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Improvement in flame retardancy of polyurethane dispersions by newer reactive flame retardant

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ABSTRACT

A novel phosphorus containing reactive flame retardant was synthesized and incorporated successfully in polyurethane backbone to obtain flame retardant aqueous polyurethane dispersions (FRPUDs). The reactive flame retardant compound was synthesized by using phosphorus oxychloride (1 mole) and N-methylaminoethanol (3 mole). The structure of synthesized phosphorus containing triol was confirmed by FTIR, ^{1}H NMR and ^{31}P NMR spectrometry. Further, polyurethane prepolymer was modified with phosphorus containing triol compound in various amounts (30, 40 and 50% on equivalent basis) and FRPUDs were prepared. PUD films were applied on wood and mild steel panels and air dried. It was then characterized for mechanical, chemical, thermal and flame retardant properties. It was observed that all FRPUDs exhibited good mechanical properties and improved flame retardancy as compared to the conventional one. The maximum limiting oxygen index (LOI) value of 37 was obtained for FRPUD containing 0.8 mass% of phosphorus and 1 mass% of nitrogen. The flame retardancy was greatly depending on the phosphorus content and increased with increase in phosphorus content.

1. Introduction

Polyurethanes (PUs) are extremely large class of polymers with wide variety of applications including surface coatings, foams, composites, adhesives etc. [1–3]. PU is well known for its excellent hardness, abrasion resistance, low thermal conductivity and low water absorption. However, the flammability of polyurethane is a major concern as it degrades very fast releasing large amount of heat when exposed to fire. Therefore, in recent years, flame retardants are incorporated in polyurethane (PU) to improve its flame retardancy [4–6]. Both, additive and reactive flame retardants are incorporated to impart flame retardant properties to the polyurethanes [7–10]. Various additive flame retardants such as boric compounds [11], aluminium polyphosphate, triphenyl phosphate [12], triethyl phosphate [13], layered silicate [14] expandable graphite [15], melamine and its derivatives [16] were extensively used in the past to improve its flame retardancy. However, additive flame retardants possess certain disadvantages like phase separation due to high loadings, loss of homogeneity, high viscosity of the formulations etc. [17].

Therefore, reactive flame retardants are gaining lots of importance nowadays. For reactive modification of polymer mainly halogenated and phosphorus based reactive flame retardants are generally used. However, some of the halogenated compounds are banned recently due to the toxicity issues associated with them and formation of corrosive smoke when exposed to fire. The phosphorus containing compounds do not possess such issues and are found to be good replacement for halogenated ones, without compromising the other properties of the polymer when incorporated. Incorporation of phosphorus compounds into the polymer is found to result in excellent thermal stability and improved flame retardant properties of the polymer. The phosphorus present in the main chain imparts more flame retardancy and is effective than the one in a side chain [18]. Commonly, phosphorus containing diols are reacted with diisocyanate compounds to prepare flame retardant polyurethanes. Park et al. synthesized two pack polyurethane systems using halogen and phosphorus modified polyesters. Both, halogen and phosphorus containing PU exhibited excellent thermal stability and improved flame retardant properties [19–21]. The regular push for developing more environment friendly and low VOC coatings has forced researchers to switch to UV curable and water based coatings. Randoux et al. synthesized UV curable systems based on PU-acrylate, in which phosphorus containing diol was first reacted with excess of diisocyanate compound and the resultant NCO prepolymer was then end-capped with the acrylate monomer to introduce unsaturation sites for UV curing [22]. Recently, aqueous polyurethane dispersions modified with phosphorus flame retardants were synthesized.

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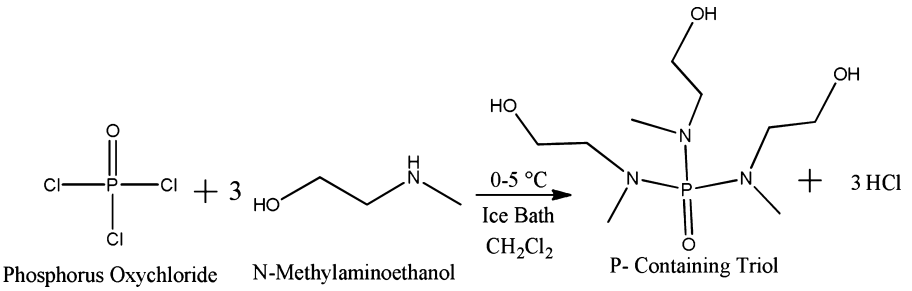

Fig. 1. Schematic representation of the reaction between phosphorus oxychloride and N-methylaminoethanol.

