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Coating characteristics of electron beam cured Bisphenol A diglycidyl ether diacrylate-co-aliphatic urethane diacrylate resins

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ABSTRACT

Electron beam (EB) was used to cure coatings of Bisphenol A diglycidyl ether diacrylate (BDGDA) containing varying proportions of aliphatic urethane diacrylate (AUA). The cured BDGDA-co-AUA polymer coatings were characterized by Fourier transformed infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), gel fraction and swelling estimation techniques. FTIR study showed that the coating formulations were completely cured at a dose of 420 kGy. The effect of AUA on the end use performance properties of BDGDA coating namely, abrasion resistance, specular gloss at 60° angle, tubular impact resistance, pencil hardness, pendulum hardness, scratch resistance, mar resistance, stain resistance, steam resistance and cigarette burn resistance was also investigated. It was observed that incorporation of urethane acrylate oligomer in the epoxy acrylate formulation improved abrasion resistance, gloss and impact resistance. However, scratch resistance, mar resistance and hardness of the BDGDA coatings decreased due to incorporation of AUA. All coating formulations exhibited excellent stains and steam resistance properties, but showed poor cigarette burn resistance.

1. Introduction

The conventional thermal curing processes use solvent-based chemical formulations, which creates environmental pollution by emitting a large amount of volatile organic compounds (VOC) and other hazardous air pollutants (HAP) into the atmosphere [1–4]. As environmental and public health concerns have become major issues in the coating processes, the radiation curing process has been found to be an effective alternative to solvent borne technology in the coating industry. Radiation curing is a polymerization/cross-linking process, initiated by high-energy radiation, to convert a reactive liquid chemical system into a non-tacky solid cross-linked network at room temperature with virtually zero emission of VOC or HAP since these systems are 100% reactive and usually contain no solvents. Radiation curing process, namely, electron beam and UV curing, offers many advantages over the thermal curing process, in relation to the ecology or environment, energy conservation, economics and in the excellent performance of products [5–14]. Further, EB curing offers advantages over UV curing such as no requirement of photo-initiators, possibility of curing of thick coatings and better process control [15].

EB curable formulations typically consist of an oligomer or prepolymer and reactive monomers. The oligomer is mainly responsible for the performance properties of the cured film. EB curing of resins containing acrylate end groups have been the subject of interest of many research groups recently because of mainly two reasons [16]. The first is the benefit offered by the EB curing process and second is a wide range of properties achieved by proper selection and combinations of the oligomers [17,18]. Epoxy acrylates and urethane acrylate resins, in particular, have been the backbone of radiation and electron beam cured coatings for over 20 years. Both the resins have their distinct properties. Epoxy acrylate resins generally are high viscosity reactive oligomers due to the strong hydrogen bonding through secondary hydroxyl groups [19] and produce hard, glossy and chemical resistance coating, whereas, aliphatic urethane acrylate is a low viscosity oligomer that provides soft and flexible coating with low shrinkage, high toughness and excellent weatherability. Due to rigid and brittle nature, epoxy resins exhibit low toughness, and poor wear and crack resistance in a real application [20–22]. To overcome these problems, a considerable amount of work has been carried out in the direction of toughening epoxies, with some research focused on introducing rubbery and flexible components into epoxy networks in an appropriate ratio [23,24]. Oligomer BDGDA has high viscosity at application temperature; hence, its viscosity is modified preferably by the addition of low viscosity multifunctional reactive monomers [25]. However, these reactive diluents show higher volatile content compared to oligomers and create shrinkage and brittleness in the coating at a higher content of reactive diluents, resulting in reducing adhesion and deterioration of gloss and aesthetic look of the coating [19,26,27]. On the other hand, aliphatic urethane acrylate, a low

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viscosity oligomer with low volatile content and unique coating properties, could be used to reduce the viscosity of BDGDA resin as well as to regulate or even improve certain properties of BDGDA coating by optimized combination of both the oligomers. To the best of our knowledge, no detail work has been reported on the use of low viscosity oligomer like AUA to regulate the performance property of the electron beam cured BDGDA coating. However, modification of epoxy acrylate oligomer by a chemical reaction of secondary hydroxyl groups with the isocyanate group from diisocyanates in order to produce more flexible and lower viscosity epoxy–urethane acrylate oligomer, have been reported [19]. Incorporation of acrylate-terminated urethanes, as a flexibilizer, was reported to improve toughness of heat cured epoxy resins and it was found that bulk properties, such as the glass transition temperature and tensile stress relaxation behavior of such toughened epoxies are strongly dependent on the characteristics of the flexibilizer used [28,29]. It was also reported that the mechanical properties like impact strength and elongation at break of epoxy–urethane acrylate interpenetrating polymer networks increase and glass transition temperature decreases with the increase in the content of urethane acrylate resin and these properties depend on the compatibility between two components [30].

