

Novel Waterborne Hyperbranched Aliphatic Polyesters Used for UV Curable Coatings

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Abstract

A series of novel waterborne hyperbranched aliphatic polyesters were prepared by modifying the multihydroxy functional hyperbranched aliphatic polyester. The polar water solubilizing functional groups such as carboxylic group were neutralized by triethylamine and unsaturated moieties such as methacrylate and acrylate. Their solubility, dispersibility, emulsification and UV curing behavior were studied. The rheological properties of these products have been determined. Water showed a favorable viscosity reduction in all of cases. The effects of degree of neutralization, counterion and dielectric constant of dispersion medium on particle size of the dispersions were investigated. Photo-DSC was used to study the photopolymerization kinetics of the resins under UV irradiation in the presence of a photoinitiator. The photopolymerization rate of the resins showed an increasing trend with higher concentration of acrylate functionality. The DMTA investigations indicated that the glass transition temperature shifted to higher temperature as increasing the content of hard segment consisting of IPDI-HEA.

Introduction

In the past markets the demands for high performance and appearance were the pacemaker in the development of resins for surface coatings. Mainly solvent borne systems were in use. With an ever increasing awareness and concern for the environment, reducing costs and improving product performance, there is a corresponding increasing interest in the characteristics of waterborne/water dispersed UV curable products as they compare with 100% solid and UV products [1, 2]. Water-based UV curable resins have started to gain commercial significance over the past few years [3], and their development has resulted in a wide variety of technical approaches in industrial applications.

The central to the utilization of polymers in an aqueous media is the fact that certain polar functional groups are capable of conferring water solubility or dispersibility to an otherwise water-insoluble polymer. The best known are carboxylic acid group, sulphonic group and tertiary amine group. However, the most common way to solubilize an organic polymer into water is to introduce highly hydrophilic ionic groups obtained by neutralization. The content of such functional groups in a polymer is highly influential in determining the state in which the polymer will exist in an aqueous environment. Because there are different synthetic routes available for the preparation of aqueous polymers, and because polymers can differ widely in terms of (1) the nature and concentration of polar solubilizing group, (2) molecular weight, and (3) the hydrophobic/hydrophilic characteristics of the other units in the polymer chain, aqueous polymer systems with a wide range of different morphological and physical characteristics can be obtained. They are classified into water thinnable, aqueous dispersions and emulsions. In all cases, the resins should have vinyl groups for

UV curing and hydrophilic groups for stabilization in water.

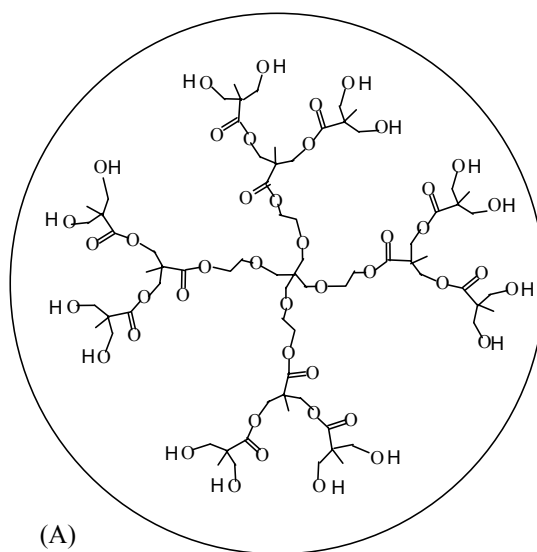
New dendritic hyperbranched polymers have provided a powerful technology in this field because of their compact three-dimensional structures of highly branched polymers. These molecules mimic the hydrodynamic volumes of spheres, which result in low viscosity even at high molecular weight, due to a lack of restrictive interchain entanglements.[4]. One potential application for these polymers is as UV curable oligomers used in coatings. In rad cure applications high molecular weight, the high crosslinking density and the high number of functionality combined with a low viscosity requirements are seem to achieve by use of dendritic hyperbranched polymers. Although the significant progress has been made in the research of dendritic polymers for various applications, there is still not much information on their use in UV curable water-based coating systems. A series of novel UV curable waterborne hyperbranched polyester (WBHP) and UV curable waterborne dispersions consisting of a multi-hydroxy functional hyperbranched aliphatic polyester core, were synthesized to explore their possible applications as UV/EB curable oligomers for coatings in our lab [5,6,7]. Photopolymerization of these UV curable waterborne prepolymers was investigated with respect to polymerization rate and conversions using Photo-DSC.

