to differentiate between the effects of different fillers on resin curing properties (Tables I and II, Fig. 3).

DISCUSSION

Figure 1 shows that filler type and quantity markedly influences gel time. Although it is known^{14,15} that as particulate content increases gel time decreases, it is noticeable that even a low quantity of kaolin retards gel time to a much greater extent than does wood flour or glass beads. Kaolin has been reported to cause severe retarding of gel time by hindering the cross-linking mechanism of the resin. This because its acid groups (e.g., silicic acid) cause ionic decomposition of the peroxide hardeners, decreasing availability of free radicals and, hence, affecting cross-linking and increasing gel time. Kaolin also absorbs some of the peroxide, rendering it inactive in the cross-linking process and contributing to increased gel times. These characteristics do not explain why wood flour does not lengthen gel times to a similar extent, as it also contains acid groups as well as being a highly absorbent filler.

When the cross-linking of an unsaturated polyester is evaluated by differential scanning calorimetry (DSC) at a lower temperature (90–100°C), a shoulder on a large exotherm peak represents residual water emission from the system. The major peak at 125–135°C represents, instead, the exothermic free-radical cross-linking of the polyester.^{14,15} This is the peak that characterizes the kinetic behavior of a particular sample, indicating a more or less rapid cross-linking reaction (steep slope) with the temperature reaching a maximum of 130–150°C.

Experimentation was conducted by selecting a standard unsaturated polyester and loading 20% of

Table I Effect of Filler Type on Thermodynamic Cross-linking Parameters of an Unsaturated Polyester Resin (Resin : Filler = 80 : 20 Rate 10°C/Min)

Filler Type	No Filler	Wood	Kaolin	Glass Beads
Mean enthalpy change (mJ)	4833	2963	3615	3857
Mean enthalpy change reported to 100% resin (mJ)	4833	3704	4518	4821
Mean activation energy (kJ/mol)	82.8	70.4	175	66.4
Mean activation energy reported to 100% resin (kJ/mol)	82.8	88.0	219	83.0
Mean reactivity (°C/min)	7.74	3.45	—	4.52
Mean reactivity reported to 100% resin (°C/min)	7.74	4.31	—	5.65

a particulate filler. The results in Table I confirm that some types of fillers can markedly influence the kinetics of cross-linking. Maximum enthalpy change is obtained when measuring the cross-linking process of a resin without fillers. Fillers reduce the curing exotherm as they absorb heat. They retard the cross-linking reaction as the particulates hinder the mobility of the free radicals. This is rather like an effect of resin dilution by an inert material: As the concentration of filler is increased, the number of reactive bonds per unit volume of the resin/filler mixture is reduced, resulting in a reduced enthalpy change. Thus, in Table I, if we report the mean enthalpy change to 100% resin, it is noticeable that silica flour, glass beads, and, to a lesser extent, even kaolin yield very similar enthalpy changes to the unfilled polyester control: They are clear examples of fillers that merely introduce a dilution effect in the curing of a polyester resin. Thus, by reducing the proportion of resin on a total sample, such inert fillers reduce the total entropy and enthalpy change of the system with increasing filler addition, without the kinetic behavior of the resin itself changing.

This is not the case with wood flour, reground polyester, and, to a much lesser extent, kaolin. In the case of kaolin, the mean enthalpy change decrease of the resin/filler system and the very small decrease in enthalpy change on the resin alone can be probably ascribed to the reasons presented by other authors and already discussed above. The very small drop in enthalpy change noticed in Table I, when 20% reground glass-reinforced polyester laminate is added as a filler indicates that the glass fiber portion of this filler appears to be as inert as are glass beads. The cured polyester portion of the filler instead appears to be involved in the mechanism of cross-linking. If we report the mean enthalpy change to 100% resin (2nd line, Table I), the noticeably apparent increase clearly indicates that residual reactivity in the cured polyester appears to exist. Its high reported compatibility with the resin and the enthalpy change behavior just outlined indicate that such a filler appears to actively participate in the resin cross-linking reaction, not hindering it but, rather, favoring it.

