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THERMAL ANALYSIS OF THERMOSETTING RESINS

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Applications of thermoanalytical methods for the study of resinification, curing and thermal degradation of phenolic and epoxy resins are reviewed. The curing properties of PF resins and various epoxy systems, determined by thermal methods, are illustrated.

Phenolic and epoxy resins are the most common thermosets utilized by the plastics-processing industry. In the cured state they are infusible, insoluble, covalently-cross-linked, thermally stable network polymer structures. The formation of this network structure is responsible for the desirable physical properties which are typical of thermosetting resins over a broad temperature range.

Owing to their intractable nature, the thermosetting resins are difficult to study by chemical means. Numerous investigations have shown that thermoanalytical techniques offer valuable tools for the study of the formation, the curing characteristics and the thermal degradation of these resins.

The purpose of this paper is to survey the thermoanalytical methods such as differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermogravimetry (TG) and thermomechanical methods, which have been successfully applied to the elucidation of the thermal characteristics of phenolic and epoxy resins.

Phenol-formaldehyde resins

When phenol reacts with formaldehyde four major reactions occur:

a) addition to give methylol phenols;
b) condensation of a methylol phenol and a phenol to give a methylene bridge;
c) condensation of two methylol groups to give an ether bridge;
d) decomposition of ether bridges to methylene bridges and formaldehyde.

The reaction is catalyzed by acids or by bases to give novolacs or resols respectively. The nature of the product is dependent on the type of catalyst and the molar ratio of the reactants. Addition and condensation are exothermic reactions, and therefore thermoanalytical methods are particularly suited for elucidation of thermal effects taking place during the resinification and the subsequent curing reactions. At higher temperatures thermal degradation of the resins occurs which may be followed by TG techniques.

Resinification reactions

Sebenic et al. [1] examined the base-catalyzed reaction between phenol and formaldehyde, using DSC combined with sealed sample cells. A two-peak curve was obtained, which points to two separate reactions namely addition and condensation of methylol phenols. Activation energies determined according to Borchardt and Daniels [2] were found to be 99.2 – 80.8 kJ/mole and 73.6 – 65.7 kJ/mole for addition and condensation reactions, respectively. Reaction orders of 2 and 1 were found for the addition and condensation reactions, respectively.

Erä et al. [3] used DSC and a pressure-tight sample holder to study the acid catalyzed novolac-type reaction between phenol and formaldehyde. A one-peak curve found indicates a simultaneous occurrence of addition and condensation reactions. A value of 94.2 – 100.4 kJ/mol was obtained for the heat of reaction which is in accordance with that measured by other methods [4]. Activation energies of 153.6 – 166.6 kJ/mole were determined for the reaction, which corresponds to the sum for the addition and condensation reactions for base-catalyzed resin. The reaction order of 1 was obtained from a Freeman-Carrol plot [5]. In both above reactions, increase of the amount of catalyst decreases the value of the activation energy.

During a PF resin cook the viscosity of the solution increases owing to the increase in polymer size. A linear correlation has been observed between the viscosity of the resin solution and the heat of reaction of the resin [6]. Further a linear correlation between the heat of reaction and the P/F ratio of the resin indicates that an increased proportion of formaldehyde greatly increases the reactivity of the components.

Curing reactions

Curing properties of PF resins have been studied by different workers using DTA techniques. White and Rust [7] examined base-catalyzed PF resin and found an exothermic peak in the temperature range of 135° – 150°. The area under the peak was related to the degree of curing. The effects of temperature, catalyst level, resin advancement and solids content on the curing rate of PF resin were further illustrated. Nakamura [8] found the presence of endothermic peaks at 70, 125 and 180° for the two-step acid-catalyzed resin. Using a similar DTA technique Katovic [9] reported two exothermic peaks at 148 and 156° in the thermal curve of a base-catalyzed resin. Burns and Orrell [10] examined the curing of PF resins in the presence of hexamine and found several different thermal curves. Using pressure DTA Ezrin and Claver [11] found two exothermic peaks at about 75° and 180° of a resol. More recently Kurachenkov and Igonin [12] studied hardening of the pulverized novolac resin with hexamine under high pressure. Three exothermic peaks were observed, at 50, 120 to 160°, and 230 to 260°. The inconsistent results obtained in these studies are due to the use of different resin components and reaction conditions, different methods of sample preparation and different instrumentation techniques.

