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Investigation of the curing kinetics of alkyd–melamine–epoxy resin system

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ABSTRACT

Properties of coatings based on alkyd resin can be improved via blending with other suitable resins. Recent studies assessed that many properties could be improved by blending with epoxy resins as well as with melamine resins. The aim of this work was to investigate the effect of epoxy resin content on the curing process in alkyd–melamine–epoxy three component blends. The coatings with two mixing ratios of alkyd/melamine (70:30 and 80:20) were formulated. They were made into baking enamels by blending with 3 and 5 wt% of epoxy resin on total resin solid. Curring kinetics was investigated by differential scanning calorimetry (DSC) and application of Ozawa isoconversional method. Fourier transform infrared spectroscopy (FTIR) was used to follow major curing reactions. The absorbance of –OH and –N–CH_2R, showed significant reduction and confirmed that the epoxy resin reacts and inserts in enamel structure. It was found that resin system with alkyd/melamine ratio of 70:30 and 3 wt% of epoxy resin has the lowest apparent activation energy of 141.5 kJ mol^{-1} and needs the shortest time of 34.2 min to reach final apparent degree of cure. Isothermal DSC experiments have confirmed these findings. The samples with 30 wt% of melamine resin had higher hardness of baked enamels then samples with 20 wt%. They also showed an increase of hardness with the increase of epoxy resin content.

1. Introduction

Alkyd-based coatings find uses in a large variety of applications, such as architectural and industrial finishes and industrial maintenance. Alkyd resins play important roles as coating binders, mainly for two reasons. Alkyds are extremely versatile with respect to their structures and properties, as they can be synthesized from a variety of natural raw materials and their overall cost is low [1–4]. However, they suffer from some major problems, such as low alkali resistance, long drying times (prepared specially from non-drying oils), moderate adhesion, and low hardness. As alkyd resins have good compatibility with a wide variety of other coating resins (nitrocellulose, amino resins, synthetic latex paints, and silicone resins) the aforementioned properties can be improved via blending with other suitable resins [5].

A combination of an alkyd resin with a melamine formaldehyde resin gives a cured film with the flexibility of the alkyd constituent, while being characterized by the high chemical resistance and hardness of the melamine resin at the same time [6]. The medium-oil-length glycerol alkyd based on Mahua oil fatty acid cured at 140 °C with 20% melamine and the cured resin showed better mechanical properties, adhesion, and was more water and alkali resistant than the commercial alkyd resin [7]. Both the alkyd and melamine resins are complex systems, in which each component can undergo a variety of reactions. Some of the cross-linking reactions are reversible, so that bonds might break and reform many times during cure of a coating, causing network structure to change continuously throughout the process [8]. In the studies of the curing reactions of palm oil alkyd/melamine enamels by Fourier transform infrared spectroscopy (FTIR) formation of methylene ether linkages was identified as the dominant reaction [9]. The amino resins can be combined with alkyd resins modified with non-drying oils such as sunflower oil and coconut oil. The alkyd resin should contain both free hydroxyl and carboxyl groups. The hydroxyl group being functional is responsible for the cross-linking reaction, whereas the carboxyl group being acidic acts as the catalyst [10]. With increases in the content of amino resin the film gains in hardness, chemical resistance and light stability. Increases in the alkyd resin result in increased flexibility and improved adhesion [10]. It has been observed that secondary amino group of the type NH–CH–OR in melamine resin is the necessary condition for resin low temperature curing under strongly acidic condition with the evaporation of alcohol for complete cross-linking [11].

Melamine-formaldehyde resins are most often used as crosslink agents in the blends with hydroxyl functionality resins such as alkyds, thermoset acrylics, hydroxyl terminated polyesters and

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bisphenol A epoxy resins.Epoxy resins are a family of oligomeric materials that can be further reacted to form thermoset polymers having a high degree of chemical and solvent resistance, outstanding adhesion to a broad range of substrates, a low order of shrinkage on cure, impact resistance, flexibility, and good electrical properties. Homogeneous and transparent epoxy/amine hybrid resins were successfully obtained through the *in situ* curing of bisphenol A epoxy and hexakis (methoxymethyl) melamine resin with 2 wt% (3-glycidoxypropyl) trimethoxysilane as a facial coupling agent. The hybrid resins showed good miscibility, high glass-transition temperatures, good thermo oxidative stability, and good flame retardancy [12]. Epoxy resins have been commercially available for more than 50 years and find uses in a diverse range of applications, especially in the adhesive and surface coating industry [13]. They possess better adhesion, alkali and water resistance, thermal stability, mechanical properties, drying times, and so forth than alkyd resins but have inferior acid resistance, gloss. Blending techniques may be used effectively to improve the inferior properties of both resins. Miscible polymer blends produce a new improved material from less superior individual components, but well established miscible polymer blends are very rarely obtained [14,15].

