T_g AS AN INDEX OF CONVERSION IN PMDI-IMPREGNATED WOOD

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It is well established that the glass transition temperature (T_g) is a sensitive measure of cure in neat thermosets. As cure advances, network mobility declines and the T_g rises in a systematic fashion. This study sought to determine if such a relationship exists for polymeric isocyanate adhesives (pMDI) cured in the presence of wood. Yellow-poplar (*Liriodendron tulipifera*) specimens were impregnated with neat pMDI and then isothermally cured for various periods in two different differential scanning calorimeters (DSCs). After this isothermal cure period, the T_g and residual heat of cure were determined. These thermal scans were performed using either constant (conventional) or modulated (MDSC) heating rates. For both methods, the degree of resin cure varied significantly under identical isothermal curing conditions; nevertheless a strong relationship was found between the degree of resin cure and the associated T_g. While the conventional DSC method yielded slightly improved sensitivity and reproducibility, results from both methods compared favorably.

Keywords: Wood adhesion, Isocyanate, Cure, Glass transition temperature

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INTRODUCTION

The classic work by Gillham and coworkers (Wisanrakkit and Gillham 1990) established that the glass transition temperature (T_g) is a sensitive measure of cure in thermosets. As cure advances, network mobility declines and the T_g rises in a systematic fashion. For the neat epoxy system studied by Gillham, the relation between T_g and percent conversion was found to be independent of the isothermal cure temperature. This fundamental relationship has since been demonstrated for a variety of other thermosets (Cook et al. 2004; Cook et al. 1997; Harismendy et al. 2000; Li et al. 2000; Malkin et al. 2005; Park et al. 2002; Scott et al. 2002; Teil et al. 2004; Toffey and Glasser 1997).

Modeling of polymeric methylenebis(phenylisocyanate), pMDI, wood adhesive cure has significant importance for optimizing industrial hot-pressing (Harper et al. 2001). Unfortunately, reliable modeling is complicated by the fact that pMDI requires moisture to undergo cure, yet pMDI is itself water immiscible. Although pMDI will cure in the presence of water or water vapor, in such a scenario pMDI's access to water is markedly different from that of pMDI impregnated in a wood substrate. In the latter scenario the water sorbed on wood promotes reaction, but wood's complicated surface is expected to influence the cure state. For instance, it has been demonstrated that the

precise moisture content of wood and, in some instances, the wood species itself affect the reaction kinetics (He and Yan 2005; He and Yan 2007). Furthermore, competing reaction pathways exist for the isocyanate conversion and the exact nature of the pMDI-wood bond is not fully understood. The relative proportion of polyurea, biuret/polyuret, allophanate, and polyurethane bonds are strongly influenced by wood moisture, cure temperature and wood species (Das et al. 2007; Harper et al. 2001; Owen et al. 1988; Weaver and Owen 1995; Wendler and Frazier 1996). As such, the cure of neat pMDI and of pMDI impregnated wood will likely differ, and this necessitates the development of *in situ* cure monitoring. The method developed by Gillham appears to lend itself to the study of pMDI-impregnated wood specimens and may be useful for developing kinetic based hot-pressing models for wood-pMDI systems. However, the fundamental relationship between T_g and isothermal cure time has only been demonstrated for neat adhesives and it is unknown if this relationship is valid for pMDI-impregnated wood. Therefore, this study was intended to determine if the wood/pMDI system will conform to the classic relationship between T_g and the degree of cure.

Yellow-poplar (*Liriodendron tulipifera)* specimens were treated with neat pMDI and then isothermally cured for various times and temperatures inside a differential scanning calorimeter, DSC. After this isothermal cure period the samples were cooled and thermally scanned to detect both the T_g and the residual heat of cure of the partially cured resin.