Westwood et al. [13–15] investigated the kinetics of curing of resol resins using sealed high-pressure cells in conjunction with DSC. Their findings showed that the heating rate exerted a considerable influence upon the resin exotherm. On increase of the heating rate, a shift of the condensation reaction to higher temperatures was observed. With the use of isothermal methods, an activation energy of 84.5 kJ/mol, a reaction order of 1, a rate constant of 0.16 min^{-1} (140°) and a heat of reaction of 263.7 J/g were deduced for a resol resin at a P/F molar ratio of 1 : 1.2. Further, the type of catalyst and the catalyst level were found to affect the resin exotherm. The curve may show one peak or two overlapping peaks, probably owing to the formation of methylene or ether bridges. The effects of the pH of the solution and the catalyst type on the formation of methylene or ether bridges were illustrated too.

Erä et al. [16] examined the heat of reaction of precured resol resins by employing DSC in combination with hermetically sealed sample cells. A linear correlation was observed between the heat of reaction and the molar ratio of phenol to formaldehyde. Precured resins with a higher proportion of formaldehyde give lower values of the heat or reaction than those having lower F/P ratios. The advancement of resin curing in the precuring stage may be assumed to be an increasing function of the proportion of formaldehyde of the resins. The relationship of the heat of reaction to the gelation time found for a series of freeze-dried resol resins suggests the use of the DSC technique for quality control of paper impregnant solutions.

Thermal degradation

In the thermal degradation of PF resins, even in an inert atmosphere, oxidation plays a major role. The oxygen originates from the initial resin [17].

Lochte et al. [18] investigated the thermal degradations of a series of resol resins using TG techniques. In the temperature range of 100°–300° distinct weight changes were observed owing to the volatilization of water, solvent and other low molecular weight components. In the temperature range 400°–700° the main degradation reactions occurred and identical TG curves were observed for resol resins with varying P/F ratios and other characteristics. It has been suggested that the thermal degradation at higher temperatures depends mainly on the stability of the dihydroxy-diphenyl-methane unit [18]. After completion of curing reaction the resins degrade similarly, despite of their differing compositions.

Friedman [19] has studied the kinetics of thermal degradation of PF resins and concluded that the changes occurring below 400° point to aftercondensation and volatilization processes. The activation energies determined from the TG curves were 209 – 301 kJ/mole and 63 – 73 kJ/mole in the temperature ranges 500° – 607° and 355° – 524° respectively.

Alaminov and Andonova [20] investigated the thermal degradation of both phenolic resins and resins modified with cyanuric acid using DTA and TG techniques. In the modified resin a considerably lower weight change was found up to 330° than in the original resin. At higher temperatures the opposite effect was noted, owing to splitting of the cyanuric ring. The activation energies of 71 – 100 kJ/mole obtained from TG curves correspond to the values found previously for lower-temperature degradation processes.

Thermoanalytical methods alone do not give a full picture of the thermal degradation of phenolic resins. As a complementary tool, the pyrolysis technique combined with gas chromatography is needed for evaluation of the degradation products. By using these techniques activation energies of –67.4 kJ/mole [21] and 63 – 73 kJ/mole [22] were deduced for the thermal degradation of PF resins. The values are in accordance with those resulted in TG-measurements.

Epoxy resins

Epoxy resins are liquid or solid low molecular products from the polymerization of compounds containing one or more epoxy groups with bifunctional aromatic, aliphatic or cycloaliphatic hydroxy compounds. Commercially, the most important are epoxy resins prepared from epichlorhydrin with bisphenol-A, 2,2-bis(4'-hydroxyphenyl)propane. Linear molecules possess free epoxy groups which may be cured by reacting either with amines, or di- and polycarbonic acids or their anhydrides. The reaction is catalyzed by either bases or acids.

Thermoanalytical methods have been used successfully in the elucidation of the degree of curing, the reactivities of resin/curing agent systems, glass transition phenomena and thermal degradation. For the practical use of epoxy resins, the characterization of both resin component and inorganic fillers and the optimization of the amount of curing agents by thermal analysis are of great importance.

