CURE BEHAVIOUR STUDY OF PHENOL FORMALDEHYDE ON WOOD SURFACE USING MICRO-THERMAL ANALYSIS

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Abstract
It is well known that wood has a marked influence on the cure mechanism of phenolic resins. Since the durability and strength of wood based composites depend on the cured state of the binder, it is important to employ a technique which can identify the wood species which can enhance or retard the curing reaction. It has been shown using the micro-thermal analysis (μ-TA™) that curing behaviour of liquid phenol-formaldehyde resin is significantly affected by the substrates. Essential thermal parameters such as glass transition temperature and cure onset were detected. It was found that certain wood species, such as pine and oak, accelerated the curing rate while other substrates, such as birch and glass substrate retarded the resin curing. The exothermic event associated with the phenol-formaldehyde curing was also detected for wood substrates which was almost absent in the case of glass substrate. This seems to suggest that wood has certain catalytic effect on the curing of the phenol-formaldehyde resin.

Introduction
Strength and durability of wood based composites depend on the cured state of the binder. Since the substrate on which adhesive is applied influences the curing process of the resin, it is important to employ a technique which can identify the wood species which can enhance or retard the curing reaction.

μ-TA is a hybrid which combines the principles of atomic force microscopy with that of thermal analysis. It has been largely used for studying of polymers [1,2]. The thermal probe used in the μ-TA is composed of a Wollaston wire which works as a heater and as a sensor measuring the tip movement and heat absorption on the sample surface [3]. With the application of a high voltage it is possible to apply high temperature to specific regions on the sample in the order of few cubic micrometers. This method is known as the local thermal analysis (LTA). The response of the tip to the increasing voltage is continuously monitored in terms of the sensor response (tip vertical displacement) and power (heat absorption) as a function of temperature.

Consolidation of the phenol-formaldehyde resin takes place through addition and condensation reactions. These reactions can be accelerated or retarded by the presence of wood. Mizumachi et al. [4] have shown using DTA that certain wood species catalytically inhibit the curing reaction. The focus of this work is to demonstrate the use of the relatively new technique μ-TA to study the influence of different wood substrates on the curing process of liquid phenol-formaldehyde resin.

Experimental procedure
Sample preparation
Liquid face phenol-formaldehyde resin and commercially available oak, birch, pine veneers and microscopic cover glass from VMR scientific Inc. were used in this study. The veneer samples were heated overnight in an oven at 103±2 ºC to determine the moisture content which was found to be ~ 5 %. The veneer surfaces were then polished using 2400P sand paper to produce even topography. The veneer and cover glass samples dimensions were of 2 x 1 x 0.68 ± 0.19 cm and 2.2 x 5 x 0.015 cm respectively. The veneers and the glass slides were carefully coated with the liquid PF on the surface using a glass rod to produce a macroscopically uniform coating. The coated veneers were weighed before and after coating to obtain a dry resin solid content of 25–30 % by weight. These coated veneers and glass slides were placed in an oven at 90 ºC for 20, 30 and 40 minutes. The cure temperature was selected to produce a resin film in a semi-cured state to facilitate the use of the thermal probe.

The tests were conducted using a μ-TA 2990 obtained from TA instruments U.S.A. The resistance probe consisted of a V-shaped 5 μm diameter tip with a temperature coefficient of 0.00165/K, a nominal resistance of 2.1 Ohms and a spring constant of 5-20 N/m. The heating rate was fixed at 25 ºC/second. At least 3 samples were measured and a minimum of 10 repetitions were done.

Results and Discussion
Figure 1 illustrates the quantities measured from the sensor response. The glass transition temperature (Tg) was detected as the temperature the probe starts to sink into the sample after the initial expansion. Cantilever deflection (CD) is measured as the probe depression depth prior to the second expansion.

