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Thermal behavior of epoxy resins [1]

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Abstract

A series of epoxy resins has been analyzed by measuring their heat capacities from 140 K up to decomposition using differential scanning calorimetry. The data for the solids were compared to the vibrational heat capacities computed using an approximate vibrational spectrum consisting of skeletal heat capacities (based on a Tarasov analysis) and group vibrations (obtained from IR and Raman data). The heat capacities for the liquid were used to construct an addition scheme for the molecules with similar groups in their repeating unit. The glass transition and the melting transition are discussed by analyzing the fast-cooled and well crystallized samples.

INTRODUCTION AND EXPERIMENTAL DETAILS

At Athas, our laboratory for Advanced THermal AnalysiS, we maintain a data bank of heat capacities and thermodynamic properties of more than 150 polymers and small molecules [1]. We are currently working on the phase behavior and thermodynamic properties of crosslinked epoxy resins. For the proper understanding of the thermodynamics of this system, it is important to understand the phase behavior of several uncured epoxy resins (monomers and prepolymers). In addition, the most common hydroxyl-containing compound, 4,4′-(2,2′-propylidene)diphenol, more commonly known as bisphenol A (RA) and used in the syntheses of several polymers including thermosetting epoxy resins, polycarbonate, polysulfones, etc., was also investigated. No detailed study of the thermal properties has been carried out for either these resins or the bisphenol. The various resins analyzed in this research are shown in Fig. 1. These were

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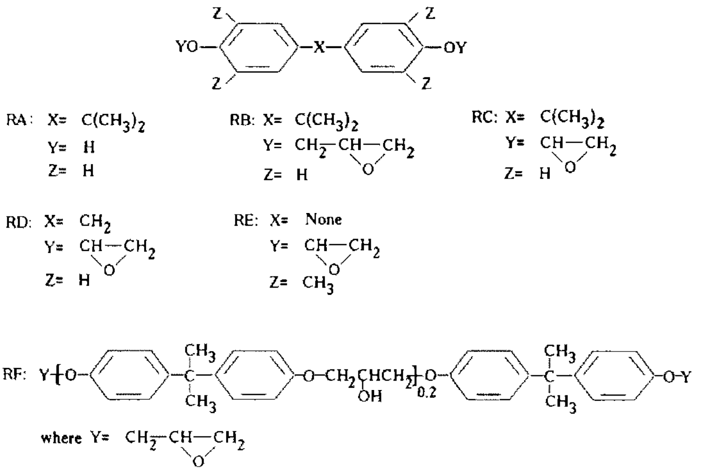

Fig. 1. Structure of the various monomers/prepolymer.

obtained from Shell Development Company, Houston, TX. For all resins, heat capacities were measured from 140 K up to the decomposition temperature. The heat capacities below the glass transition were analyzed by fitting to approximate vibrational spectra. The liquid heat capacities were compared with those derived using an empirical addition scheme. These data enable us to interpret quantitatively the various phase transitions and to determine the thermodynamic functions, the enthalpy *H*, entropy *S*, and Gibbs function *G*.

Phase transition measurements were performed with both a Perkin-Elmer DSC-7 and a TA Instruments 2100, a dual-sample thermal analyzer modified to carry out low-temperature measurement [2]. Heat capacities were measured using our specially calibrated dual-sample DSC at a heating rate of 10 K min^{-1} with a nitrogen flow rate of 20 ml min^{-1}. Typical sample masses used were 15–20 mg. The error is estimated to be <1% above 300 K, <3% below 200 K and <2% between 200 and 300 K.

RESULTS

Investigation of the transition behavior of the as-received samples from 140 K up to decomposition showed only one distinct endothermic transition for RA, RB, RC and RE, indicating that these were of high crystallinity. The peak temperatures and heats of transition are shown in Table 1. The glass transition could only be observed when these samples were quenched in liquid nitrogen from the melt. On heating, RB and RC remained completely amorphous while RA and RE showed a small amount of crystallization. The other two resins (RD and EF) never crystallized and showed only a sharp glass transition.