Curing reactions

Curing characteristics of epoxy resins have been studied by different workers using DSC techniques. Prime [23] examined an epoxy resin and an aromatic diamine and applied his dynamic kinetic equation for the curing reaction. Activation energies of 51.9 – 64.0 kJ/mole and reaction orders of 0.6 – 1.0 were determined for the reaction. For the heat of reaction a value of 473 – 510 J/g was obtained. Acitelli et al. [24] have concluded that the curing reaction may be diffusion-controlled and occurs in the temperature range of 23 – 157° leading to expansion of the network structure. Barton [25] studied the curing of epoxy/aromatic diamine system by DSC. Activation energies of 49.8 kJ/mole and 52.7 kJ/mole were obtained from isothermal and dynamic measurements respectively which correspond to the values reported previously. Horie et al. [26] investigated the hardening reactions of epoxy resins and aliphatic diamines by isothermal DSC methods. The model reaction between phenylglycidylether and butylamine was further illustrated. They concluded that the advancement of both above reactions takes place via the same mechanism and the hardening reaction becomes diffusion-controlled at the final stages of the process. Activation energies of 54 – 58 kJ/mole were obtained for both reactions and the hardening reaction kinetics were third-order.

Prime et al. [27, 28] examined the curing system of epoxies with polyamide. Three separate curves were obtained, which point to three different stages in the process. A reaction scheme was proposed where the first stage is due to the reaction between amine and epoxy groups, while in two subsequent stages amide bonds are formed. The activation energies of 60.7 – 63.2 kJ/mole determined for the first reaction are of the same magnitude as resulted for the amine curing system. For the heat of reaction, values of 343 – 376 J/g were obtained. More complicated hardening effects have been observed when dicyandiamide is used as a curing agent [29]. This is due to the degradation of dicyandiamide to melamine during the curing process. For the activation energy of this system a value of 54 kJ/mole was reported.

Barton and Shepherd [30] have studied the reactions between epoxy resins and 2-ethyl-4-methyl-imidazole. The results suggested that notable amounts of intermediate products are formed, which act as strong catalysts in the curing process. Dynamic DSC measurements showed that the formation of reaction products followed first-order kinetics and the activation energies were 79 – 92 kJ/mole.

Fava [31] has investigated the curing of epoxies with hexahydrophthalic acid anhydride using isothermal and dynamic DSC-methods. A linear correlation was obtained between the rate of reaction and temperature and an activation energy of 74.5 kJ/mol was deduced for the process. On the basis of isothermal DSC measurements, Malavašič et al. [32] have concluded that the reaction order changes during the advancement of epoxy/anhydride curing. Order of 0.5 and 1 and activation energies of 58.2 kJ/mole and 56.1 kJ/mole were obtained for conversions of 18 – 80% and 80 – 98% respectively. The heats of reactions determined from isothermal DSC curves were 302.2 – 333.2 J/g (107.5°) depending on the components of the reaction system. According to Peyser and Bascom [33] the reaction is second-order despite the two-stage process. From dynamic DSC measurements an activation energy of 62.8 kJ/mole resulted for the first stage of the hardening process with a 12% conversion. After this stage the rate of reaction increases and the activation energy yields a considerably higher value, 159 kJ/mole. For the heat of reaction, the values between 160.3 – 264.5 J/g were obtained, depending on the heating rate. The lowest values are suggested to be due to an incomplete hardening process.

Further, the catalyst type was found to affect both the curing mechanism and the structure of the resin. Variations between the heat of reaction, the activation energy and the kinetic rate have been observed [34]. The concentration of the catalyst affects the kinetic parameters giving an exponential relationship with the temperature [35].

Among different investigators, the opinions as to the kinetics of epoxy resin hardening differ considerably. Whereas the order and the rate constant show considerable discrepancies, most activation energies determined by DSC methods are consistent with the values of 58 – 67 kJ/mole and 58 – 71 kJ/mole obtained from the gel point [36] and electrical resistance [37] measurements. On this basis it can be concluded that the network structure formed has very little effect upon the activation energy of the hardening of epoxy resins.

Glass transition and curing

The polymerization of epoxy resins decreases considerably in the final stages of the reaction, owing to the formation of large amounts of cross-linked molecules. For evaluation of the final steps of curing, the determination of the glass transition point has shown to be of special value. The relationship of the change of the glass transition with respect to molecular weight and cross-linking density has been established [26].