EXPERIMENTAL

Separate DSC experiments were conducted using modulated (MDSC) and constant (conventional DSC) heating rates. In each case a commercial pMDI (Rubinate® 1840 from Huntsman Polyurethanes) was used: viscosity 166 mPa•s (25°C), NCO content 31%. Yellow-poplar flakes 0.3-0.5mm (conventional DSC) or 1.5 mm (MDSC) in thickness were sliced from the tangential wood surface using a disk flaker. The flakes were equilibrated to 7-8% moisture content over saturated aqueous K_2CO_3. Disks 3 mm in diameter were punched from the equilibrated wood specimen and soaked in pMDI for 5 min (conventional DSC) or 1 min (MDSC). For the MDSC specimen the excess resin was simply wiped off with tissue paper. For the conventional DSC specimen the excess resin was removed by placing the impregnated disks between tissue papers and pressed under a 10kg mass for 1 minute. The average weight increase from resination (based on the moisture equilibrated wood mass) was 52 +/-2% for the MDSC specimens and 32 +/-11% for the conventional DSC specimens. While these resin loadings were far in excess of those used in commercial applications, they approached the minimum necessary to obtain adequate heat flow responses for all DSC experiments. All specimens were analyzed immediately following impregnation.

MDSC experiments were conducted on a TA Instruments 2920 DSC equipped with a nitrogen purge (50 cm^3/min) and a refrigerated cooling system. Sapphire was used for the heat capacity calibration; indium was used for the temperature and cell constant calibrations. The resin impregnated disks were sealed in hermetic aluminum DSC pans and isothermally cured within the DSC at 80, 60 or 50°C for prespecified times between 0

and 16 hours. The partially cured specimens were then quench cooled to -90°C and thermally scanned at 2°C/min with a modulation amplitude of 0.4°C and a period of 60s.

Conventional DSC experiments were conducted on a TA Instruments Q100 DSC equipped with a nitrogen purge (50 cm^3/min) and a refrigerated cooling system. Indium was used for the temperature and cell constant calibrations. The resin impregnated disks were sealed in stainless steel high volume sample pans and isothermally cured at 80, 60 or 40°C for prespecified times between 0 and 24 hours. The partially cured specimens were then quench cooled to -90°C and thermally scanned at a constant heating rate of 20°C/min to 200°C. After this initial scan the sample was again quench cooled and rescanned over the above temperature range. This latter scan served as a fully-cured baseline and was subtracted from the initial scan, providing more reproducible measurements of the T_g and the heat of reaction. For both methods, heat of reaction calculations were made with TA Instruments Universal Analysis 2000 software using the sigmoidal baseline fit model. Reported T_g's are for the transition's midpoint.

RESULTS AND DISCUSSION

Detection of T_g and Residual Cure Using MDSC

Typical MDSC thermograms for specimens precured for 0, 4 and 6 hrs (60°C) are shown in Figure 1. The non-reversible heat flow exhibits the respective cure exotherms.

