Properties of radiation curable hyperbranched polyurethane acrylate from palm oil oleic acid Postprint

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Abstract

Radiation curable hyperbranched urethane acrylate (HBPUA) from oleic acid of palm oil was synthesized aided by p-toluene sulfonic acid as a catalyst. This mixture was then used as the core (HBP-1) and reacted with palm oil oleic acid to form the hyperbranched polyol (HBP-2). HBPUA was prepared by reacting HBP-2 resin with diisocyanate and hydroxyl-containing acrylate monomer with the presence of 0.1 2wt% dibutyltin dilaurate as a catalyst. The reaction was confirmed by several analytical data i.e. hydroxyl value (OHV), Fourier Transform infrared (FT IR) spectroscopy gel permeation chromatography (GPC) and nuclear magnetic resonance (NMR) spectroscopy analyses. The HBPUA was easily curable when subjected to electron beam (EB) or ultraviolet (UV) radiation.

Full Text

Preamble

Properties of Radiation Curable Hyperbranched Polyurethane Acrylate from Palm Oil Oleic Acid

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Abstract

Radiation curable hyperbranched urethane acrylate (HBPUA) was synthesized from oleic acid of palm oil with p-toluene sulfonic acid as catalyst. This mixture served as the core (HBP-1) and was subsequently reacted with palm oil oleic acid to form the hyperbranched polyol (HBP-2). HBPUA was prepared by reacting HBP-2 resin with diisocyanate and hydroxyl-containing acrylate monomer in the presence of 0.1–2 wt% dibutyltin dilaurate as catalyst. The reaction was confirmed through several analytical methods including hydroxyl value (OHV) determination, Fourier Transform infrared (FTIR) spectroscopy, gel permeation chromatography (GPC), and nuclear magnetic resonance (NMR) spectroscopy. The HBPUA was readily curable upon exposure to electron beam (EB) or ultraviolet (UV) radiation.

Key words: Radiation, Hyperbranched polymers, Oleic acid, Urethane acrylate

Introduction

In recent years, vegetable oils have emerged as promising raw materials for resin production. The long fatty acid chains in vegetable oils impart desirable flexibility and toughness to otherwise brittle resin systems such as epoxy, urethane, and polyester. Linear palm oil-based urethane acrylate resin has been employed as a prepolymer for free radical polymerization with encouraging results [1]. However, the curing speed and hardness of the resulting films remain relatively low compared to commercial resins. Hyperbranched polymers have attracted considerable attention due to their benefits of low viscosity, good solubility, and highly branched molecular structures containing numerous functional end groups that facilitate chemical modification. Among all classes of acrylic oligomers, urethane acrylates exhibit the highest mechanical strength and chemical resistance. The objective of this work was to synthesize hyperbranched palm oil-based urethane acrylate resin. Hyperbranched urethane acrylates demonstrate very rapid curing rates and lower shrinkage than their linear counterparts. The cured films exhibit excellent hardness, high chemical resistivity, good scratch resistance, minimal residual unsaturation, and low extractables [2,3]. This paper presents the synthesis and characterization of urethane acrylates based on second-generation hyperbranched polyester polyol derived from palm oil oleic acid [4].

2.1 Materials

Dipentaerythritol (DPE), dimethylol propionic acid (DMPA), isophorone diisocyanate (IPDI), p-toluene sulfonic acid (PTSA), and dibutyltin dilaurate (DBTDL) were supplied by Merck-Schuchardt Germany. 2-hydroxyethyl acrylate (2-HEA) was obtained from Aldrich Chemicals Co., USA. Trimethylolpropane triacrylate (TMPTA) was purchased from UCB Chemicals, Belgium, and oleic acid (palm oil source) was acquired from Acid Chemical Co., Malaysia. All chemicals were used as received without further purification.

2.2 Synthesis of Hyperbranched Polyester Polyol (HBP)

The first-generation hyperbranched polyester polyol (HBP-1) was synthesized via melt polycondensation using DPE as the core and DMPA as the chain extender, following established methods described elsewhere [2,3,8,9]. The reaction was conducted at 130–150°C under nitrogen atmosphere in the presence of p-TSA catalyst (0.4 wt% of DMPA) and monitored periodically by acid value determination until reaching an endpoint below 10 mg KOH/g. The HBP-1 was subsequently reacted with palm oil oleic acid at 190–220°C to produce the second-generation hyperbranched polyester polyol (HBP-2), with reaction progress monitored through hydroxyl value (OHV) determination.