Results and Discussion

1. Waterborne hyperbranched polyester (WBHP)

The combination of the advantages of waterborne formulations with higher crosslinking density achievable by UV curing is, therefore an attractive approach towards environmentally friendly coatings with improved properties.

The UV curable waterborne hyperbranched polyester (WBHP) consisting of a multi-hydroxy functional aliphatic polyester core, which is endcapped with methacrylic and salt-like groups in different ratios were synthesized as shown in Fig 1. The core is the second generation of hyperbranched aliphatic polyester Boltorn™ H20, produced by perstorp AB, Sweden, having molecular weight of 1747 g mol^{-1} with approximately 16 hydroxyl groups. The stoichiometry for the modification of carboxylic groups into methacrylate groups and salt-like structure was adjusted in four different ratios, i.e.10:6, 8:8, 6:10, 4:12. The obtained products were named WBHP-10.6, WBHP-8.8, WBHP-6.10, WBHP-4.12, respectively.



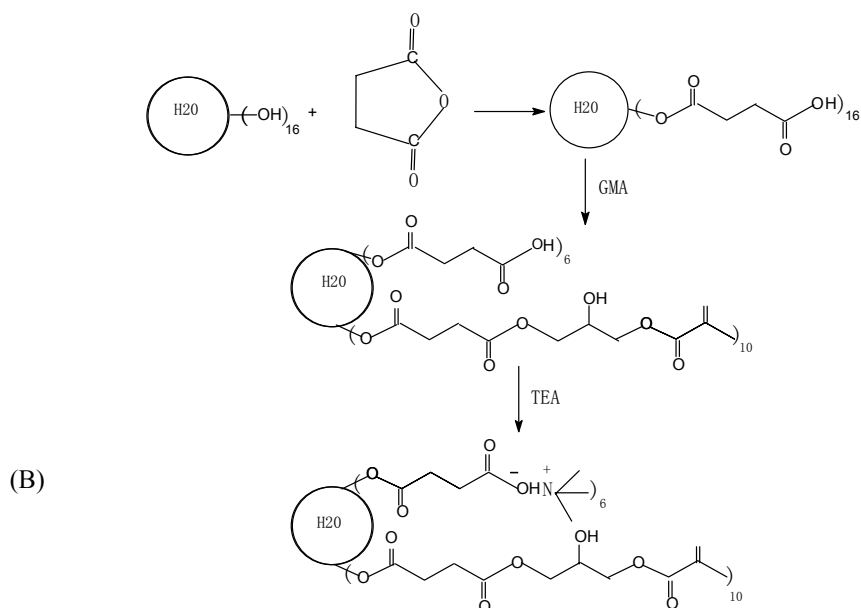


Fig.1 (A) Idealized formula of BoltornTMH20; (B) Schematic description of synthesis for the WBHP-10.6

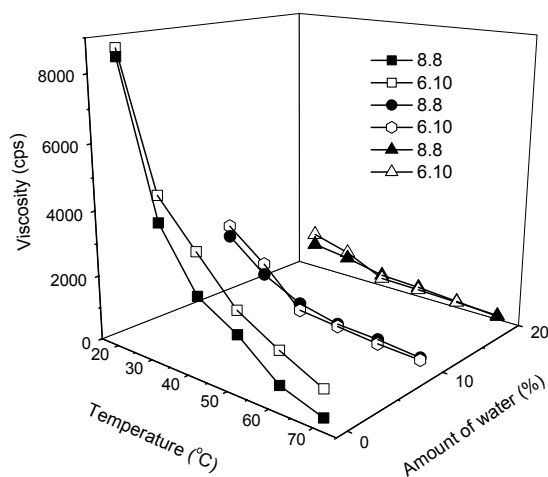


Fig.2. Viscosity profiles of WBHP 8.8 and WBHP-6.10 versus amount of water and temperature.