Celebi et al. synthesized reactive flame retardant diol, phosphorus phenyl dihydroxy (PPhDH) and incorporated in carboxyl functional polyurethane backbone to yield polyurethane dispersions. It was observed that with increase in phosphorus content LOI value increased but upto a certain limit after which it decreased. Maximum LOI value of 27 was obtained when phosphorus content in the formulation was 1.5 mass% [23]. Celebi et al. modified PU backbone with an amine functional flame retardant chain extender. The resultant dispersions exhibited excellent flame retardant properties showing maximum LOI of 27 [24]. Shao et al. synthesized aziridine compounds based on phosphorus were suggested as curing agents for PU dispersions. These compounds were introduced at carboxyl pendant of PU Prepolymer [25].

Following research work reveals the synthesis of hydroxyl functional reactive flame retardant based on phosphorus and its incorporation in polyurethane backbone to obtain flame retardant aqueous polyurethane dispersions. Reactive flame retardant containing three hydroxyl groups was reacted with diisocyanate compound and used for preparation of dispersions. The flame retardant aqueous polyurethane dispersions were applied on wood and metal substrates. The performance of coatings was evaluated by characterizing mechanical, chemical, optical, thermal and flame retardant properties.

2. Materials

All the chemicals including phosphorus oxychloride (density: 1.645 g/cm^3, B.P. – 105 ^{0}C), N-methylaminoethanol (density: 0.935 g/cm^3, B.P.-158 °C), diethyl ether, acetone, dimethylol propionic acid (DMPA) (solid powder, M.P.: 189–191 °C), polyethylene glycol (PEG Mol wt: 400), triethylamine (TEA) (density: 0.725 g/cm^3, B.P.: 90 °C), ethylene diamine (EDA) (density: 0.9 g/cm^3, B.P.: 116 °C) were purchased from SD Fine Chemicals Ltd., Mumbai, India and were used as received. Isophorone diisocyanate (IPDI) (density: 1.06 g/cm^3, NCO content: approx. 37.5%) was supplied by Bayer Materials Science, Mumbai, India. Commercial PUD was obtained from Perstorp Chemicals India Pvt. Ltd. (solids: 35%). Conventional PUD is synthesized in laboratory using same raw materials as that of FRPUDs but only without any flame retardant compound.

3. Experimental

3.1. Synthesis of phosphorus containing reactive flame retardant

In the first step, stoichiometric amount of N-methylaminoethanol (3 mole) dissolved in dichloromethane was reacted with phosphorus oxychloride (1 mole) in an ice bath as shown in Fig. 1. The temperature was maintained at around 0–5 °C throughout the reaction. To attain maximum conversion, the reaction was allowed to stir overnight (18–20 h) at 400 rpm. After completion of the reaction, the product obtained was filtered to separate quaternary ammonium salt out from the reaction mixture. Further, the filtrate was washed with diethyl ether to remove unreacted compounds.

3.2. Synthesis of flame retardant aqueous polyurethane dispersions (PUDs)

Synthesized trihydroxy functional phosphorus containing reactive flame retardant was then used for preparation of flame retardant aqueous polyurethane dispersions. Raw materials selected for formulations were DMPA, IPDI, PEG-400, dibutyl tin dilaurate as a catalyst, EDA as a chain extender and TEA as a neutralizing agent. Various formulations were designed by replacing part of conventional polyol (in this case PEG-400) with reactive flame retardant compound on equivalent basis but maintaining NCO/OH ratio constant in all the formulations. Recipes of all the PU formulations are given in Table 1.

Aqueous polyurethane dispersions were synthesized using Acetone Process [26,27]. The reaction was carried out in a four necked flask equipped with condenser, mechanical stirrer, thermometer and nitrogen inlet. In first step, all the reagents including DMPA, PEG-400, flame retardant compound and acetone were charged in a flask and stirred till homogeneous mixture was obtained. The mixture was then heated to 60–65 °C. Stoichiometric amount of IPDI and required amount of DBTDL was then added to the above mixture drop wise for next one hour. The reaction was continued till isocyanate content reached to its theoretical value and was evaluated by dibutylamine back titration method according to ASTM D 2572-97. Once the desired isocyanate value was attained, the temperature was lowered to 50 °C and chain extension was allowed using ethylene diamine for next 50 min. Finally neutralizing agent, triethylamine was added to make the prepolymer water dispersible. These flame retardant aqueous PUDs were applied on wood panels and were air dried. The cured coatings were evaluated for mechanical, optical, chemical and flame retardant properties.

Table 1
Formulation for flame retardant polyurethane dispersions.

Raw materials	Mol. wt	Eq. wt	No. of NCO and/or OH equivalents			
			Conventional	PUD-30	PUD-40	PUD-50
IPDI	222	111	4.4	4.4	4.4	4.4
PEG-400	400	200	**1.3**	**0.91**	**0.78**	**0.65**
FROH	269	89.67	–	**0.39**	**0.52**	**0.65**
DMPA	134	67	0.7	0.7	0.7	0.7