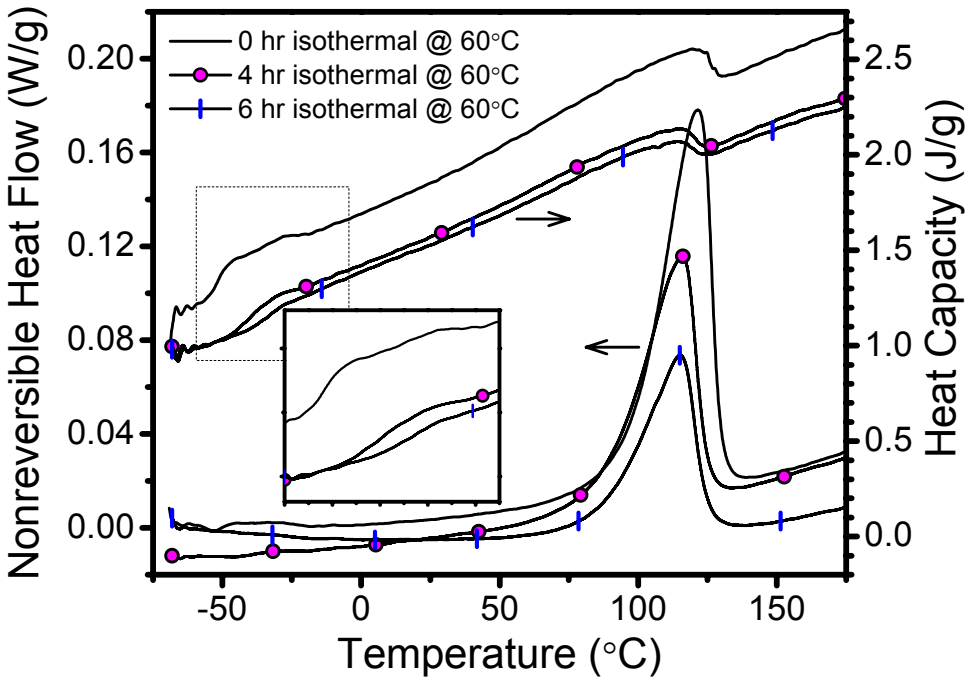

Figure 1. MDSC thermograms of pMDI impregnated yellow-poplar previously cured for various times at 60°C (Heating Rate = 2°C/min; amplitude = 0.4°C; period = 60s). Inset shows an expanded view of heat capacity (Tg traces).

The residual heat of reaction (ΔH_R) decreased with increasing isothermal cure time, relative to the total heat of reaction (ΔH_T) measured for the uncured specimen. The heat flow trace does not clearly show the resin glass transition. The heat capacity curve does reveal the T_g (near -50°C), and vitrification is also seen in the high temperature region corresponding with the heat flow exotherm. As expected, the Tg rose following isothermal pre-curing. However, as the T_g rose its magnitude was proportionately reduced, making accurate detection more difficult.

The fractional conversion, *x*, defined as

$$x = 1 - \frac{\Delta H_R}{\Delta H_T} \quad (1)$$

is plotted versus isothermal cure time at various temperatures in Fig. 2. Using the MDSC method, T_gs were unambiguously detected for factional conversion only below approximately 0.6. Figure 2 shows significant variation between fractional conversion and isothermal cure time. For example the 60°C, 4 hr cure data varied about the mean value by as much as +/- 50%. Similarly, the 50°C fractional conversions were somewhat uniform, but the corresponding cure times ranged from 6 to 15 hours. The reason for this great variation was unknown, nor was it investigated. With a 52% resin content, the MDSC specimens likely contained both adsorbed and free liquid pMDI. Perhaps the data scatter reflects differential degrees of resin adsorption and penetration. However, the corresponding plot of T_g versus fractional conversion (Fig. 3) displays a clear trend that is not discerned in Fig. 2. While some scatter remains, the T_g rises in a systematic fashion with increasing fractional conversion. Furthermore, this relation between T_g and fractional conversion was independent of the isothermal cure temperature. While Fig. 2 exhibits a complex relationship between fractional conversion and isothermal cure time, Fig. 3 demonstrates that T_g is an accurate indicator of resin cure. Furthermore, Fig. 3 validates the accuracy of the fractional conversions that varied so drastically with isothermal cure time.

Detection of Tg and Residual Cure Using Conventional DSC

Using conventional rather than modulated heating it was possible to use a significantly greater heating rate (20°C/min vs. 2°C/min). This larger heating rate and, to a lesser extent, the greater sensitivity of the Q100 DSC increased the intensity of the observed Tg's. As such, using the conventional DSC method the Tg's were unambiguously detected in the heat flow signal even at fractional conversions greater than 0.9.

Typical conventional DSC 1st and 2nd heating scans are shown in Figure 4 along with the difference (subtraction) of these two scans. The subtraction trace exhibits an improved baseline relative to the 1st heating scan, and this made the definition of the Tg and the heat of reaction more reproducible.