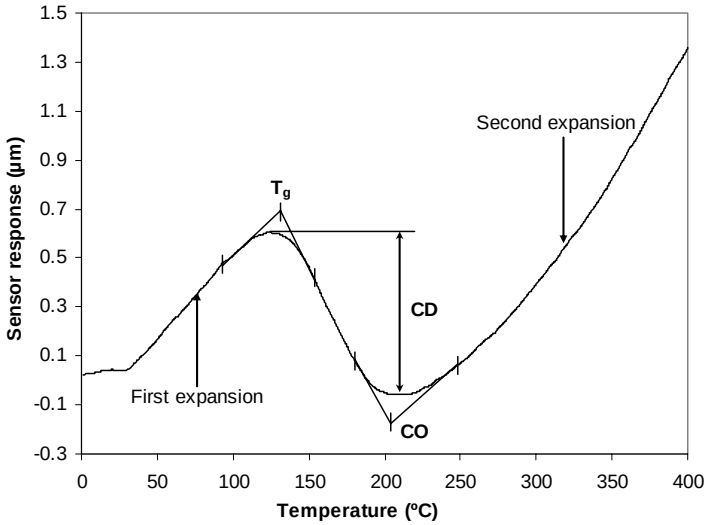

Figure 1. Glass transition temperature, cantilever deflection and cure onset detection illustrated.

Cure onset (CO) is detected prior to the second expansion. It should be emphasised that the expansion detected includes the expansion of the Wollaston wire. The effect of the tip expansion will be small, since the same tip was used in all experiments.

Effect of wood on Tg measurement

One of the most useful thermal parameter for characterising a polymer is glass transition temperature (Tg) which is controlled by cross-link density of the polymer. The cross-link density of the polymer increases with the pre-cure resin temperature which results in the increase of Tg. Therefore, the Tg can be directly related to the modulus (stiffness) of the resin. Figure 2 shows that Tg increases with the pre-cure time as expected.

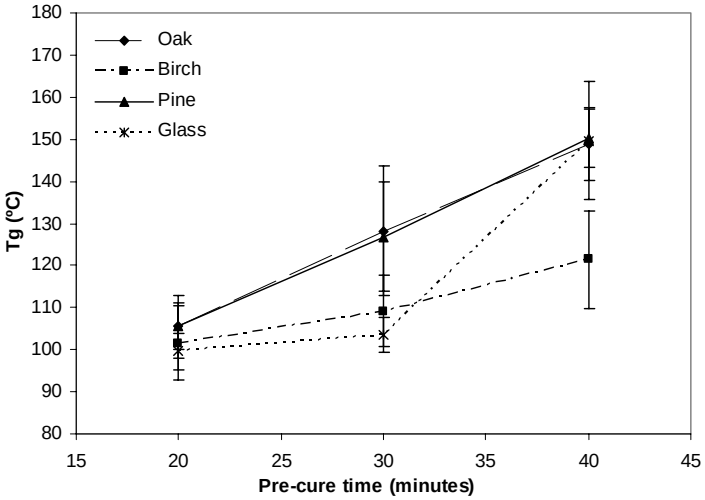

Figure 2. Tg of pre-cured PF resin on different substrates at different time intervals. Pre-cure was carried out at 90 ºC in an oven.

The observation is in agreement with the work by Schmidt et al. [5] on the PF resin. In the case of the pine and oak the variation in Tg values are comparable throughout the pre-cure schedule signifying analogous cure state. However, in the case of birch and glass the Tg values are considerably lower until 30 minutes of pre-cure time. This implies that cross-linking and polymerisation reactions proceed at a much faster rate with pine, oak substrate resulting in a higher modulus in PF resin compared to birch, glass substrates. The rapid increase in Tg of PF on microscopic glass after 40 minutes of pre-cure is attributed to the higher heat absorption by the resin on glass.

Effect of wood on cure onset (CO)

Cure onset is the phase in which the resin begins to cure with physical expansion and release of heat (Figure 4). The CO and the cure exotherm would be specific to the measured region due to the inhomogeneous wood surface.

