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Synthesis and characterization of interpenetrating polymer networks with hyperbranched polymers through thermal-UV dual curing

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ABSTRACT

The aim of this study was to investigate the possibility of using acrylated hyperbranched polyesters (HBP) as UV curable component in dual curing automotive applications. Dual curing is one of possible ways to obtain fast curing, scratch resistant coatings for use in OEM and car refinish applications. Dual curing systems, upon hardening, can give interpenetrating networks (IPNs).

All the IPNs were obtained by UV-thermal dual cure process and they consisted of an UV curable acrylic component and a classic 2-pack urethane component. The acrylic component was acrylated hyperbranched polyester (HBP(A)) and 2-ethyl hexyl acrylate (EHA). The classic 2-pack urethane component consisted of a hydroxyl functional acrylate copolymer (HA) and Desmodur® N3390. The weight ratio of HBP(A) and EHA in the IPNs was varied from 100/0 to 25/75, while the urethane component remained the same in all the IPN samples.

The IPNs were characterized by dynamic-mechanical analysis (DMA), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The mechanical properties of the IPNs were also investigated. A single glass transition temperature, T_g, indicated that a homogeneous material with no separation domain was obtained. DMA showed that with increasing HBP(A) in the IPNs, the crosslink density increased, while the flexibility decreased. The data obtained by DMA and DSC showed a decrease of the T_g values with increasing amount of HBP(A). There were slight differences in the thermal stability of the IPNs.

1. Introduction

Jonas Aylsworth and Thomas Edison made the first interpenetrating polymer network (IPN) in 1914 [1] by mixing natural rubber and sulphur with crosslinked phenol–formaldehyde resin in the hope of obtaining a material with more toughness. Edison patented this material but they never called it an IPN. Millar [2,3] was the first researcher who systematically investigated the properties of IPNs and published the first paper on the subject in 1960. Frisch [4,5] and Sperling [6–10] independently came across the concept of IPNs composed of two different polymers in 1969.

An interpenetrating polymer network is a non-bonded combination of two polymers both in network form and strongly entangled together [11]. Materials known as IPNs involve the preparation of crosslinked polymer I, subsequent swelling in a network of monomer II plus crosslinker, and the *in situ* polymerization of monomer II [12,13]. Because they combine the properties of the components forming the networks, IPNs have become the subject of extensive studies [14–17].

Hyperbranched polymers can be synthesized by random polymerization of A_xB monomers, using condensation or addition. Highly branched polymers with a large number of end-groups are obtained. The properties of HBP depend on several parameters, especially the backbone and the end-group structure. HBP are more soluble than linear polymers. HBP normally exhibit amorphous non-entangled behaviour, making them very brittle. The thermal properties of HBP depend on the nature of the end-groups. The T_g of HBP decreases with decreasing end-group polarity [18]. The unique combination of low viscosity, high molecular weight and large number of reactive end-groups can be exploited in coatings [19–27].

Although other authors have used the UV-thermal dual cure process to produce IPNs [14,17], to the best of our knowledge, the use of an acrylated HBP in IPNs obtained by dual curing have not yet been investigated. In the present study acrylated HBP was a part of the component of the IPN. The investigated systems were first

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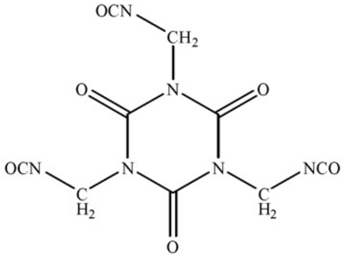
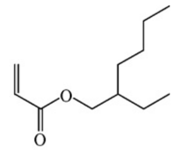
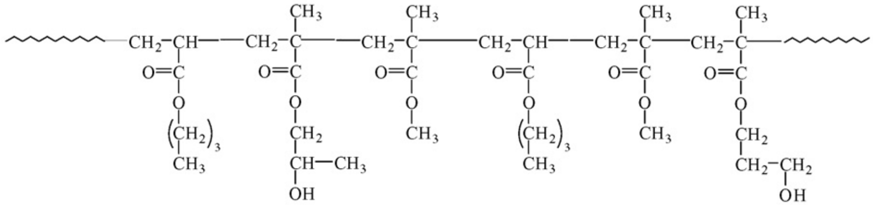
Table 1
Structure of the employed monomers



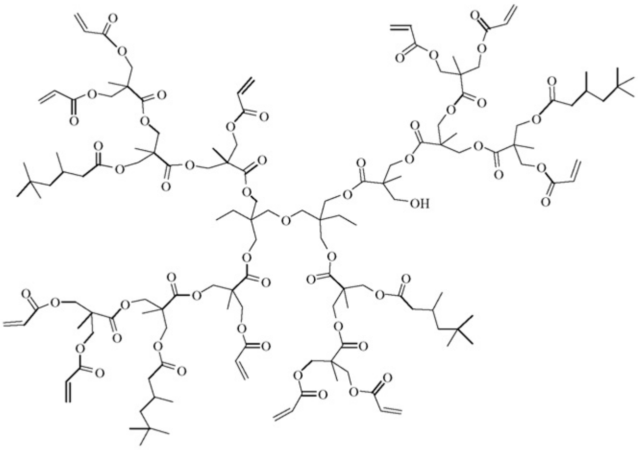
Desmodur N3390



Acrylic acid, 2-ethyl-hexyl ester EHA



Hydroxyl functional acrylate copolymer HA



HBP(A)

subjected to UV induced acrylate double bond conversion with the formation of a polyacrylic network, followed by the thermal radical polymerization of the urethane component. The properties of the obtained IPNs were analyzed by DMA, DSC and TGA. The film properties were also investigated with respect to hardness and flexibility.

This investigation is part of an effort to explore the possibility of using HBPs in dual-cure coatings in order to obtain coatings with superior properties with respect to scratch resistance.

2. Experimental

2.1. Materials

Desmodur® N3390 (19.4×10^{-3} of NCO for 1 g of Desmodur), BAYER, Germany, used as 90% solution in butyl acetate, MERCK, USA, methyl methacrylate (MMA), BASF, Germany (purity ≥ 99.9%), butyl acrylate (BuA), BASF, Germany (purity ≥ 99.5%) and 2-hydroxypropyl methacrylate (HPMA) Cognis, were used with no further purification. 2,2′-Azobis(2-methylpropionitrile) (AIBN), DuPont, was used as the radical polymerization initiator.

2-Ethyl hexyl acrylate (EHA) BASF, Germany (purity ≥ 99.6%), was used as reactive diluent, while acrylated hyperbranched polyester HBP(A) was used as acrylated oligomer in UV component of IPNs. 1-Hydroxy-cyclohexyl-phenyl-ketone (Irgacure 184), CIBA, USA, was used as the photo-initiator.

The structures of the employed monomers are presented in Table 1.

2.2. Synthesis of hydroxyl functional acrylate copolymer HA

A four-necked round bottom flask, equipped with an inert gas (nitrogen) inlet, a temperature regulation lug for the contact thermometer, a mechanical impeller lug with a condenser