In order to obtain a resin for applications needing high performance properties important factors like the curing degree, time, and temperature of curing process should be considered. For this reason, studies of the curing kinetics of these materials have considerable importance. Differential scanning calorimetry (DSC) is the most popular technique for monitoring curing and has been extensively used in curing studies, especially since the appearance of high pressure crucibles. In an attempt to explain the curing behavior, many mechanistic models have been applied. These models become extremely complex in case of the kinetic analysis where multiple and parallel reactions are in competition and their products can take part in the reaction with the starting reactant [16]. Several authors have applied different approaches based on fitting kinetic data to previously assumed reaction models [17–20]. Nevertheless, this type of approaches has resulted in some inconsistencies as are not effective in explaining complex reactive systems particularities [21]. Thus, empirical models are preferred to study the cure kinetics. If isothermal methods are used it is not possible to conduct the reaction at very high temperatures, since part of the total reaction heat is lost during the stabilization time and so high conversions cannot be attained. If the reaction is carried out at very low temperatures, some of this heat is likewise lost, since the sensitivity threshold of the appliance is low [22]. Dynamic methods do not usually present these problems, but in some cases they are not equivalent to isothermal ones. Model-free kinetics (MFK) is well suited to depict the kinetics of complex reactions such as the cure of resins. In recent years, model-free approaches have been described for the kinetic analysis of the cross-linking of resins such as epoxy [23–25], lignin-based phenolic resins [26,27] and melamine formaldehyde resin [28] based on thermo-chemical data obtained from DSC.

A study of cure kinetics of epoxy resin based on a diglycidyl ether of Bisphenol A (DGEBA), with poly(oxypropylene)diamine (Jeffamine D230) as a curing agent has shown that system with stoichiometric content of amine, can be successfully described with Kamal model [29]. System DGEBA-20a with sub-stoichiometric content of amine showed evidence of two separate reactions, second of which was presumed to be etherification reaction. An autocatalytic equation was applied to determine the isothermal curing kinetics of the diglycidyl ether of bisphenol A/melamine phosphate system (DGEBA/MP). The DGEBA/MP system exhibits autocatalytic behavior in the isothermal curing procedure, whose kinetics fits well with the autocatalytic mechanism [30]. Study of curing kinetics of two epoxy resins with different structures diglycidyl ether with bisphenol A and diglycidyl ether of hydroquinone epoxy resins in the presence of diglycidyl aniline as reactive diluent and triethylenetetramine as the curing agent established that two parameter autocatalytic model is the most suitable for the description of the process [31].

The mechanism and kinetics of cure od aklyd–melamine–epoxy resin have not been elucidated in this way. As known, the curing reaction is a very complex process, because many reactive processes occur simultaneously. The final properties of the crosslinked alkyd–melamine–epoxy resins depend on the kinetics of the curing reaction. The study of the cure kinetics contributes both to a better knowledge of the process development and to improving the quality of the final product. The mechanism and curing kinetics of alkyd–melamine–epoxy resin have not been yet elucidated in this way. The aim of the present paper was to develop a method based on thermal analysis and infrared spectroscopy to elucidate the mechanism of curing of alkyd–melamine–epoxy resin systems. Additionally, Ozawa isoconversional method was employed to calculate kinetic parameters and to analyze how they are influenced by the presence of epoxy resin. Program based on MathCAD software package that automatizes the calculation process of the kinetic parameters in curing reaction was developed.

Table 1
Sample designation and composition.

Sample name	Alkyd/melamine ratio	Amount of epoxy resin (wt%)
A/M/E-7/3/0	70/30	0
A/M/E-7/3/3	70/30	3
A/M/E-7/3/5	70/30	5
A/M/E-8/2/0	80/20	0
A/M/E-8/2/3	80/20	3
A/M/E-8/2/5	80/20	5

2. Experimental

2.1. Materials

In this study, commercially available alkyd, melamine and epoxy resins were used. Alkyd resin, commercial name ®Vialkyd AR 308 is short oil alkyd resin containing 30 mass% castor oil, produced by Cytec Surface Specialties Austria GmbH, was used as a 60% solution in xylene/butanol alcohol mixture. The characteristic of the resin was: acid number on solid resin = 20–30 mg KOH g^{-1}; OH number = 120 mg KOH g^{-1}; dynamic viscosity at 23 °C = 710–1100 mPa s; density (20 °C) = 1.02 g cm^{-1}. Melamine resin, commercial name ®Maprenal MF 514/60IB, produced by Ineos Melamines Gemany GmbH, was used a 60% solution in isobutanol. The characteristic of the resin was: acid number <2 mg KOH g^{-1}; dynamic viscosity at 23 °C = 710–910 mPa s; density (20 °C) = 1.01 g cm^{-1}. A bisphenol A epoxy resin commercial name Araldite® GZ 7071 X 75 (Ciba Geigy, Ltd), was used as a 75% solution in xylene. The characteristic of the resin was: epoxy equivalent = 182–192 g/equiv; epoxy content = 1.49–1.67 equiv/kg; dynamic viscosity at 25 °C = 8000–12,000 mPa s; density (25 °C) = 1.08 g cm^{-1}.

Resin blends were obtained by mixing first appropriate amount of alkyd and melamine resin and then adding small amount of epoxy resin 3–5 wt% on total resin solid, with vigorous stirring. Sample compositions and designations are given in Table 1.

These compositions were chosen since it has been observed that, when a 30% concentration of a ketonic resin was blended with an alkyd resin, a significant improvement in adhesion, hardness, gloss, storage stability, acid resistance, and drying time was achieved over that of the alkyd resin alone [32]. Among various compositions investigated, most favourable coating properties could be achieved with an alkyd/melamine resin ratio of 75/25 [33].