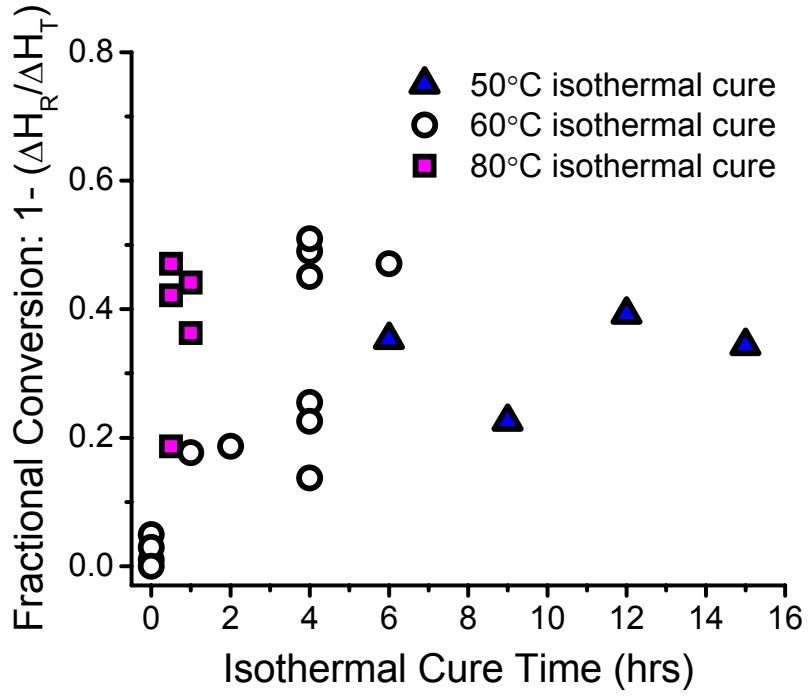

Figure 2. Comparison of fractional conversion versus isothermal cure time at different temperatures analyzed using MDSC.

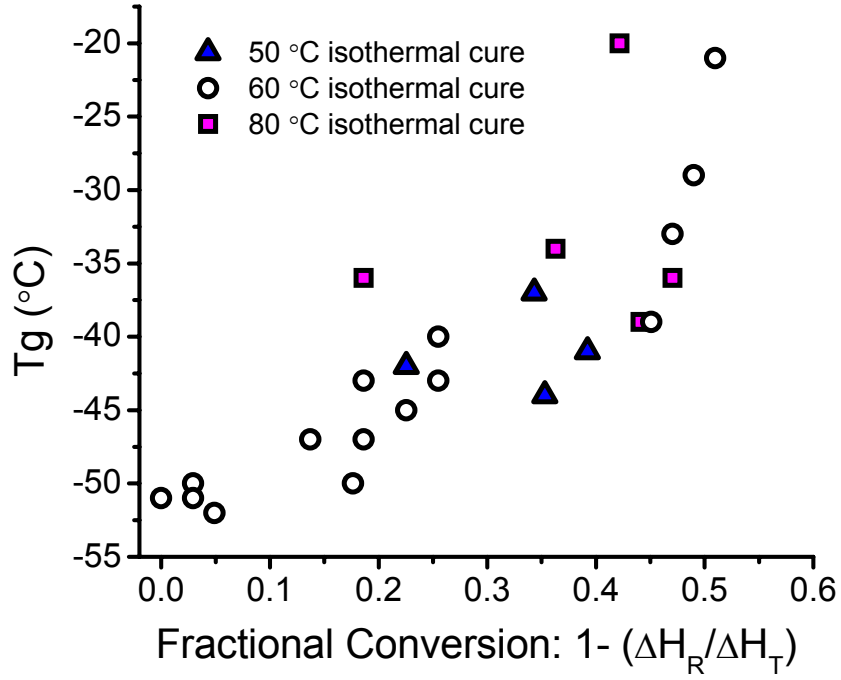

Figure 3. Comparison of Tg versus fractional conversion for MDSC specimens.