2.3 Synthesis of Hyperbranched Polyurethane Acrylates (HBPUA)

HBPUA prepolymers/resins were prepared in a 250 mL five-necked flask equipped with a thermometer, dropping funnel, mechanical stirrer, and nitrogen gas inlet. IPDI was reacted with HBP-2 at an NCO:OH ratio of 9:1 for 3 h at 40–75°C with 0.1%–2.0% DBTDL as catalyst, following our earlier work [1] to produce NCO-terminated prepolymers. Subsequently, 2-HEA was added dropwise at the same NCO ratio. The synthesis procedure followed established literature methods [5], with dioxane added to control viscosity. Reaction progress was monitored by tracking the consumption of –N=C=O (IPDI) and –OH (HBP-2) groups at approximately 2250–2270 cm^{-1} and 3400–3500 cm^{-1}, respectively [1,6,7,8].

2.4 Electron Beam (EB) Curing of HBPUA-Based Formulations

The HBPUA prepolymers were dissolved in acrylate monomers such as TMPTA to reduce viscosity. Coating formulations were prepared at least one day prior to curing. The formulated resins were applied to glass plates using a manual bar coater (RDS 30, Japan) and subsequently irradiated with a 200 keV electron beam machine (Curetron type EBC-200-AA2, Nissin High Voltage, Japan) at an accelerating voltage of 200 keV, beam current of 2 mA, and dose rate of 10 kGy/pass.

2.5 Characterization of the Resin

FTIR spectroscopy was performed using a Perkin Elmer Spectrum 2000 spectrometer. Samples were spread as thin layers on NaCl cells and scanned from 4000 cm^{-1} to 400 cm^{-1}. Molecular weight (Mw) distributions were determined using a Polymer Laboratories GPC Model PL-GPC 50 Plus with PLgel 10 µm Mixed-B column, using tetrahydrofuran at 1.0 mL/min as mobile phase. Calibration was performed using linear polystyrene standards of known molecular weight and dispersity. Viscosity was measured at 25°C using a Brookfield Viscometer Model RVTDV-IICP with spindle #42. ^{13}C-NMR spectra were recorded on a JEOL ECP 400 MHz NMR using dimethylsulfoxide (DMSO-d_6) as solvent. Hydroxyl values (OHV) and acid values (AV) of HBP were determined using ASTM D4274-99 and MPOB Test Method c2.7:2004, respectively.

2.6.1 Determination of Gel Content of Cured Films Thin film samples were weighed (W_1) in a SUS 304 stainless steel wire-mesh filter (#100) and placed in a Soxhlet extractor. Extraction was performed for at least 24 h in acetone. The residue was removed, vacuum-dried, and weighed until constant weight (W_2) was achieved. The gel content was calculated using the following equation:

Gel Content (%) = (W_2/W_1) × 100

where W_1 is the initial mass of the sample before extraction (g) and W_2 is the mass after extraction (g).

2.6.2 Pencil Hardness Test Cured films were subjected to pencil hardness testing using Standard Mitsubishi-Uni Pencil (JIS 5400). Pencil hardness ranges from 9H (hardest) to 9B (softest), with H indicating harder grades and B indicating softer grades.

2.6.3 Determination of Thermal Properties Thermal decomposition profiles of cured hyperbranched polyurethane acrylate were studied using a Mettler Toledo TGA 851 analyzer. Samples of approximately 2–3 mg were placed in alumina pans and heated at 10°C/min in nitrogen atmosphere from 50°C to 550°C.

2.6.4 Morphological Studies The morphology of cured HBPUA films coated on medium density fiberboard (MDF) was investigated using a Philips XL-30 scanning electron microscope.

3.1 Characterization of HBP-1, HBP-2, and HBPUA

The FTIR spectra of oleic acid, HBP-1, HBP-2, and HBPUA are shown in Fig. 1. For HBP-1 resin, FTIR (KBr, cm^{-1}) showed peaks at 3200–3600 cm^{-1} (–OH), 2943 cm^{-1} ($–CH_3$), 2872 cm^{-1} ($–CH_2$), 1717 cm^{-1} (C=O), 1464 cm^{-1} (aliphatic $–CH_2$), 1371 cm^{-1} (aliphatic $–CH_3–$), and 1240 cm^{-1} (C–O). ^{13}C-NMR (300 Hz, DMSO-d_6) showed signals at \$ \$174.75 ppm (–C–CO–O–), \$ 70.9*ppm(–C–CH{2}\$-O–), \$*65.43*ppm*(–*CH*{2}\$–OH), and \$ \$39.5 ppm (–C–C–C–). These bands confirm successful reaction between DPE and DMPA to produce HBP-1, validating the formation of hyperbranched polyester polyol resin.

