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Synergistic effect of P—S and crosslink density on performance properties of epoxy coatings cured with cardanol based multifunctional carboxyl curing agents

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ABSTRACT

In the present study, phosphorus-sulphur containing di and tetra functional carboxyl curing agents were synthesized from renewable resource, cardanol and used in the preparation of high performance epoxy coatings. Structure of the curing agents was analysed by evaluating its acid and iodine number as well as spectroscopic and chromatographic techniques. Coatings were formulated by varying the ratio of epoxy adduct to curing agents on equivalent basis such as 1:0.6, 1:0.8 and 1:1. Further, the prepared coatings were characterized for mechanical, chemical, optical, thermal, anticorrosive and flame retardant properties. It was concluded that, with increase in concentration of flame retardant curing agents, anticorrosive as well as flame retardant properties of the coatings improved. This enhancement in the properties could be related to the synergistic effect of phosphorus and sulphur as well as chemical structure of curing agents.

1. Introduction

Owing to its excellent solvent and chemical resistance, adhesion to various substrates, superior corrosion resistance, toughness, low shrinkage on cure and good mechanical and insulating properties, epoxy resins are important class of thermosetting polymers [1–3] and finds variety of applications in surface coating, adhesive, laminates, composites, electrical applications, transport and aerospace etc. [4,5] However, their thermal and fire retardant properties need to be improved to maintain their valid status in the advanced applications [6–8].

To confer flame retardancy, generally additive or reactive flame retardants are incorporated in epoxy resins. Inorganic materials such as aluminium trihydrate, magnesium hydroxide, antimony oxides etc. are widely used as additive flame retardants. Major problems with these flame retardants are they require higher loadings which sometimes may result in phase separation as well as increase in viscosity [9]. To resolve this, halogenated flame retardants were incorporated in epoxies. They improved flame retardancy of the system but also generated toxic and corrosive fumes. Due to this they are banned in most of the countries and search for the halogen free flame retardants began [10]. Later, phosphorus based reactive flame retardants were explored and soon received great attention as they are able to sustain the flame retardance for longer time and reduce the influence on physical and mechanical properties of polymers.

In conventional epoxies, phosphorus can be added in the main backbone of epoxy [10–14] or can be incorporated in curing agent [15–20] which would later use for crosslinking epoxy. In both the cases, excellent flame retardancy was achieved however, crosslinking with phosphorus containing compound is much easier than to graft phosphorus on polymer backbone. In this regards, various flame retardant curing agents were developed in the past including phosphated amines [21,22], DOPO and its derivatives, [22–25], phosphazene compounds [26–29] etc.

All these curing agents are based on petroleum resources and needs to be replaced with compounds derived from renewable resources for their sustainable production. Amongst various renewable resources, cardanol is inexpensive, easily available and one of the most commonly used agricultural product derived from cashew nut shell liquid [30]. The presence of phenolic hydroxyl group and C15 alkyl chain makes it suitable for chemical modification through variety of chemistries [31]. Cardanol and its derivatives finds wide applications in the field of coatings, curing agents, antioxidants etc. [32–38]. Recently, cardanol has been modified with various flame retardant compounds to improve flame retardancy of epoxy resins [39], polybenzoxazines [40] and polyurethane foams [41]. It has been concluded that the addition of cardanol based flame retardant, not only improved flame retardant properties but also mechanical properties of the system they were

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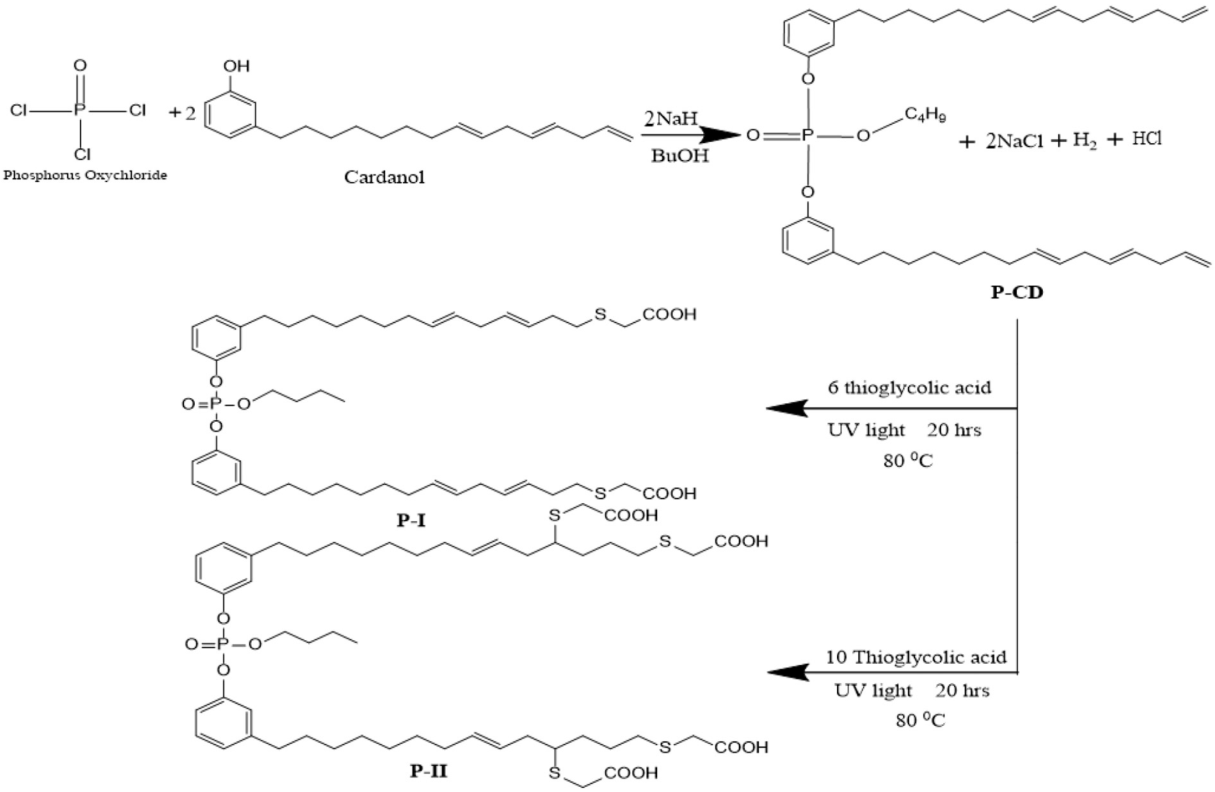