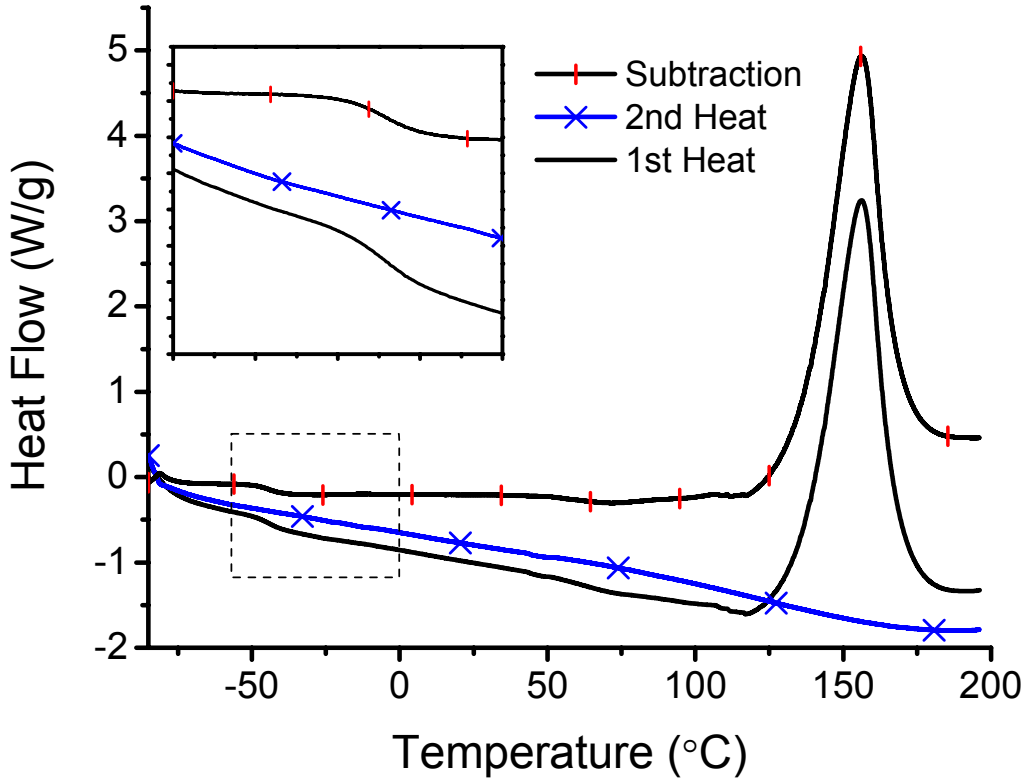

Figure 4. Typical conventional DSC 1st and 2nd heats and the difference thereof (subtraction) for pMDI impregnated yellow-poplar (heating rate = 20°C/min)

Analogous to Fig. 2, the plot of fractional conversion versus isothermal cure time for the conventional DSC specimens is presented in Fig. 5. Despite some improvement relative to the data in Fig. 2, Fig. 5 still shows significant variation (e.g. the 80° data at 0.66 hours and the 60°C data at 3 hrs isothermal cure). With a 32% resin content, the conventional DSC specimens should contain mostly adsorbed pMDI, in comparison to the MDSC specimens that had 52% resin. Again, it is unknown why the relationship between fractional conversion and isothermal cure time was so varied. As previously mentioned, perhaps the micro- and nanoscale penetration varied and influenced the cure rate. While the wood specimens were very small, yellow-poplar has a very uniform grain. Perhaps during wood preparation (punching from a flake) the specimens experienced different degrees of compression and damage that could influence resin penetration.