Fava [31] has investigated the curing of the diglycidylether of the bisphenol A/acid anhydride system by DSC. Thermal curves of the partially cured resins showed the shift of Tg to higher temperatures. The glass transition increases in relation to the curing temperature and coincides with the curing temperature at a definite temperature. Simultaneously, the exotherm decreases, indicating aftercondensation. At 400 K no exothermic changes are observed, which shows the completion of curing reaction. Additional studies have shown the relationship between the glass transition and the degree of curing [38], the curing time [39] and the curing temperature [40].

Thermomechanical characteristics

The dynamic mechanical behaviour of the polymer may be determined by torsional braid analysis (TBA) and linear thermal expansion measurements. Both methods have been used for elucidation of the curing process of epoxy resins.

Gillham et al. [41, 42] investigated the curing of epoxy/anhydride systems by using TBA. In isothermal curing at different temperatures, two types of dynamic mechanic behaviour are observed, namely a shift to the glassy state and the gelation of the system. On the basis of the corresponding critical temperatures $T_{g\infty}$, the glass transition, and T_{gg}, the gelation point, three different types of isothermal behavior may be detected, depending on the curing temperature (T_c) as follows:

1) $T_c < T_{gg}$, glass transition only;

2) $T_g < T_c < T_{gg}$, both glass transition and gelation;

3) $T_c > T_{g\infty}$, gelation only.

Similar thermomechanical behaviour has been observed in the curing of bisphenol *A* with aromatic diamines [43]. The gelation time and the maximum curing time determined by TBA are suited for the optimization of the resin formulations [44].

Cuthrell [45] has conducted linear thermal expansion measurements for epoxy/diamine curing system. Two characteristic phase transitions were observed at definite temperatures. The method may be used for following the curing process if the rate of linear expansion is related to the degree of cross-linking of the system.

Thermal degradation

The chemical structures of both the initial epoxy monomer and the curing agent affect the thermal stability of the polymer. TG studies on the diglycidylether of resorcinol showed that replacement of the phenyl group by the of 2,2-diphenylpropyl group decreased the thermal stability. Simultaneously, a shift of the degradation peak to higher temperatures was noted [46].

The type of curing agent affects the activation energy of thermal degradation. The cycloaliphatic epoxy resins degrade according to a multiphase mechanism, and the process may be characterized by an average activation energy of 86.2 – 151.9 kJ/mole, depending on the curing agent [47].

The substituents in epoxy resins decrease the thermal stabilities of the polymers. Brominated epoxy resin degrades at considerably lower temperatures than the initial polymer, owing to the catalytic effect of HBr formed during the degradation process. Thermal degradation takes place in three stages, the respective activation energies being 83.7, 282.5 and 105.9 kJ/mole [48]. In nitro-substituted epoxy resins the similar tendency of decreased thermal stability has been observed [49].

The curing temperature exerts a considerable influence upon the thermal stabilities of epoxy resins. Lee and Levi [50, 51] have determined by TG the overall activation energy of thermal degradation of epoxies as a function of the curing temperature. Values of 83 – 134 kJ/mole were found in the curing temperature range of 100° – 200°. The results of dynamic and isothermal measurements clearly show that resins cured at higher temperatures possess improved thermal stabilities, owing to the more extensive degree of cross-linking attained at elevated temperatures.

Generally, epoxy resins are thermally stable polymers whose degradation temperature are in the range 300° – 400°. By means of TG it is possible to obtain a good picture of the factors such as structural parameters, curing agents and curing conditions which affect the thermal stability of the resin.

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Résumé — On donne un aperçu de littérature sur l'application des méthodes thermoanalitique dans l'examination de formation, durcissement et décomposition thermique des résines phénoliques et epoxydes. On rend compte des caractéristiques de durcissement des résines PF et de divers systèmes d'epoxyde déterminé à l'aide de méthodes thermiques.

Zusammenfassung — Die Literatur über die Anwendung von thermoanalytischen Methoden für die Untersuchung von Bildung, Härtung und thermischen Zersetzung der Phenol/Formaldehyd und Epoxy Harzen wird besichtigt. Die Härtungseigenschaften der PF Harzen und verschiedenen Epoxy Systeme bestimmt auf Basis von thermischen Methoden werden illustriert.

Резюме — Представлено обозрение по применению термоаналитических методов для изучения процессов смолообразования, вулканизации и термического разложения фенольных и эпоксидных смол. Приведены вулканизационные свойства PF резин и различных эпоксидных систем, определенные термическими методами.