

Organic/inorganic nanocomposite coating of bisphenol A diglycidyl ether diacrylate containing silica nanoparticles via electron beam curing process

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ABSTRACT

The paper presents the fabrication of organic/inorganic nanocomposite coatings via a solvent free, environment benign-electron beam curing process using Bisphenol A diglycidyl ether diacrylate (BDGDA) as an oligomer, 1,6-Hexandioldiacrylate (HDDA) as a reactive diluent, and SiO₂ nanoparticles as inorganic nano-reinforcing component. Silica nanoparticles were modified by ⁶⁰Co-gamma radiation induced grafting of glycidyl methacrylate (GMA) and 2-hydroxyethyl methacrylate (HEMA), before dispersing them into coating compositions for their better compatibility with coating formulations. Surface modified silica nanoparticles were characterized by FTIR spectroscopy and thermogravimetric analysis (TGA). The rheological behavior of coating formulations was evaluated using Brookfield viscometer; formulations with surface modified SiO₂ nanoparticles exhibited pseudoplastic type non-Newtonian behavior. EB cured nanocomposite coatings were characterized by TGA, differential scanning calorimetry (DSC), atomic force microscopy (AFM), scanning electron microscopy (SEM) and contact angle (wettability) measurement. AFM and SEM analysis showed that the dispersion of silica nanoparticles in the coatings improved after surface modification. DSC analysis showed that the modification of SiO₂ increased the glass transition temperature (*T_g*) of the EB cured coatings. Coatings were further analyzed for performance properties, viz. abrasion resistance, gloss at 60° angle, pencil hardness, pendulum hardness, chemical and steam resistance properties, as per standard test methods. It was found that incorporation of silica nanoparticles into coating formulation improves abrasion resistance significantly. Gloss of coating reduced significantly upon addition of silica nanoparticles suggesting that the silica nanoparticles could be used as effective matting agent. Moreover, modification of silica nanoparticles further improved abrasion, pencil hardness and gloss significantly. EB cured nanocomposite coating passed chemical and steam resistance tests and exhibited excellent chemical and stain resistance properties.

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1. Introduction

The conventional curing formulations are generally based on isocyanates, epoxies or other polymeric resins mixed with different organic solvents, such as toluene, methyl ethyl ketone and acetates. Curing of these formulations to get solid coatings is achieved using hot forced air ovens or infrared heaters to evaporate the solvents in the form of volatile organic compounds (VOC) and other hazardous air pollutants (HAP) into the atmosphere. As environmental and public health concerns have become major issues in the coating processes, various advanced coating technologies, including radiation curing process have been proposed as alternative to the conventional solvent borne thermal curing process [1–4]. Furthermore, increased awareness regarding the environment, energy conservation, economics and better performance of products has

emerged as the driving force to switch from conventional curing to radiation curing process [1–5]. Radiation curing is a polymerization/crosslinking process initiated by radiation energy to convert liquid chemical system into non-tacky solid matrix. A large number of reports are available in the literature on radiation cured coatings including UV curing and EB curing [6–9]. However, EB curing offers certain advantages over UV curing, such as instantaneous complete curing, no requirement of photoinitiators, and possibility of curing of thick and pigmented coatings. Considering these advantages of EB curing, several research groups have studied varieties of EB curable resins including acrylates, methacrylates, vinyl esters and epoxies to develop high-performance polymer matrix composites for novel applications [8–11].

Properties of EB cured coatings can be further improved by fabrication of nano-composite coatings through incorporation of inorganic nano-fillers in the coating formulation [12–15]. Most widely used inorganic nano-sized reinforcing fillers include SiO₂ nanoparticles, [14–17], clays, [12] and carbon nanotubes [18] among others. In the conventional composites, the filler and polymer combine on micro scale, which results in poor

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interaction at the interface of organic matrix and reinforcing filler. The poor interaction results in weak adhesion between two components and hence drops performance properties. The macroscopic reinforcing elements cause structural imperfections. These structural imperfections however diminish as the size of reinforcing element decreases. In principle, the ultimate properties of reinforced composite elements may be expected if filler dimension reaches molecular or atomic levels. Nano-composite materials that exhibit a change in structure and composition over nanometer scale (1–100 nm) have been reported to show remarkable enhancement in hardness, scratch resistance, wear and abrasion resistance, impact resistance, gas barrier properties, flame retardancy, mechanical properties and electrical properties that arise from the synergism between the properties of the components [12–18]. The extent of property enhancement of inorganic/organic nano-composite depends on two factors: (i) how uniformly the nano-fillers are distributed inside the polymer matrix and (ii) how strong is the interaction between the fillers and the matrix.