Water offers a promising alternative of monomers and solvents in UV/EB curing systems. It gives a very efficient viscosity reduction of formulations. Fig. 2 shows the viscosity profiles of WBHP-8.8 and WBHP-6.10 versus temperature at 0%, 10% and 20% addition of water, respectively. The viscosity drops from 8500 cps^{-1} to 4000 cps^{-1} for the resin WBHP-8.8 by increasing the temperature from $20 \text{ }^\circ\text{C}$ to $30 \text{ }^\circ\text{C}$. It can be interpreted that the reduction in viscosity with raising temperature is due to decreasing intermolecular hydrogen bonding in the resin. Moreover, the viscosity reduces 4 times after addition of 10 wt% water at room temperature. For the resin WBHP-6.10 the viscosity also drops from

8750 cps⁻¹ to 4800 cps⁻¹ with raising the temperature from 20 °C to 30 °C. WBHP-6.10 has higher viscosity than WBHP-8.8, which may be due to the higher ionic group concentration in the former and the mutual repulsions of the same charges result in more expansion of the molecules.

Different photoinitiators and their contents in resin formulation are important factors in determining the curing rate and extent of cure for the dried films. Fig. 3 shows the unsaturation conversions versus UV dose curves obtained for WBHP-8.8 and WBHP-6.10 resins containing two different photoinitiators in different concentrations. These measurements were performed at 2.04 mW cm⁻² UV light intensity. This relatively low intensity was chosen to slow the reaction, so that the key features of the conversion profiles could be conveniently measured. As shown in Fig. 3 (a) for the resin WBHP-8.8 the final conversion drops from 80% to 74% with decreasing the concentration of Darocur 1173 from 4 wt% to 2 wt%. The WBHP-8.8 resin has higher final conversion than the WBHP-6.10, not only by varying the photoinitiator type but also increasing its concentration as it is clear from Fig. 3(b).

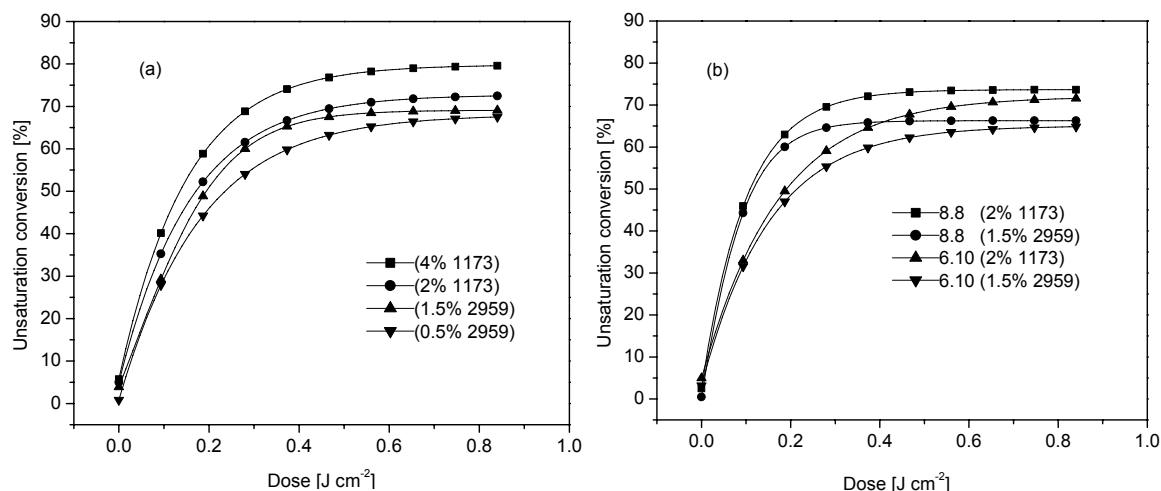


Fig.3. Unsaturation conversion profiles as a function of photoinitiator type and concentration. (a) WBHP-8.8 (b) WBHP-8.8 and 6.10

It can also be concluded from Fig. 3 that for both of the resins Darocur 1173 was found to be the most efficient initiator than Irgacure 2959. This may account for more rapid reaction rate and greater extent of cure for the waterborne system with Darocur 1173 addition. These results are in good agreement with the observation obtained by Masson. This implies that Darocur 1173 has good miscibility and ease of incorporation into aqueous systems. In spite of greater aqueous solubility of Irgacure 2959, its solid state may be the cause of less evenly dispersed in the system, thus longer irradiation time was required to level off unsaturation conversion. Moreover, the resin containing 4 wt% Darocur 1173 absorbs less dose to arrive at the maximum conversion than that containing 2 wt% of it. This phenomenon attributes to a large number of photoinitiator radicals produced in the initiation stage of the former formulation.