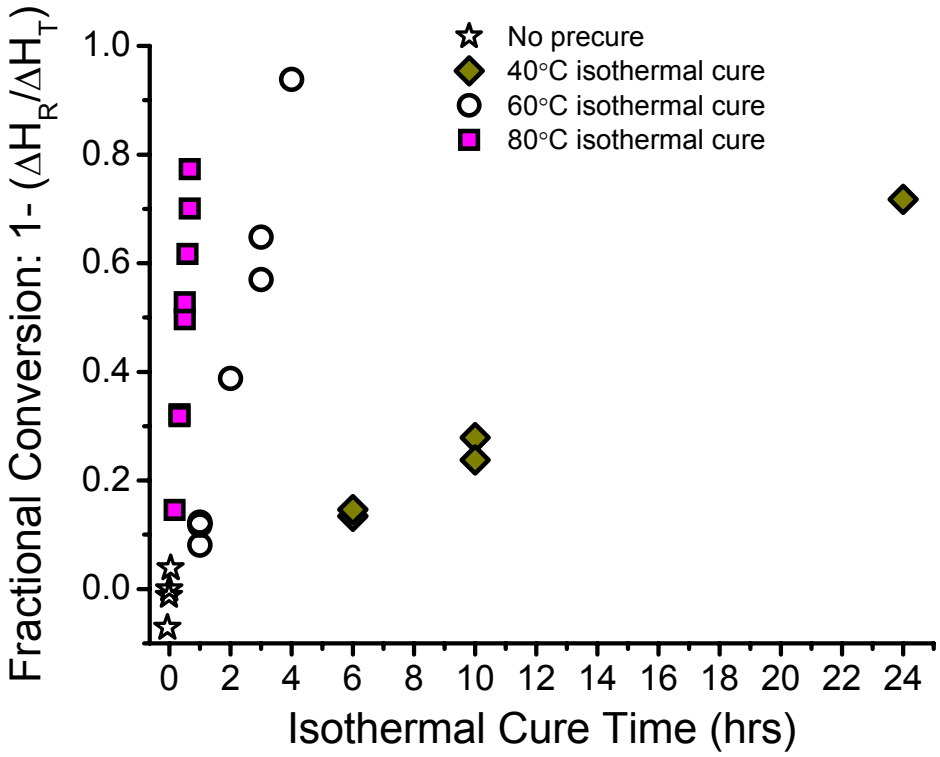

Figure 5. Comparison of fractional conversion versus isothermal cure time at different temperatures for samples analyzed using conventional DSC.

The corresponding plot of T_g versus fractional conversion is presented in Fig. 6. The overall trend was similar to that observed in Fig. 3 using the MDSC method. Again, the T_g serves as an accurate indicator of fractional conversion despite the noted variation between fractional conversion and isothermal cure time. However, the techniques employed in the conventional DSC method result in less scatter with discernable Tg's even at very high fractional conversions. This greater sensitivity and lower variability of the conventional DSC method is especially significant, considering that the conventional specimen contained approximately 60% less pMDI than the MDSC specimen.

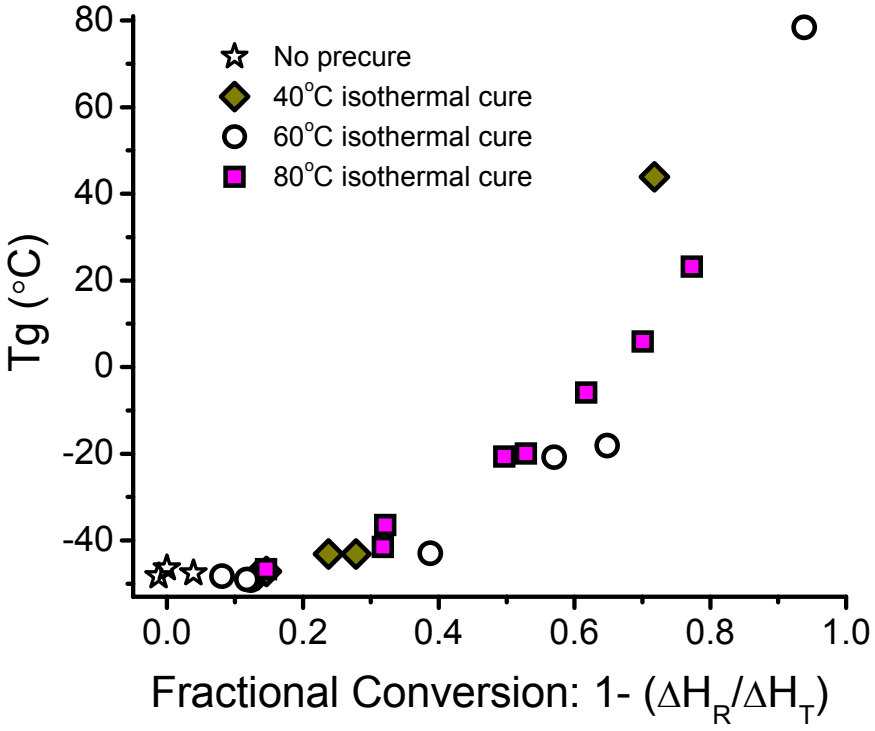

Figure 6. Comparison of T_g versus fractional conversion for conventional DSC specimens.