Wood flour instead reduces the enthalpy change more noticeably. At first this was thought to be because it is a highly absorbant filler. Although its high absorbancy may limit the mobility of the polymer chains by secondary forces' interaction, the extent of the enthalpy change decrease is such that the existence of a covalent bond between curing resin and filler can be suspected. The enthalpy changes

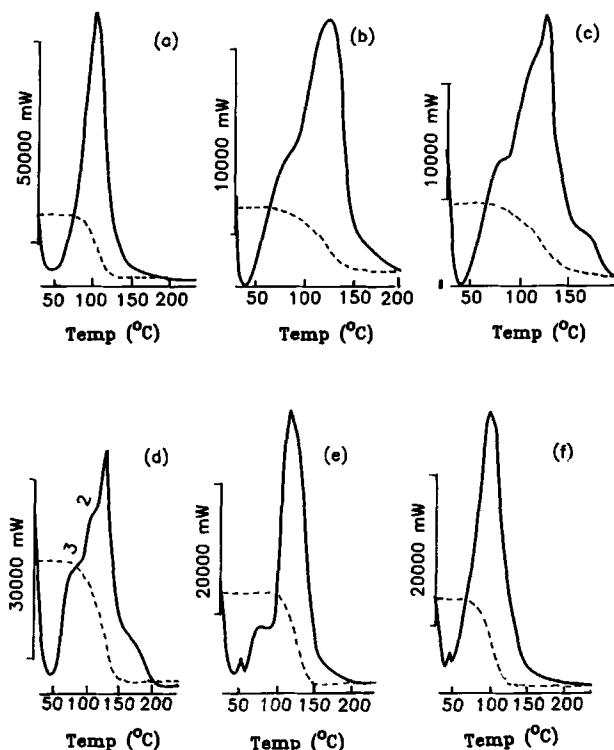


Figure 2 DSC traces of the cross-linking reaction of (a) an unsaturated polyester resin alone, (b) polyester/glass beads 80/20, (c) polyester/reground polyester 80/20, (d) polyester/wood flour 80/20, (e) polyester/bagasse lignin 98/2, and (f) polyester/hardwood kraft lignin 98/2.

are also supported by comparing the mean reactivities of the unfilled and filled systems (Table I).

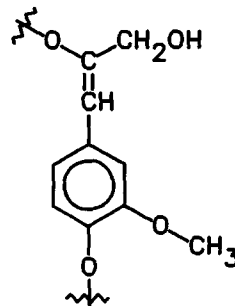
It is also of interest to compare enthalpy and activation energy changes. The mean activation energies of the filled systems as they are, and reported to 100% resin, are shown in Tables I and II. They indicate again that glass beads, which should not participate at all in the reaction, do, instead, appear to have some effect, at minimum also acting as a heat-sink in the system, and that wood flour participates in the reaction, that reground polyester might to a minimal extent participate in the reaction, and that silica flour does not appear to participate to the reaction, but that both silica and particularly kaolin slow down the reaction and create conditions that are less favorable to the cross-linking reaction proceeding. Thus, from Figure 1 and Table I, kaolin is acting as a characteristic heat-sink filler, and as its proportion increases, the enthalpy change decreases. Glass beads, which should be nonabsorbant, their surface reputedly being inert, and which should not

Table II Additional Data Comparing Reactive and Nonreactive Fillers with Unfilled Polyester Resin Curing

	No Filler	20% Wood Flour	20% Glass Beads
Time to reach 35°C (min)	20	24	35
Peak temperature (°C)	156	130	153
Time to reach peak temperature (min)	36	49	59
Reactivity (°C/min)	7.56	3.8	4.82

show any tendency to immobilize the polymer chains on their surface, instead appear to reduce reactivity and slow down the time to reach 35°C (Table II). The reaction, however, remains highly exothermic as the proportion of glass beads increases, notwithstanding the fact that Figure 2(b) clearly indicates that this filler does function as a heat-sink. What this peculiar behavior might indicate is difficult to understand, unless a reaction at the interface between resin and glass beads also occurs.

An interesting phenomenon is observed in DSC scans of polyester resins containing wood flour (Fig. 2). There are three distinct shoulders present on the exothermic peak and an additional shoulder at 118°C, indicating that an additional exothermic reaction, possibly between the filler and the resin, occurs. This could be a free-radical reaction, reducing free radicals available for resin cross-linking and contributing to the enthalpy reduction. The appearance of the additional shoulder at 118°C in DSC scans of polyester/wood flour proved interesting, as a third shoulder did not appear on any of the other filler thermograms other than that of reground polyester. The wood flour constituent that is most likely to react with the resin is wood lignin, an amorphous random polymer that constitutes between 25 and 28% of wood¹⁸ and is composed of phenylpropane units mostly of the following structure:



To verify whether lignin was the reactive constituent in the wood flour, isolated sugar cane bagasse lignin and hardwood kraft lignin were added to the polyester resin, without filler, at the rate of 2% by mass (equivalent to 7–8% wood flour). The DSC scans are shown in Figure 2. In the polyester resin without filler, only one exothermic peak of 115°C is visible. With bagasse lignin, two additional peaks are visible at 70 and 56°C. With hardwood kraft lignin, one additional peak at 50°C is detected, although this is much smaller than in bagasse lignin. This is due to the kraft lignin having been obtained by a drastic sulfuric acid precipitation process that results in a much lower level of unsaturation being present. The peaks observed are much more marked when 5–6% lignin is used (equivalent to 20% wood flour).

