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Study of performance properties of itaconic acid based acrylic-modified polyester for industrial baking finishes

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ABSTRACT

Itaconic acid based unsaturated polyesters have been synthesized followed by their co-polymerization with commonly used acrylic monomers. Series of such acrylic-modified polyesters have been prepared and examined their physical and performance characteristics. Apart from determining various physico-chemical characteristics, these resins were also characterized for their molecular weight distribution and grafting of acrylic on polyester using gel permeation chromatography (GPC) and FT-IR techniques respectively. The performance of cured film and the effect on cross-linking density of the synthesized acrylic-modified polyesters were investigated through dynamic mechanical analyzer (DMA) using melamine formaldehyde resin as a cross-linker at elevated temperature. The resultant polymeric film showed excellent hardness, flexibility, impact resistance, adhesion, and cupping with improved weathering resistance over non-acrylated polyester.

1. Introduction

Conventionally thermosetting acrylics and polyester resins in combination with amino resin or blocked isocynate are widely used in variety of industrial baking finishes for household appliances, coil coatings, auto OEM, auto ancillary, etc. Such coatings are primarily designed to meet the performance criteria in line with service life expectation of the coated object.

Polyester is the most commonly used resin in pre coated metal (PCM) application for its excellent mechanical performance and workability during the coating process. Since polyesters provide better hardness, adhesion, flexibility and impact resistance and acrylics impart superior weathering, it was considered to incorporate acrylic functionality into the polyester backbone to enhance overall performance.

There are number of research articles and patents available on the preparation of acrylic-modified polyesters [1–11] and aqueous acrylic-modified polyesters [12–22] meant for powder coatings [3], antifouling coatings [4], PCM [9], protective coatings [11], automobile coatings [19] and textile coatings [18,21]. These research articles generally deal with various synthetic routes like: (1) acrylation of unsaturated polyester, wherein unsaturated polyesters are synthesized by reacting polyester polyol with glycidyl methacrylate [2,7]/isocynato methacrylate [4]/maleic anhydride or fumaric acid [1,6,8–10]. (2) Condensation of hydroxyl polyester with acrylic resin using trans-esterification catalyst [3]. Unsaturated polyester based on maleic anhydride or fumaric acid have been commonly studied by several researchers for their subsequent acrylic grafting for coating application. However, itaconic acid based unsaturated polyesters are not vastly studied for their potential applications in baking finishes.

In the present work, base polyester was synthesized and reacted with itaconic acid to obtain unsaturated polyester intermediate. Such unsaturated polyester was grafted with acrylic monomers in various concentrations resulting in a series of acrylic-modified polyesters. These resins were characterized for their physical properties, molecular weight through gel permeation chromatography (GPC) and grafting of acrylic on polyester through FT-IR.

Designed acrylic-modified polyesters were also cured with melamine formaldehyde resin (MF) in various ratios at elevated temperature. Clear coatings thus obtained were tested for mechanical properties. The effect of varying grafting percentage of acrylics on polyester as well as varying curing ratios of acrylic-modified polyester to MF on cross-linking density of the polymer film was investigated using DMA analysis.

2. Experimental

2.1. Materials

Itaconic acid (Multichem Specialty Ltd., Mumbai) was used as such for incorporation of unsaturation into polyester. Diethylene

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glycol (India Glycols Ltd.), neopentyl glycol (Perstorp Chemicals), trimethylol propane (Perstorp Chemicals), isophthalic acid (Perstorp Chemicals) and adipic acid (Chemo India) were used for synthesis of polyester without further purification. Styrene (Bayer ABS Ltd.), methyl methacrylate (Vam organic Chemical Ltd.), Butyl acrylate (BASF chemicals) and tert-Butyl peroxybenzoate (Trigonox C, AkzoNobel Polymer Chemicals) were used as such for acrylic modification.

Setamine US 138 BB70 (partially butylated melamine formaldehyde resin, Nuplex) was used as cross-linker and Cycat 600 (CYTEC) as catalyst in baking system.

2.2. Preparation of acrylic-modified polyester

Acrylic-modified polyester was synthesized as described below (Scheme 1).

2.2.1. Synthesis of unsaturated polyester

Unsaturated polyester resin was synthesized in two stages. The first stage involves the synthesis of pure polyester followed by the itaconic acid modification in the second stage. This process is followed because itaconic acid is bio-based poly acid and decomposes above its melting point (162 °C) [23]. If itaconic acid is added along with other polyacids and polyols and processed at high temperature (225 °C) then it can undergo decomposition/isomerization due to unsaturated C–C bond.