For HBP-2 resin, FTIR (KBr, cm^{-1}) exhibited peaks at 3200–3600 cm^{-1} (–OH), 2936 cm^{-1} and 2843 cm^{-1} (CH_3–, $–CH_2–$), 1744 cm^{-1} (–C=O–), 1468 cm^{-1} ($–CH_2–$, aliphatic), and 1240 cm^{-1} (–COO–, ester). ^{13}C-NMR (300 Hz, $CDCl_3$) showed signals at \$ \$174.75 ppm (–C–CO–O–), \$ 70.9*ppm(–C–CH{2}\$-O–), \$*65.43*ppm*(–*CH*{2}\$–OH), and \$ \$39.5 ppm (–C–C–C–). The hydroxyl value (OHV) of HBP-2 was 700 mg KOH/g. These spectral features indicate successful reaction between HBP-1 and oleic acid to produce HBP-2 resin.

For HBPUA, FTIR (KBr, cm^{-1}) showed peaks at 3300–3360 cm^{-1} (–NH– bending), 1562 cm^{-1} (–CN stretching), and 1635 cm^{-1} and 810 cm^{-1} (double bonds of acrylate groups), confirming successful bonding of both acrylate and amine groups to HBP-2 resin.

[Figure 1: see original paper]

Figure 2 [Figure 2: see original paper] shows the ^{1}H-NMR spectrum of HBPUA. A peak at 6.4 ppm corresponds to the acrylic group in HBPUA (–NHCO–). Signals at $ $5.1–5.2 ppm are assigned to hydrogen atoms attached to unsaturated carbons (–CH=CH–), while peaks at 3.8–4.2 ppm correspond to methylene hydrogens connected to ester groups (–CH–COO–). These observations confirm successful bonding of both acrylate and amine groups to HBP-2 resin to form HBPUA. Both FTIR and ^{1}H-NMR analyses thus verify the successful synthesis of HBPUA.

[Figure 2: see original paper]

Table 1 summarizes gel permeation chromatography data, viscosity measurements, and hydroxyl values for HBP-2 and HBPUA. The low viscosity suggests that HBP-2 and HBPUA molecules are less entangled due to their spherical architecture. One of the most notable properties of hyperbranched polymers is their combination of high molecular weight and low viscosity compared to linear analogues [3,9]. The low polydispersity index supports these findings.

3.2 Characterization of Cured Resins

Curing of HBPUA: HBPUA contains unsaturated sites capable of undergoing polymerization through double bond reactions. A thin layer of HBPUA applied to a glass plate polymerized into a solid film upon EB radiation exposure. The prepolymer HBPUA cured effectively at 100 kGy.

Figure 3 shows FTIR spectra of cured and uncured HBPUA. The cured sample exhibits no peaks at 1634 cm^{-1} and 810 cm^{-1} corresponding to acrylate groups, confirming their consumption during polymerization upon EB radiation exposure.

[Figure 3: see original paper]

Properties of cured film: Formulations based on HBPUA were developed to evaluate the effects of radiation dose on hardness and gel content, as summarized in Table 2 . Increasing TMPTA content from 40% to 60% resulted in higher pencil hardness and gel content in the cured films. TMPTA, possessing multifunctional acrylic groups, formed cross-links with HBPUA to produce hard films. The higher reactivity of acrylates in TMPTA contributed to a high degree of cross-linking, enabling curing at lower radiation doses.

The TGA and DTG thermograms of HBPUA formulations are shown in Fig. 4. Thermal decomposition of HBPUA commenced at 200°C with 98% weight loss. For HBPUA-1:TMPTA at a 6:4 ratio, weight loss was 95% at 200°C. Figure 5 demonstrates that thermal stability of HBPUA increased in the presence of TMPTA, with Tmax shifting from 450°C to a higher temperature of 455°C. This improvement in thermal stability is attributed to chemical cross-linking induced by TMPTA.

Figure 6 [Figure 6: see original paper] shows the interfacial adhesion between HBPUA/TMPTA and MDF as revealed by scanning electron microscopy (SEM). The micrographs demonstrate good interaction between the cured film and substrate.

4 Conclusion

Hyperbranched polyurethane acrylate prepolymers/resins (HBPUA) were successfully synthesized from palm oil-derived oleic acid. The cured HBPUA films exhibited high cross-linking density (gel content) and high pencil hardness index. Thermal decomposition studies revealed good thermal stability with negligible weight loss up to 450°C. The hyperbranched acrylate structures offer significant advantages for various coating industry applications, including wood coatings, printing inks, and pressure-sensitive adhesives (PSA).

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