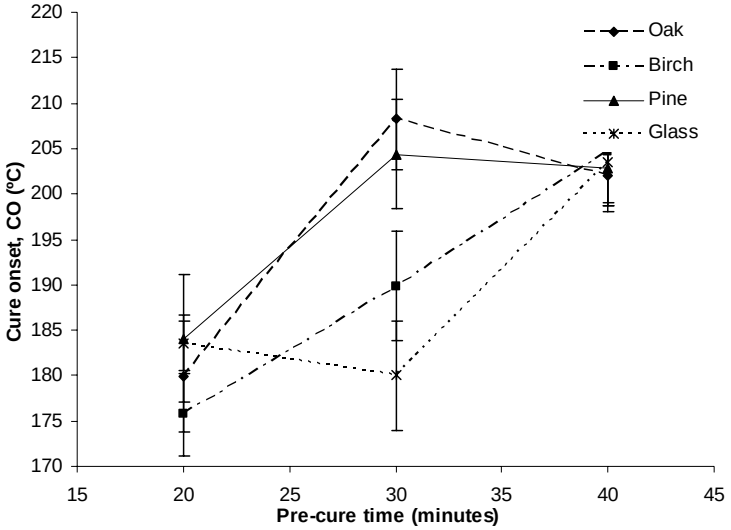

Figure 3. Cure onset of PF on different substrates pre-cured at different time intervals at 90 ºC.

From Figure 3 it can be seen that except for glass the CO increased for oak, birch and pine with pre-cure time. This is because resin with a greater degree of cure would require less heat for further completion of the condensation reaction.

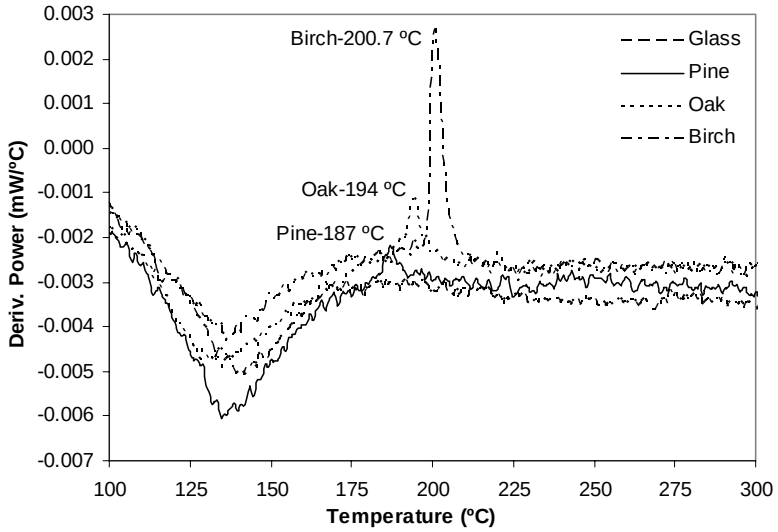

Figure 4. Cure exotherm detected for PF on different substrates pre-cured at 90 ºC for 20 minutes.

The curing reactions of PF resin is typically exothermic in nature, which results in release of heat at some phase in the polymerisation reaction. Since the sample used was semi-cured the amount of heat released could be expected to be small. The heat liberated is also dependent on the degree of cure of the resin which decreases with the increase in the degree of cure. No significant exotherms were observed with glass substrate.

One of the major advantages of this technique is its versatility. Any resin could be used to study its curing behaviour. Cure information pertaining to a particular location on the resin could be studied.

The major limitation of this technique is its inability to work on liquid resins due to probe contamination by sticky resin. The occurrences of exothermic events in PF were detected however, varied in temperature at different locations on the same sample, which may be caused by non-isothermal test conditions and inhomogeneous wood surface.

Conclusion

μ-TA was successfully used to identify the differences in the curing behaviour of PF resin caused by different substrates. Important thermal parameters such as glass transition temperature and cure onset were measured for partially pre-cured PF resin on different substrates. Pine and oak veneer substrates were found to accelerate the curing process while birch veneer retarded the cure process. Cure exotherm associated with resin cure were detected for all wood substrates. However, for glass substrate no significant exotherms were detected. This suggests catalytic activity of wood substrates on the curing mechanism of the phenol-formaldehyde resin.

References

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