The hydrophilic character of a cured film is well characterized by the polar component of the surface energy, which can be determined by measuring its contact angle of water. Waterborne coatings are expected to be more sensitive to moisture because of their hydrophilic character, brought on by the introduction of polar groups. The surface energy characteristics of UV cured WBHP films and WBHP-8.8 blended films with 20% 2002 are summarized in Table 1.

Table 1. Surface tension characteristics of the UV cured films.

UV cured coatings	$\theta_w^{\circ a}$	$\theta_d^{\circ b}$	γ_p (mJ m ⁻²)	γ_d (mJ m ⁻²)	γ_{total} (mJ m ⁻²)
WBHP-10.6	52.5	36.7	8.5	42.3	50.8
WBHP-8.8	49.5	36.7	9.5	42.3	51.8
WBHP-6.10	45.5	36.1	10.6	42.6	53.2
WBHP-4.12	42.7	35.5	11.3	42.9	54.2
WBHP-8.8 +20% EB 2002	50.5	36	9.1	42.6	51.7
EB 2002	62	36.1	5.1	42.5	47.6

^a contact angle by water

^b contact angle by diiodomethane

The obtained results indicate that the value of dispersive component of the surface energy remains almost constant, because of the contact angle measurements with dim on polymer surface should be very little affected by hydrophilic characteristics. It can be seen that the contact angles of water (θ_w) follows the order of WBHP-10.6 > WBHP-8.8 > WBHP-6.10 > WBHP-4.12 as the acid content increased. The addition of EB 2002 in WBHP-8.8 to obtain two blends results into the decrease of polar component, which leads to decrease in surface energy. This can also be interpreted in terms of decrease in the concentration of hydrophilic groups on the surface.

2. Waterborne hyperbranched polyurethane dispersions (WHPUD)

Aqueous polyurethane dispersions have received considerable attention in the past few decades because of their applications in adhesives and coatings for various substrates including textile fabrics, plastic, wood, glass, fibers and metals [8]. A series of UV curable waterborne hyperbranched polyurethane dispersions can be prepared by modifying some of hydroxyl groups of Boltorn™ H20 as a polyol to acidic groups and tipping remaining OH-groups with diisocyanate and acrylic functionality such as IPDI and HEA, respectively. They are different from conventional waterborne urethane acrylate ionomers having only one ionic site in the center or at the end of a molecule. The UV curable waterborne dispersions prepared in this study have n ionic sites (n = 6, 8, 10) and 16-n acrylate functionality in Boltorn™ H20 based prepolymer [7]. The aqueous dispersions were electrostatically stabilized with carboxyl groups incorporated into their structures, which were neutralized by triethylamine. The schematic presentation for the reaction procedure

is shown in Fig. 4. The effects of chemical structures of end groups on various properties of WHPUD, such as particle size and rheological behaviors were investigated.

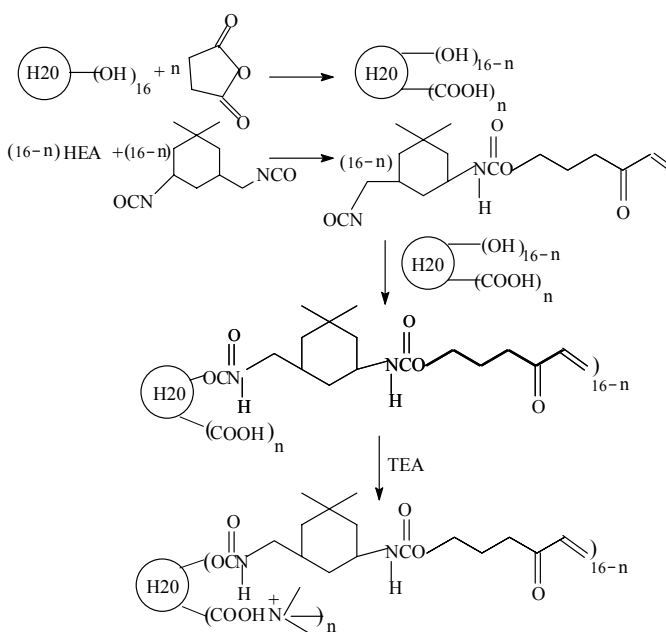


Fig.4. The schematic description of the synthesis for WHPUDs.