Table III Effect of 2% Different Lignin Types, as Reactive Components of Wood Flour Filler, on Cross-linking Reaction Parameters of Unsaturated Polyester Resin
(Note: Heating Rate = 5°C/Min; Hence, Higher ΔH and E_a Values)

	ΔH (mJ)	Peak Temperature (°C)	Energy of Activation (kJ/mol)
Resin alone	9533	115	115
Resin + 2% bagasse lignin	3685	132	303
Resin + 2% hardwood kraft lignin	5712	107	141
Resin + 2% softwood kraft lignin	8176	112	96

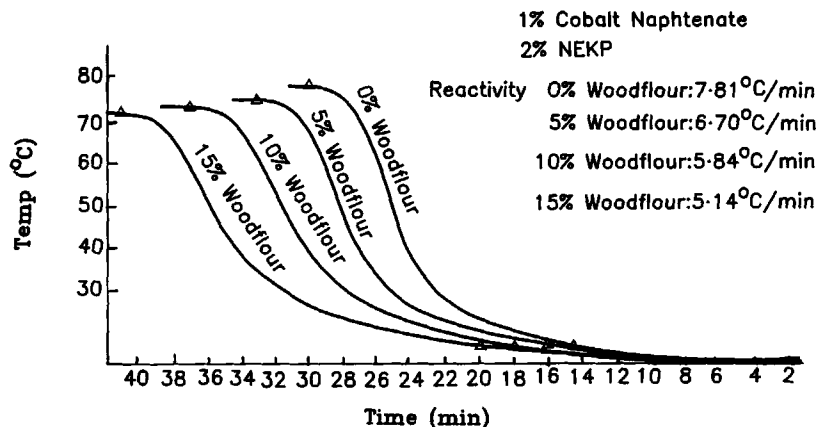


Figure 3 Evaluation of increasing wood flour content on the reactivity of an unsaturated polyester resin.

When evaluating the enthalpies of the curing reaction (Table III), a marked decrease in enthalpy occurs when bagasse lignin is present as a result of additional chemical reactions. A smaller drop in enthalpy occurs when hardwood kraft lignin is added as the additional chemical reactions occur to a lesser extent. A marked increase in activation energy also occurs when bagasse lignin reacts, indicating that although the activation energy is relatively high the chemical reaction between the filler and resin unsaturation is exothermic enough to allow the reaction to proceed. This is unusual as this chemical reaction is a heterogeneous reaction occurring between separate phases—solid substrate and a liquid resin. Only a very reactive substrate will allow a chemical reaction to occur between separate phases as large activation energies need to be overcome.

The influence of wood flour on the kinetic curing behavior of unsaturated polyester resins can be evaluated by performing a reactivity analysis. Figure 3 illustrates the changes in reactivity with a wood flour loading from 0 to 15%. When performing a linear regression analysis on the data, a correlation coefficient of .9947 is found, indicating that there is a linear relationship between the quantity of wood flour present and the resin reactivity. The relationship can be presented as

$$y = 7.7030 - 0.1774x$$

where y is reactivity ($^{\circ}\text{C}/\text{min}$) and x represents % wood flour on resin mass. As the amount of wood flour increases, the resin reactivity decreases. However, when evaluating overall reaction rates, as a

result of the wood flour contributing a reactive species, and the reaction being a second-order reaction, the overall reaction rate increases. Table II shows data that also support a chemical reaction between the resin and the wood flour.

An analysis of this chemical reaction can be made using FTIR. It is, however, difficult as the relative concentration of unsaturation is low and peak changes are small and easily masked. Nevertheless, one can detect the increase in unsaturation when 20% wood flour is added to the unsaturated polyester by the IR bands at $1550\text{--}1650\text{ cm}^{-1}$, characteristic of the $\text{C}=\text{C}$ stretching vibrations.¹⁹

The presence of the lignin in wood flour is also confirmed by strong transmissions at $1175\text{--}1125$, $1125\text{--}1090$, and $1070\text{--}1000\text{ cm}^{-1}$, representing the 1 : 2 : 4 trisubstitution of the aromatic ring, indicating that the wood flour contains a guaiacyl-type softwood lignin.

Kinetic evaluation of the system of reactions between wood flour components and polyester resins, due to difficulties in properly analyzing a heterogeneous reaction of this kind by DSC, was followed by FTIR of model compound reactions and reaction kinetics applied to particular industrial problems and are reported elsewhere.^{17,18}

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