In first stage, the synthesis of polyester polyol (PE) was carried out in 500 mL four-necked kettle. Kettle was equipped with a temperature controller, heating mantle, nitrogen purger, overhead stirrer and Dean Stark assembly. Polyester monomers such as, diethylene glycol (DEG), neopentyl glycol (NPG), trimethylol propane (TMP), isophthalic acid (IPA), adipic acid (AA), dibutyl tin oxide (DBTO) as esterification catalyst and o-xylene as azeotropic solvent were added into the reactor and the temperature was initially set at 160 °C for 1 h. Subsequently, the reaction temperature was increased from 160 to 225 °C for 4 h. During the polyester synthesis, the batch was monitored on acid value and viscosity (70% in o-Xylene at 25 °C on Gardner Scale).

In the second stage, polyester resin and itaconic acid (ItA) were charged into the reactor vessel. The reaction was carried out at 150–160 °C for 2–3 h to incorporate unsaturation into the polyester backbone. Unsaturated polyester intermediate, i.e. itaconic acid polyester has Gardener viscosity of Y-Z1 @ 70% solids and an acid value of 16 mg KOH/g.

2.2.2. Synthesis of acrylic-modified polyester (AMP)

Acrylic-modified polyester was synthesized by solution polymerization technique using a free radical initiator. A mixture of styrene, methyl methacrylate (MMA), butyl acrylate (BA) and tert-butyl peroxy benzoate (TBPB) were added drop wise into the unsaturated polyester resin at 140 °C for 3 h followed by 2 h digestion at same temperature for complete conversion of monomers. Clear polymers were obtained showing complete homogeneity in the resins. Series of acrylic-modified polyesters (AMP) were prepared using compositions shown in Table 3.

2.2.3. Preparation of the acrylic-modified polyester coating

Acrylic-modified polyesters were cross-linked with melamine formaldehyde resin (MF), i.e. Setamine **US**-138 BB-70 at 70:30 and 80:20 ratios. Clear films of 30–35 μm dry film thickness (DFT) were applied on mild steel panel and baked at 140 °C for 30 min. Cured films were characterized for mechanical properties and cross-link density.

2.3. Test methods

2.3.1. Characterization of acrylic-modified polyester

Molecular weight and polydispersity of AMPs were measured using Varian Pro star Model No. 210 GPC instrument equipped with an auto sampler, pump, RI detector and PL gel column. Polystyrene and poly (methyl methacrylate) were used as a calibration standards. Tetrahydrofuran was used as an eluent with the flow rate of 1 ml/min.

FTIR spectra were recorded using PerkinElmer-Spectrum One instrument in spectral range 4000–650 cm^{-1} with resolution of 4 cm^{-1}.

2.3.2. Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis (DMA) was performed using Dynamic Mechanic Analyzer Q-800 (TA-instrument, USA. Test method was a tension-film mode under conditions; a frequency of 1 Hz, strain of 0.3% and temperature from −60 to 150 °C at the rate of 3 °C/min). For DMA analysis, film was coated on silicon release paper using 150 μ applicator and cured at 140 °C for 30 min.

2.3.3. DSC analysis

Thermal analysis was carried out using DSC Q-10 (TA instrument, USA) under a nitrogen atmosphere.

2.3.4. Hardness test

Scratch hardness of the cured polymeric film was tested using Sheen make automatic scratch tester Ref. No. 705 with 1 mm tungsten carbide tip. The results are given in Table 5.

2.3.5. Adhesion test

The cross-hatch adhesion test was performed on the coated steel panels after 7 days of application. The test was carried out according to ASTM D 3359. The distance between cuts is 1 mm with a cutting guide. The classification of adhesion test results is 0B when over 65% flaking of the cross-cut area is occurred and 5B when no flaking is observed. The rating of 1–4B was for in between results based on extent of flaking. The results are given in Table 5.

2.3.6. Flexibility test

Flexibility of the cured films was evaluated using the conical Mandrel bend test (ASTM D522) and Erichson Cupping tester (Model 202, as per BS 3900: Part E4: 1969). The cured films were placed over the 1/8 in mandrel with the uncoated side in contact with mandrel and was bent 180° around it. The bent plates were examined visually for cracks or loss of adhesion. If film passed through 1/8 in mandrel then it was said to pass the flexibility test. The results are given in Table 5.

2.3.7. QUV test

Cured films of acrylic-modified polyesters were evaluated for accelerated weathering resistance (QUV 313B, ISO 4892/3, light source: UV B (313 nm), irradiance: 0.63 W/m^2, cycle: 8 h light at 60 °C and 4 h condensation).

3. Result and discussion

3.1. Preparation of acrylic-modified polyester

In order to synthesize acrylic-modified polyester resin, polyhydric alcohol, e.g. NPG, DEG, TMP and a polybasic acid IPA and AA were condensed to give the polyester polyol (Table 1). Key physical properties of the above synthesized polyester polyol is listed in Table 2. Polyester resin was then reacted with unsaturated polybasic acid (ItA) to give the unsaturated polyester resin intermediate having the carbon–carbon double bond. In earlier reports