TABLE 1

Various thermodynamic parameters

Sample	Θ_1/K (range) [a]	$N_{skl}/(N_{grp})$	$T_m^{\ominus}$/K	$\Delta H_m^{\ominus}$/ (kJ mol^{-1})	T_g/K	ΔC_p[b]/ (J K^{-1} mol^{-1})
RA	293 (140–160)	14/(85)	434.7	30.9	313.0	73.1
RB	552 (140–210)	34/(113)	322.5	27.1	254.4	173.8
RC	523 (160–250)	30/(99)	320.3	20.0	257.6	172.3
RD	742 (140–160)	24/(87)	–	–	252.4	219.9
RE	639 (170–250)	34/(104)	382.1	19.9	267.1	236.7
RF	743 (160–240)	39.2(132.4)	–	–	260.0	213.9

[a] The experimental range for averaging Θ_1 is given in parentheses. For crystalline heat capacity, Θ_3 was assumed to be 54 K and for amorphous, 40 K. [b] This value was obtained from the experimental heat capacity of the liquid and the calculated solid heat capacity, except for RA where the melt heat capacity was obtained by an addition scheme (see text).

The details of the computation of the heat capacity for the solid state have been previously described in detail [3]. The vibrational contribution to the heat capacity C_v was calculated based on an arbitrary separation of the vibrational spectrum into group and skeletal vibrations. The strongly coupled skeletal vibrations are usually well approximated by the Tarasov equation in which the parameters Θ_3 and Θ_1 represent the intermolecular and intramolecular frequencies; $\Theta = h\nu/k$, where ν is the frequency in Hz and h and k are Planck's and Boltzmann's constants, respectively; Θ is expressed in kelvin (1 cm^{-1} ≡ 1.4388 K). In this research, Θ_1 was obtained by fitting the limited experimental heat capacities below the glass transition temperature to the Tarasov equation. The group vibrations were obtained from the frequencies retrieved from IR and Raman data and normal-mode calculations for the various groups. Because the heat capacities could only be obtained from 140 K, Θ_3 was assumed to be the same as the value used for the crystalline and amorphous states of the phenylene-containing polymers in our data bank. Table 1 shows the various parameters used for the computation of heat capacities from 0.1 to 1000 K for all the samples. To convert heat capacity at constant volume to that at constant pressure C_p a modified Nernst–Lindemann equation was used [4, 5].

DISCUSSION

Figure 2 shows the vibrational heat capacities plotted together with the experimental data. The computed vibrational C_p value agreed with the experimental value to a precision of better than ±3%, as was observed earlier for more than 100 polymers and a series of paraffins analyzed in our laboratory. The separation of the vibrational spectrum into skeletal and group vibrations and the use of the Tarasov analysis to represent the skeletal heat capacities for bisphenol (RA) and all the resins (RB–RF) seemed to be an acceptable analysis, as justified by the agreement of the computed data with the experimental data. Because no experimental heat capacities were available below 140 K for any of the samples analyzed, the data below 140 K are only approximate. The value of Θ_1 represents the upper frequency limit of the average of the intramolecular skeletal vibrations. A much lower Θ_1 is observed in RA than in the other resins (Table 1) and in addition Θ_1 decreased from a value of 322.5 K at 140 K to 109.1 K at 190 K. The skeletal heat capacities showed only a slight change, from 115.9 J K^{-1} mol^{-1} at 190 K to 121.5 J K^{-1} mol^{-1} at 250 K indicating that the skeletal vibrations are probably close to being fully excited in the experimental range. Bisphenol differs from the other resins in having strong intermolecular hydrogen bonding which results in a strong coupling of the skeletal vibrations, thus making the use of the Tarasov analysis problematic. In addition, the representation of two low vibrational frequency modes between 60 and 90 K for each phenylene unit derived from polyparaphenylene as group vibrations, would also affect the skeletal heat capacities [6]. In all the remaining resins, Θ_1 was relatively constant over a wide temperature range, indicating that the Tarasov analysis could be used with greater confidence.

The analysis of the glass and melting region is shown in Fig. 3 for

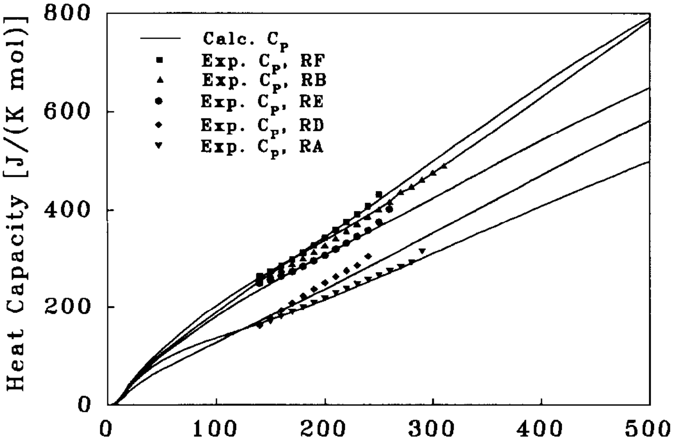

Fig. 2. Computed heat capacities compared with the experimental heat capacities for the various resins.