In light of these reports, we have targeted the improvement of certain end use performance properties of EB cured BDGDA coating by the simple physical blending of AUA with BDGDA before electron beam curing reaction. Therefore, the objective of the work was to use a low viscosity AUA oligomer to adjust and regulate the application viscosity of BDGDA for better applicability of the coating and the study of the effect of AUA concentration on end use performance properties of BDGDA coatings.

2. Experimental

2.1. Materials

The oligomers used to prepare different coating formulations were procured from M/s Cognis Corporation, USA, with the chemical structures and properties given in Scheme 1. The composed veneer plywood samples from Durian industries limited and glass plates were purchased from local suppliers, Mumbai, India.

2.2. Electron beam curing of epoxy acrylate resin

Oligomers BDGDA and AUA were mixed in different proportions with continuous stirring at ~40 °C to get homogeneous mixtures. Different coating formulations, namely, A, B, C, D and F were prepared by mixing 10, 20, 30, 40 and 50 phr AUA in BDGDA oligomer, respectively (Table 1). These formulations were applied onto wood and glass samples of desired sizes using a doctor blade film applicator (Elcometer, UK). The coated samples were cured at 420 kGy dose using electron beam accelerator ILU-6, BARC, at beam current = 2.0 mA, beam energy = 1 MeV, dose rate = 20 kGy/pass and conveyor speed = 1.5 cm/s.

Table 1
Thermogravimetric analysis: decomposition temperature at different percentage weight loss of coatings with varying ratios of BDGDA and AUA, cured at 420 kGy electron beam dose under aerated conditions

Coating formulations	BDGDA/ phr	AUA/ phr	Temperature (°C)			
			10% wt. loss	20% wt. loss	80% wt. loss	90% wt. loss
A	100	0	373	400	455	519
B	100	10	361	392	453	520
C	100	20	342	378	441	470
D	100	30	341	385	439	468
E	100	40	340	381	438	466
F	100	50	339	380	439	456

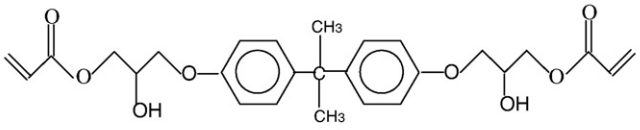
The thickness of the EB cured coatings was found to be ~50 μm as estimated by a thickness gauge 'coat measure M12' (Yuyutsu, JAPAN). Non-tacky coatings (A to F) with no visible shrinkages on the surfaces were obtained under optimized electron beam curing conditions described above. Incorporation of AUA did not affect the EB curing behavior of BDGDA oligomer.

2.3. Fourier transformed infrared spectroscopy (FTIR)

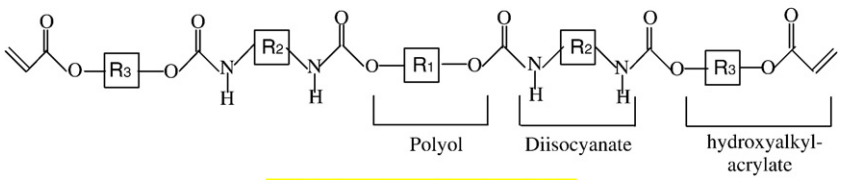
Fourier transformed infrared spectroscopy (FTIR) measurements were performed on a FTIR spectrophotometer (FT/IR-660 from JASCO, Japan). FTIR spectra were recorded in the range 400–4000 cm^{-1} with a resolution of 4 cm^{-1} and averaged over 100 scans. Cured film samples were thoroughly ground at liquid nitrogen temperature and mixed with KBr to prepare discs by compression. In case of the uncured liquid coating formulations, samples were dissolved in acetone and then a drop of sample was sandwiched between two KBr discs and dried to record the spectra.

2.4. Thermogravimetric analysis (TGA)

The non-isothermal thermogravimetric measurements were carried out with Mettler thermogravimetric analyzer (TG 50) coupled with a Mettler TC 10A processor to determine the thermal degradation behavior of BDGDA-co-AUA coatings. The thermograms were recorded in air atmosphere at a heating rate of 10 °C min^{-1} in the temperature range 50–700 °C.



Bisphenol A diglycidyl ether diacrylate (BDGDA)
(Viscosity=8.0 Pa.s (at 60°C), volatile content=1.0 %, specific gravity=1.17 g.ml^{-1}(at 25°C))



(Aliphatic urethane diacrylate (AUA)
(Viscosity=13 Pa.s (at 25°C), volatile content=2.0 %, specific gravity=1.13 g.ml^{-1}(at 25°C))

Scheme 1. Chemical structure and properties of BDGDA and AUA oligomers.