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The Effect of Lignin Content on the Cure Properties of Phenol-Formaldehyde Resin as Determined by Differential Scanning Calorimetry

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Summary

The thermochemical behavior of lignin combined with phenol-formaldehyde (PF) thermosets has been investigated through Differential Scanning Calorimetry (DSC). The effect of the lignin type and content as well as of its methylolation effect have been investigated through the kinetic parameters of the curing reaction. The linearity of the Arrhenius plots of lnK vs 1/T justifies the use of the Borchardt and Daniel's nth order model to characterize the curing reactions of thermosets. The activation energy, the heat of the reaction and the order of the reaction have been used in order to evaluate the effect of lignin addition on the curing of phenolic resin. Results showed a decrease of the heat of the curing reaction of lignin-phenol-formaldehyde (LPF) resins as the lignin content increases but in a lesser extent for methylolated lignins containing thermosets. The smaller decrease of the heat of the curing reaction observed after the addition of the methylolated type of lignins compared to the non-methylolated lignin is an indication that the methylolation increases the reactivity of lignins. The heat of curing seems to give a better correlation with the amount of lignin content than does the activation energy. An increase of the order of the phenolic resin cure reaction after addition of methylolated or non-methylolated lignins by 50 to 100% was also observed.

Introduction

The relatively high increase of petrochemicals cost renders PF resin very expensive and it has become increasingly necessary to find out how to reduce the amount of the resin used in wood composite manufacture. The use of fillers or extenders with PF resin as an alternative bonding system has been explored in plywood manufacture (Sellers Jr. 1985) and, very recently, in flakeboard manufacture (Waage *et al.* 1991). Lignin is a renewable by-product of pulp industry and has a polyphenolic structure which is similar to that of PF resins. This structural similarity makes lignin a good candidate for a partial replacement of PF in the amount of resin used in fiberboard manufacture. Also, due to this similarity, the possibility of incorporating it into the PF with and without chemical modification may be considered.

Much work has been done in this area and the use of non-modified as well as modified lignins has been reported. Studies on the curing of PF thermosets have been developed in many laboratories and reported in the literature in the last years, Muller *et al.* (1986), Kelley *et al.* (1986), Chow and Steiner (1974), Sebenik *et al.* (1974), Chow *et al.* (1975), Ebewele *et al.* (1986), White and Rust (1965), Katovic (1967), Ezrin and Claver (1969), Kay and Westwood (1975), Mizumachi and Morita (1975), Muller *et al.* (1984), Christiansen and Gollob (1985) and Gupta *et al.* (1986).

The aim of the present study is to investigate the changes in the kinetic parameters of the curing process of a PF resin as a function of the content of modified or non-modified lignin, and also as a function of the type of the lignin.

Experimental

Methodology

The bond performance of LPF resin systems is studied through a series of experiments in order to evaluate the effect of the lignin type and content, as well as the effect of lignin modification by means of methylolation.

Resin preparation

The PF resins used in this work have all been taken from the same batch and were furnished by a private resin producer. Some properties of this resin determined in our laboratory are as follows: the viscosity corresponds to T in the Gardner scale, pH is 12 and solid content about 60%.

Methylolation of lignins

Two types of softwood lignins (black spruce), a sodium based lignosulfonate with 15% reducing sugars and a molecular weight $\overline{M}w$ of 50000 (L1) and an ammonium based lignosulfonate with 10% reducing sugars and a molecular weight $\overline{M}w$ of 37000 (L2), were furnished in powder form by a lignin producing company. We used