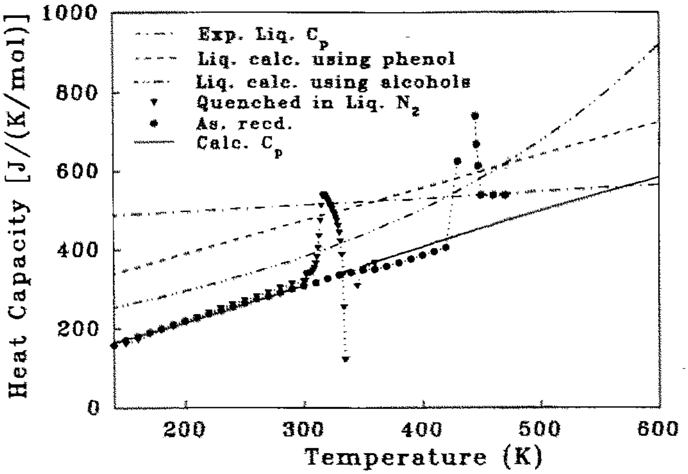

Fig. 3. Analysis of the various transitions in bisphenol A.

bisphenol (RA). A more detailed description of the thermal properties of bisphenol A of varying degrees of purity has also been analyzed and will be reported separately [7]. Figures 4 and 5 show a similar analysis for samples RC and RE. For the amorphous samples RD and RF, the glass transition was analyzed quantatively using the calculated baselines for the solid and the liquid. The results of the analysis are shown in Table 1. A large hysteresis peak is evident in Fig. 3, interrupted by crystallization of the quenched sample. A completely amorphous sample could be obtained for RC when the sample was quenched from the melt in liquid nitrogen (Fig.

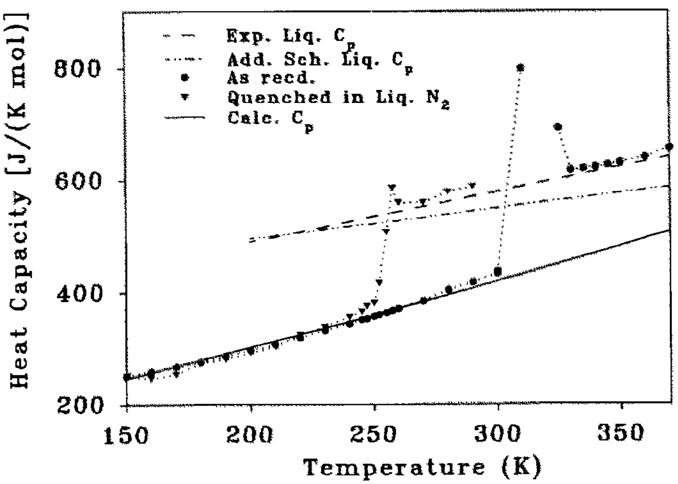

Fig. 4. Analysis of the various transitions in resin RC.

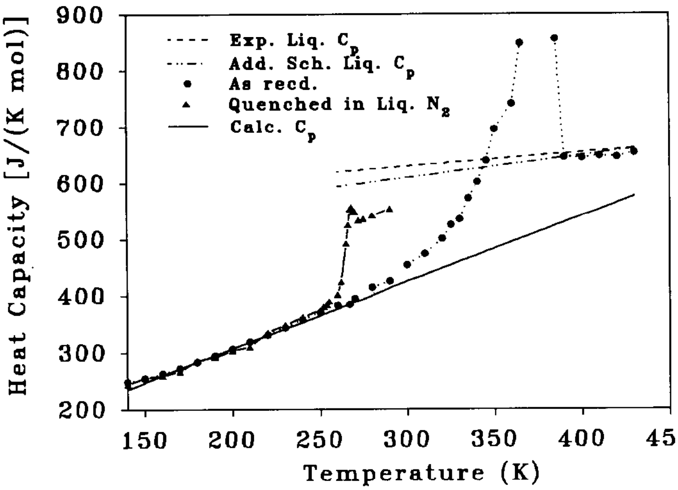

Fig. 5. Analysis of the various transitions in resin RE.