As shown in Table 2 the study of particle size using laser light scattering method has revealed that the particle sizes of WHPUDs are sensitive to the carboxyl content, degree of neutralization and dielectric constant of a dispersion medium. The lower is the concentration of carboxyl groups per polymer the larger is the particle size of dispersion. The particle sizes decreased as the degree of neutralization increased, because the dissociated carboxyl groups are capable of stabilization. As the dielectric constant of a dispersion medium decreased, the dissociation of carboxyl groups decreased causing the particle size to increase.

Table.2. Average particle sizes of WHPUD.

Sample	Average Particle size (nm)		
	Degree of neutralization		
	100 %	70 %	40 %
WHPUD-10.6	70.69	97.58	125.02
	113.72 ^(a)		
	237.18 ^(b)		
WHPUD-8.8	59.83	89.63	113.82
WHPUD-6.10	43.75	81.40	99.74

(a) Methyl alcohol

(b) Butyl alcohol

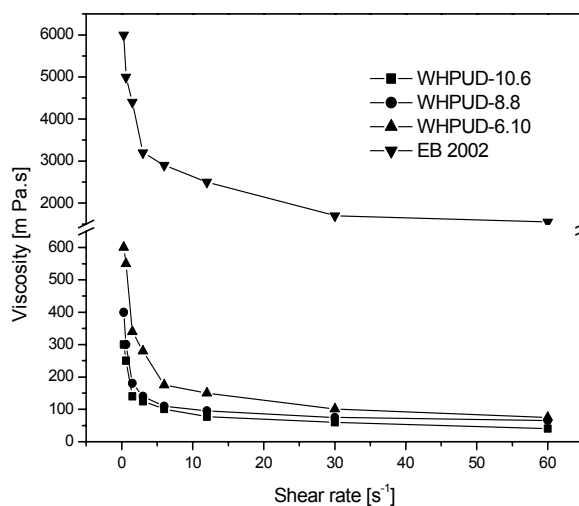


Fig.5. Effects of carboxyl content on rheological behavior of WHPUDs with 40% solid content.

The viscosity arises from the interactions among the particles of dispersions. Therefore, it is considered that there are many factors such as molecular architecture, molecular weight, solid content and dispersion medium, which affect the rheology of a coating. In addition, the rheology of water dispersible system can be easily controlled by the addition of water.

Fig. 5 shows the rheological behavior of WHPUD-10.6, WHPUD-8.8, WHPUD-6.10 and EB 2002. It has been observed that the viscosity for all dispersions decrease drastically when the shear rate increased from 0.3 s^{-1} to 6 s^{-1} , whereas decreased gradually from 6 s^{-1} to 60 s^{-1} . When the shear rate increases, the physical crosslinks are broken down, thus leading to the drastic decrease in viscosity. This implies that WHPUDs exhibit shear thinning or pseudoplastic behavior, which arises in common polymer dispersions. It seems from the results illustrated in Fig. 5 that the IPDI-based dispersions exhibit pronounced deviation from Newtonian flow behavior. The chain entanglement and hydrogen bonding between urethano and urea linkages can be more rapidly formed in the IPDI-based prepolymer because of the flexibility of the chains. Fig. 5 reflects clearly that at each shear rate the viscosity of commercial waterbased resin EB 2002 is higher than those of all WHPUDs synthesized in our lab.