Fig. 1. Schematic representation of preparation of P—S containing multifunctional curing agents.

added in. Despite such advantages of cardanol based flame retardants, their use in flame retardant applications are yet to be explored.

Hence, we have made an attempt to improve flame retardancy of epoxy resin by curing with novel phosphorus-sulphur containing multifunctional carboxyl curing agents. The preparation involved the reaction of cardanol with phosphorus oxychloride followed by thiol-ene reaction of thioglycolic acid across the unsaturation of cardanol. The structure of curing agents were analysed by chemical as well as ^{1}H NMR, ^{13}C NMR, GPC and EDAX analysis. The carboxyl curing agents thus synthesized were mixed with epoxy resin in various proportion and characterized for mechanical, chemical, anti-corrosive, flame retardant properties etc. and structure property relationship was established.

2. Materials and methods

2.1. Raw materials and chemicals

Cardanol (NC-700) was provided by Cardolite Specialty Chemicals Ltd., Mangalore, India. Commercial epoxy resin (diglycidyl ether of bisphenol-A; % solids- 70 and EEW- 180/eq) was kindly supplied by Huntsman India Ltd. Mumbai, India. All the reagent grade chemicals including phosphorus oxychloride, thioglycolic acid, *N*,*N*-dimethylbenzylamine (BDMA), 1,8-Diazabicycloundec-7-ene (DBU), Irgacure-184, sodium hydride, sodium hydroxide, butanol, tetrahydrofuran, ethyl acetate was purchased from SD Fine Chemicals, Mumbai, India. All reagent grade chemicals were used as received without further purification.

2.2. Synthesis of phosphorus containing cardanol (P-CD)

In the first step, 100 ml of THF was poured into the four necked flask fitted with water condenser, thermometer pocket, nitrogen inlet and dropping funnel. The entire assembly was put into an ice bath and stoichiometric amount of sodium hydride was slowly added into the flask. The reaction mixture was stirred using magnetic stirrer. To the above mixture, drop wise addition of cardanol was done for a period of 20–25 min without exceeding the temperature of the reaction mixture beyond 10 °C. After complete addition of cardanol, the temperature of the mixture was gradually increased to 60 °C and the mixture was allowed to stir for an hour. Further, the reaction mixture was again cooled to 0–5 °C and phosphorus oxychloride was added in a drop wise manner for a period of 1–1.5 h. The stoichiometric ratio of cardanol: phosphorus oxychloride: sodium hydride was 2:1:2. After complete addition of phosphorus oxychloride, temperature of the mixture was gradually raised to 70 °C and allowed to stir for 8 h. Further, one mole of butanol was added to the above mixture to block the remaining chlorine atom of $POCl_3$. The product abbreviated as "P-CD" was diluted in ethyl acetate and washed several times with 1% aq. sodium hydroxide solution followed by washings with lukewarm water to ensure complete removal of unreacted species. The formation of product was analysed by chemical and spectroscopic analysis.

2.3. Thiol-ene coupling of P-CD with thioglycolic acid

In the second step, thiol-ene coupling of P-CD was performed in a single necked round bottom flask. Molar ratio of P-CD to thioglycolic acid was varied as 1:6 and 1:10 to prepare di and tetra functional carboxyl curing agents. Entire quantities of P-CD and thioglycolic acid along with 1 wt% (of total batch) Irgacure-184 and 1.5 wt% (of total batch) DBU catalyst were poured into the flask and allowed to reflux at 80 °C for 20 h in the presence of UV light. After completion of the reaction, the products were washed several times with 1% aq. sodium hydroxide solution followed by washings with lukewarm water. The viscous maroon colour products were then analysed by acid and iodine value determination as well as spectroscopic techniques. Products with di and tetra functional curing agents were abbreviated as "P-I" and "P-II" respectively. (as shown in Fig. 1).