4). Sample RE (Fig. 5), however, was semi-crystalline as is evident from the heat capacity above the glass transition region which does not reach that of the melt as in RC. For bisphenol A (sample RA), the as-received samples were of high crystallinity and showed only a melting transition. The ΔC_p obtained from the extrapolation of the experimental C_p of the liquid to T_g and the solid, vibration-only C_p was rather large, 193 J K^{-1} mol^{-1}. On average, ΔC_p has been established to be about 11 J K^{-1} per mol of "small" mobile bead [8]. If phenylene and isopropylidene groups are considered as large beads that contribute about twice the ΔC_p of a "small" bead, then, empirically, ΔC_p should not be more than about 90 J K^{-1} mol^{-1}. To resolve this discrepancy, melt heat capacities were obtained via an addition scheme based on additivity of the heat capacities of the various groups. The heat capacity for the dimethylmethylene group was obtained from polyisobutylene [9], while the heat capacities of phenol [10] and various other alcohols [11] were retrieved from the literature. In the case of phenol, the heat capacity of two extra hydrogens was assumed to be within the error of the addition scheme. It is obvious from Fig. 3 that neither of the addition schemes seems to represent the heat capacity of bisphenol. A ΔC_p value of 73.1 J K^{-1} mol^{-1} is, however, obtained by using the heat capacity from the –OH groups of alcohols, a value close to that expected from the "bead analysis". The heat capacity of the solid, obtained empirically using the solid data from phenol, reproduced the experimental heat capacity within 1%. Obviously the melt heat capacities need further attention. It seems most likely that the limited experimental data do not establish the proper temperature dependence.

Similarly, for the other resins an empirical addition scheme was used to

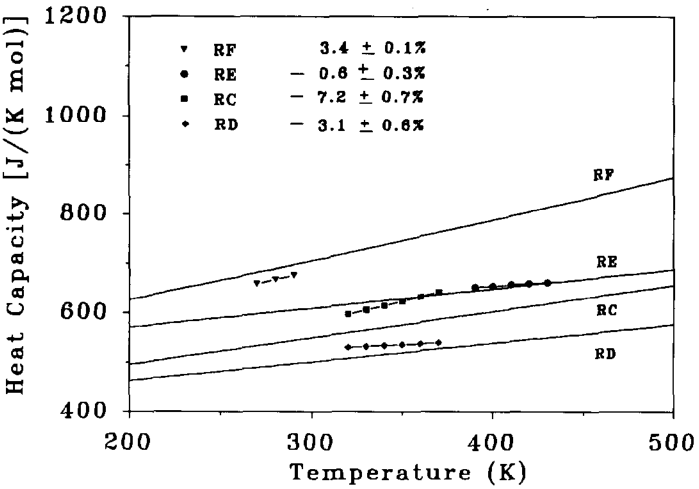

Fig. 6. An addition scheme for the melt heat capacities of the various resins.

determine the heat capacities of the melt and to compare with the experimentally derived data. Figure 6 shows a plot for the heat capacities of the melt. The epoxide contribution was obtained from RB while the contribution of the remaining groups was obtained from our data bank. The average and RMS errors were RC, −7.2 ± 0.7%; RD, −3.1 ± 0.6%; RE, −0.6 ± 0.3%; RF, 3.4 ± 0.1%, over the experimental range. Using the addition scheme, heat capacities ΔC_p could be determined as RC; 157.7; RD, 186.6; RE 211.7; and RF, 238.0 J K^{-1} mol^{-1}, and compared to the experimental data listed in Table 1. All samples show a larger value for ΔC_p than expected using the standard interpretation of mobile beads, described above.

For all the samples analyzed, the thermodynamic functions (enthalpy, entropy and Gibbs function) were determined and detailed tables are available from the data bank [1]. The recommended heat capacities for the solid are computed vibrational data, while the melt heat capacities are those determined experimentally, except for bisphenol (RA) where liquid heat capacities were obtained from the empirical addition scheme.

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