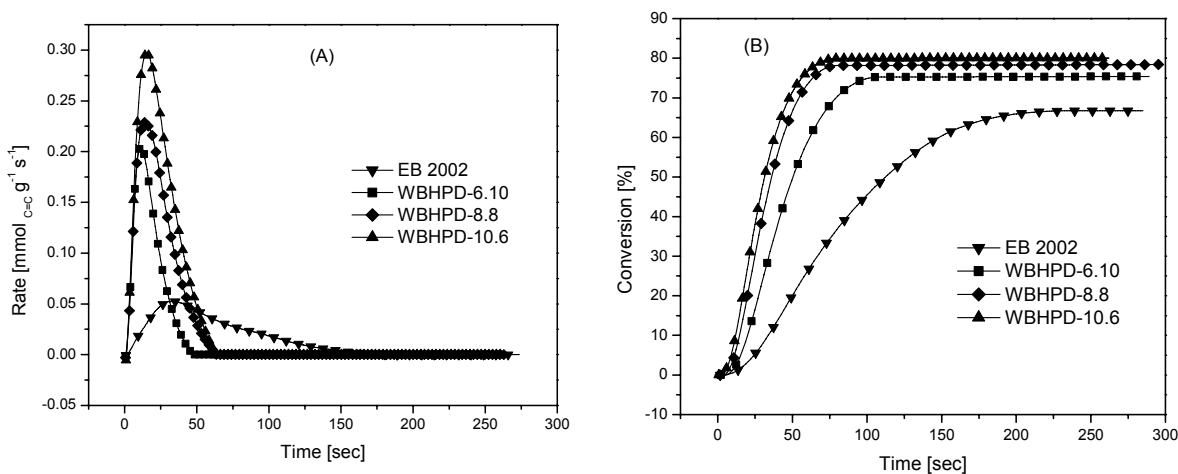


Fig. 6. Photopolymerization kinetics of WHPUD-10.6, WHPUD-8.8, WHPUD-6.10 and EB 2002 using 1.5% Irgacure 2959. (A) Photopolymerization rate (B) Unsaturation conversion comparisons

Fig.6(A). shows the time dependencies of photopolymerization rate R_p for each of the waterborne hyperbranched polyurethane dispersions (WHPUDs). Immediate auto-acceleration (initial increase in polymerization rate with conversion) was observed for all three prepolymers. From Fig.6, it can be seen that WHPUD-10.6 has highest R_p^{\max} among all because of its high unsaturation concentration. The R_p^{\max} for WHPUD-10.6, WHPUD-8.8, WHPUD-6.10 and EB 2002 decreases from $0.29 \text{ mmol}_{\text{C=C}} \text{ g}^{-1} \text{ s}^{-1}$, $0.23 \text{ mmol}_{\text{C=C}} \text{ g}^{-1} \text{ s}^{-1}$, $0.20 \text{ mmol}_{\text{C=C}} \text{ g}^{-1} \text{ s}^{-1}$ and to $0.05 \text{ mmol}_{\text{C=C}} \text{ g}^{-1} \text{ s}^{-1}$ respectively. These values indicate that the high concentration of acrylate end groups located at the outer layer of the sphere-like structure leads to a high value of R_p^{\max} .

As shown in Fig. 6(B), the unsaturation conversion over 80% was obtained after a longer irradiation time for three resins while 65% for EB 2002. The highest conversion was observed for WHPUD-10.6, followed in order by WHPUD-8.8, WHPUD-6.10 and EB 2002. Overall conversions were 80%, 78%, 74% for WHPUD-10.6, WHPUD-8.8, WHPUD-6.10 respectively compared to 65% for EB 2002. Their curves of P^f versus irradiation time illustrates that more the ionic content, the less is the unsaturation conversion. For the resins WHPUD-10.6 and WHPUD-8.8 the conversion is much higher than others before 100 seconds irradiation time because they have higher concentration of acrylic end-groups. This is also due to the fact that, as the ionic group content (carboxylic group neutralized with TEA) in WHPUD increases, the strengthened electrostatic repulsion among the same charges makes the chain propagation difficult.

The dynamic mechanical properties of the UV cured samples of WHPUD-10.6, WHPUD-8.8, WHPUD-6.10 and EB 2002 are shown as function of temperature in Fig.7. Storage modulus (E') generally increases and the major transition temperature move toward the higher temperature as hard segment concentration increases. It seems that soft and hard segments of these WHPUDs are virtually phase-mixed to show a single glass transition (T_g). The microphase miscibility is likely to be due to the strong hydrogen bonding between oxygen of carbonyl group and the hydrogen atom of urethane groups and coulombic forces between ionic centers.