Generally, silica nanoparticles are hydrophilic in nature due to surface OH groups, and therefore, are difficult to disperse homogeneously in apolar organic polymer resins due to intrinsic non-compatibility between the two components. In addition, due to high specific area of nanofillers, the probability of agglomeration is quite high. Physical mixing of SiO₂ nanoparticles and polymer resin, where the shear forces are too low to break up agglomerates leads to inhomogeneous, viscous and sticky solution which yields nanocomposites with properties even poorer than that of neat resin. Therefore, the SiO₂ nanoparticle surfaces need to be modified beforehand using different processes involving some specific chemical coupling agents, which can improve the compatibility, dispersion as well as interaction between two components [17,19]; examples of the coupling agents include trialkoxy silanes having acrylate end group like 3-methacryloxypropyltrimethoxysilane [20], trimethylchlorosilane, dimethyloctylchlorosilane, 3-aminopropyltrimethoxysilane, etc. [21]. Aim of the present study is to develop organic/inorganic nanocomposites coating by radiation (EB) curing method using epoxy acrylate resin and silica nanoparticles. In order to improve the performance properties of the nanocomposite coating, silica nanoparticle surfaces were modified via radiation induced grafting of vinyl monomers for their better compatibility with the polymer resins [16].

2. Experimental

2.1. Materials

The oligomer Bisphenol A diglycidyl ether diacrylate (Photomer 3016, Cognis Corporation) and reactive diluent 1,6-Hexanediol diacrylate (Photomer 4017, Cognis Corporation) and silica nanoparticles (particle size = 20 nm, specific surface area = 400 m²/g, Aldrich) were used as received without further purification. The chemical structures of oligomer and reactive diluent are given in Fig. 1.

2.2. Surface modification of SiO₂ nanoparticles

Surfaces of SiO₂ nanoparticles were modified by radiation induced grafting of vinyl monomers, namely, glycidyl methacrylate (GMA) and 2-hydroxyethyl methacrylate (HEMA) using ⁶⁰Co- γ radiation source. A known amount of vacuum dried (150 °C, 24 h) silica nanoparticles were mixed with dilute solution of vinyl monomers in acetone (~2%, v/v) under vigorous stirring in a high speed mechanical stirrer. The mixture was irradiated by ⁶⁰Co γ -ray at a dose rate of 2.5 kGyh⁻¹ at room temperature. After being

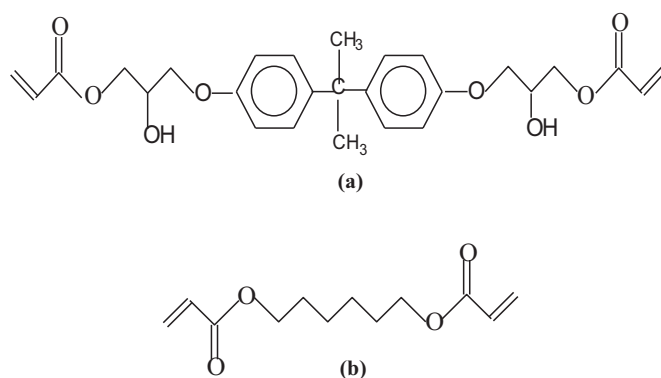


Fig. 1. Chemical structures of (a) bisphenol A diglycidyl ether diacrylate (BDGDA) and (b) 1,6-hexanediol diacrylate (HDDA).

exposed to a total radiation dose of 20 kGy, solution containing grafted silica nanoparticles was centrifuged and washed in acetone by stirring and centrifuging several times, finally dried and characterized by FTIR and TGA.

2.3. Preparation of polymeric nanocomposite coating

Silica nanoparticles (5%, w/w) pre-dispersed in acetone were mixed in epoxy acrylate based resin BDGDA containing 30 phr of HDDA at 50 °C under intensive stirring for 8 h. It was observed that the untreated silica particle resulted in a thick, viscous and inhomogeneous mixture with lump like structures, due to incompatibility of unmodified SiO₂ nanoparticles with the resin. On the contrary, the surface modified silica particles gave homogeneous mixture suggesting better compatibility. The coating formulations containing silica nanoparticles were applied onto glass plates using doctor blade film applicator (Elcometer, UK) and subsequently cured with electron beam (ILU6 EB Accelerator) to get non-tacky coatings, at irradiation parameters: EB dose = 400 kGy, beam current = 2 mA, beam energy = 1 MeV, dose rate = 20 kGy/pass and conveyor speed = 1.5 cm/s. The thickness of the EB cured coatings was found to be ~100 μ m as estimated by a thickness gauge 'coat measure M12' (Yuyutsu, Japan).

2.4. Fourier transformed infrared spectroscopy (FTIR)

Fourier transformed infrared spectroscopy (FTIR) measurements were performed on a FTIR spectrometer (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. Silica nanoparticles were thoroughly mixed with KBr powder and discs were prepared in a compression die press for FTIR measurements carried out in transmission mode.

2.5. Thermogravimetric analysis (TGA)

The non-isothermal thermogravimetric (TG) measurements were carried out with Mettler thermogravimetric analyzer (TG 50) coupled with a Mettler TC10A processor to determine the thermal degradation behavior of EB cured coatings. The thermograms were recorded in air atmosphere at a heating rate of 10 °C min⁻¹ in the temperature range 50–800 °C.

2.6. Differential scanning calorimetry (DSC)

Glass transition temperature (T_g) of the samples was determined by a differential scanning calorimetry (DSC) using Mettler-Toledo DSC 823e system. For all experiments, ~10 mg of

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