An investigation on the hydrolysis of polyphenolic cyanate esters using near-IR spectroscopy

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High temperature organic polymers have been described as polymers that retain useful properties after thousands of hours of exposure at 300°C in air under static conditions. Cyanate esters fall within this class of polymers. They offer properties such as good fracture toughness, excellent adhesion, low shrinkage, excellent dielectric properties, low dissipation factor and low moisture uptake: 1 - 3 % in boiling water (but found to be 5% in our work). However, such polymers suffer from poor resistance to hydrolytic degradation. Although much work has been reported concerning the cure and mechanical behavioral characteristics of these polymers, there are fewer reports of work that aims to understand their degradation behavior. In this study a detailed understanding of degradation by hydrolysis was sought by measuring fractional increase in weight and chemical changes using near infrared (NIR) spectroscopy. Evidence of the degradation reaction being a chain scission event was also obtained based on the analysis of dynamic mechanical behavior following exposure to controlled humidity and temperature environments. The experimental techniques developed in this work were found to be a reliable and reproducible method to characterize the hydrolysis reaction. The principal goals of this project were to determine the kinetics of hydrolysis and to evaluate associated changes in mechanical properties. Two methods were developed to determine the fractional conversion of hydrolysable bonds. Based on these values a kinetic rate expression was obtained. The fractional conversions of hydrolysable bonds when compared to the resulting Tg did not show a linear relationship as assumed by other researchers. Moreover it was found that unlike other reports, Tg could not be recovered by drying after several hundred hours hot-wet conditioning. The diffusivity of water in the polymer network was also measured and the characteristic times for reaction and diffusion were compared for the sample geometry investigated. Very low values of Damkohler number were obtained suggesting that the hydrolysis process for the specimens studied was reaction controlled.