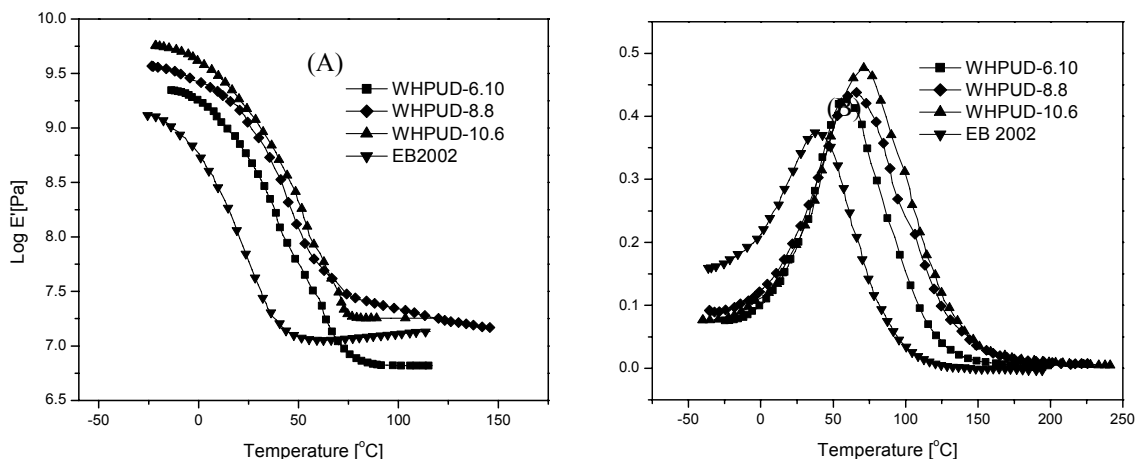


Fig. 7. Dynamic mechanical properties of WHPUD-10.6, WHPUD-8.8, WHPUD-6.10 and EB2002 (A) Tensile storage modulus E' (B) Tensile loss factor ($\text{Tan } \delta$)

$\text{Tan } \delta$ of WHPUDs is shown in Fig. 7(B). The sharper $\text{tan } \delta$ transition observed for the EB 2002, suggests more uniform cross-links compared to WHPUDs. However the peak temperature moves toward the higher temperature and the peak becomes broader as the IPDI-HEA content increases. It can be explained due to higher double bond concentration of the system, which leads to higher crosslink density of the UV cured films. The broadening of peak may indicate that the relaxation is not a single one and comprises of consecutive ones. As shown in Table 3 the pendulum hardness of the UV cured WHPUD-

10.6, WHPUD-8.8, WHPUD-6.10 and EB 2002 films were 265 s, 204 s, 187 s and 128 s respectively.

Table 3. Dynamic mechanical properties and pendulum hardness of WHPUDs and EB 2002

Sample	T _s (°C)	T _g (°C)	T _s /T _g	V _e (mmol/ml)	Pendulum Hardness (sec)
WHPUD-10.6	20	72	0.975	2.32	265
WHPUD-8.8	18	63	0.958	2.14	204
WHPUD-6.10	14	58	0.968	1.34	187
EB 2002	7	40	0.980	1.09	128

Conclusions

The development of waterbased system has been motivated primarily by environmental considerations. Many advances in the synthesis of polymers for aqueous coatings have been made over the past years. The versatility in designing the hyperbranched polymer for waterborne rad-cure applications makes it a unique tool for structure/properties relationship allowing to reach unique combinations of properties. The high crosslinking density, inherent backbone flexibility and easy accessibility of the double bond allow to reach a high ultimate conversion (around 80 %) in combination with a high glass transition temperature and hardness. Moreover, waterborne system will contribute to a wider use of radiation curing technology in coming years and are able to bridge the performance gap between waterbased and 100% radcure technologies. Novel UV curable waterborne hyperbranched aliphatic polyesters may meet requirement for coatings and adhesives as oligomers or using as modifiers in linear resins.

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