Finally, T_g versus fractional conversion data for the two different DSC techniques (Figs. 3 and 6) is overlaid in Fig. 7. Despite the differences in sample preparation, DSC operation, and data analysis techniques, the two methods compared favorably. As such, using DSC to measure the T_g of pMDI impregnated wood appears to be a robust and reproducible method for determining the degree of conversion.

Curing of pMDI impregnated wood significantly differs from that of most neat thermosets; wood provides a complex and catalytic surface. Perhaps arising from this complexity, both the conventional and MDSC methods exhibited significant variability between T_g and isothermal cure time. Despite these complexities the fundamental relationship indeed still exists between the T_g and the fractional conversion of the wood-pMDI system. However, it remains questionable whether this method can actually be extended to the study of commercial OSB. Certainly the resin loadings used in this study were significantly greater than those of commercial OSB. Furthermore, actually adopting this method to a pilot-scale press system seems rather challenging. Perhaps this method's greater utility will be in investigating the species dependence of pMDI performance or as a general method for analyzing various wood/adhesive systems.

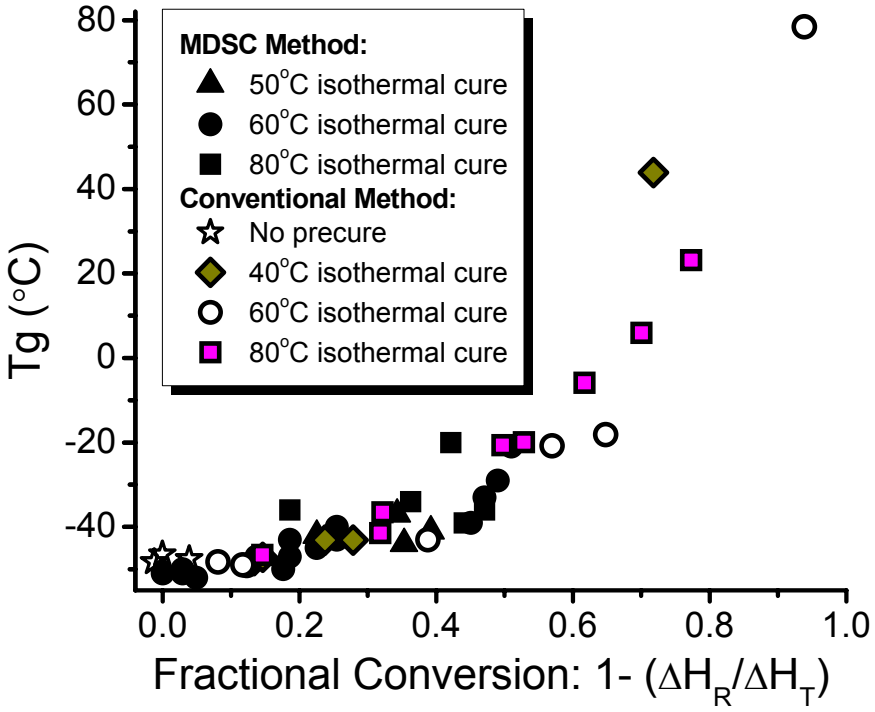

Figure 7. Overlay of Tg versus fractional conversion for both the MDSC and conventional DSC specimens.

CONCLUSIONS

1. This study demonstrated a fundamental relationship between the T_g and the fractional conversion of pMDI impregnated wood. Whereas this relation has previously been demonstrated for neat thermosets, the pMDI impregnated wood introduces an added layer of cure complexity involving catalytic interactions between the water, wood, and resin.
2. For both the MDSC and conventional DSC techniques significant variability was noted in the T_gs of specimens cured under identical conditions. However, despite the inability to accurately predict T_g from the isothermal curing conditions, both methods demonstrated that the T_g remains a good indicator of the system's fractional conversion.
3. The MDSC method was limited to fractional conversions below approximately 0.6, beyond which the T_g could not be accurately detected. The conventional DSC techniques provided greater sensitivity with accurate T_g detection possible at fractional conversion greater than 0.9. The conventional DSC results also exhibited less variability than those of the MDSC method.

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