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ORIGINAL CONTRIBUTIONS

Anila Asif
Cheng Yu Huang
Wen Fang Shi

Photopolymerization of waterborne polyurethane acrylate dispersions based on hyperbranched aliphatic polyester and properties of the cured films

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A. Asif · C. Y. Huang
W. F. Shi (✉)
State Key Laboratory of Fire Science and
Department of Polymer Science
and Engineering, University of Science
and Technology of China,
Hefei, Anhui 230026,
People's Republic of China
E-mail: wfshi@ustc.edu.cn
Tel.: +86-551-3606084
Fax: +86-551-3606630

Abstract A series of novel waterborne hyperbranched polyurethane acrylates for aqueous dispersions (WHPUD) based on hydroxy-functionalized hyperbranched aliphatic polyester Boltorn™ H20 were investigated and used as UV curable oligomers. The aqueous dispersions were electrostatically stabilized with carboxyl groups incorporated into their structures, which were neutralized by triethylamine. The photopolymerization kinetics of these WHPUDs was studied with respect to polymerization rates and unsaturation conversions in the presence of a photoinitiator using differential scanning calorimetry. The polymerization rates of the resins under UV irradiation and the gel contents in the cured films showed an increasing trend with higher concentration of acrylate functionality, which is in favor of the theory of radical chain polymerization. The mechanical and thermal behaviors of UV cured films of aqueous dispersions were evaluated by tensile testing and dynamic mechanical thermal analysis (DMTA). The results of DMTA investigations indicated that the glass transition temperature shifted to higher temperature as the content of the hard segment consisting of IPDI-HEA increased. Moreover, the storage modulus and pendulum hardness also increased with increasing the hard segment content. As the degree of neutralization increased, the T_g and tensile strength decreased, whereas, the elongation at break increased.

Keywords UV curable · Waterborne hyperbranched polyurethane ionomer · Aqueous dispersion · Photopolymerization kinetics · Thermal behavior · Mechanical property

Introduction

UV radiation curing has become a well accepted technology, which, because of its distinct advantages, has found manifold industrial applications, mainly as fast drying protective coatings, printing inks and adhesives. The growing concerns in environmentally friendly coating industries have led to the development of solvent free formulations that can be thoroughly cured within a fraction of a second upon UV exposure at ambient temperature, to generate polymer materials without emission of volatile organic compounds [1, 2]. In recent years, notable progress has been made in the qualitative understanding of the cross-linking mechanism, in particular that of the widely used acrylate systems, under conditions similar to those in most industrial applications [3]. Photoinitiated polymerization of highly branched and telechelic oligomers is a complex process, which exhibits a number of anomalous behaviors such as initial autoacceleration followed by autodeceleration due to gelation and radical trapping. There is a general trend today to replace toxic monomers, or at least reduce their content, and develop UV curable formulations where its disadvantages are eliminated. In this respect, waterbased UV curable systems appear as a promising supplement by eliminating the use of acrylate monomers, water being used as the only diluent. The formulation viscosity, which is determined by the solid content, can thus be reduced to the precise level required for spraying and rolling applications to any type of substrate. Moreover, waterbased UV curable coatings may combine the flexible properties of high molecular weight polymers with the hardness of strongly cross-linked acrylate polymers [4]. The potential of waterbased systems and their performance in UV radiation curing have been thoroughly investigated in the past decade [5–7]. Most of them consist of a dispersion or emulsion of acrylate functionalized oligomers, which are photocross-linked in the solid state, after the removal of water.

Aqueous polyurethane (PU) dispersions have been used for a wide range of commercial applications such as coatings or adhesives for various substrates, including textile fabrics, plastics, leather, wood, glass fibers and metals. The development of these aqueous PU dispersions has been motivated primarily by environmental considerations to reduce the emission of organic solvents into the atmosphere. In addition, the quality of these dispersions, notably excellent adhesion to polymeric and glass surfaces and film forming ability at ambient temperature, makes them suitable for a myriad of applications. Conventionally, PU is insoluble in aqueous media and forms phase separation into large domains. For PU to be dispersible in water, ionic and/or nonionic hydrophilic segments should be incorporated in PU structure. A PU ionomer can be defined as a copolymer consisting of a PU backbone with a minority of the repeat units carrying pendant acid groups, which are partially or completely neutralized to form salts. The chemistry and preparation processes of aqueous PU dispersions are well reviewed in the literature [8–10]. The presence of ionic species in ionomers has a considerable effect on many of their physical properties. The ionic centers in the hard segments generally favor segregation and cohesion within the hard segment domains due to their strong electrostatic forces and thermodynamic incompatibility with the polymer matrix. Extensive attention has been devoted to understanding the factors controlling ionic association. The compatibility of the backbone and the ionic groups, the content of ionic groups, degree of their neutralization and the length of the spacer groups between the polymer backbone and ionic groups have all been shown to have important effects on the mechanical and dynamic mechanical properties of ionomers [11].

Waterborne radiation curable systems are expected to overcome disadvantages of both waterborne systems and radiation curable systems. The combination of the advantages of waterborne formulations with higher cross-linking density achievable by UV curing is therefore an attractive approach towards coatings with improved properties. The formulators in coating industries always balance the viscosity, cure speed and final properties for a given UV formulation. It is a difficult compromise to achieve both rapid cure speed and lower viscosity for an oligomer by a conventional technique. PU dispersions can also be prepared with high solid content and high molecular weight, as the viscosity of dispersions is generally independent of the molecular weight of the dispersed polymer particles.

The residual water in cured films affects the mechanical properties. So, it is necessary to flash off residual water completely. As a consequence, the advantages offered by these environmentally friendly systems are, however, partly offset by the necessity to introduce a drying step before UV exposure. It is well known that the addition of water has a plasticizing effect on the UV curing of acrylic resins. In any industrial application of waterbased UV curable coatings, the drying step will be the bottleneck, which will control the speed of the curing line, because it is the slowest process.

Moreover, owing to unique properties such as compact three-dimensional structures, a large number of end group functionalities and little chain entanglements in the melt state, hyperbranched polymers have attracted considerable attention as materials with new application potentials in comparison with their linearly homologue polymers. Dendritic hyperbranched polymers can provide a powerful technology in this field. The high-density functional terminal groups on a hyperbranched polymer offer the potential for tailoring their compatibility through the conversion of end groups to chemically suitable moieties. Two properties, i.e., low viscosity due to the architecture, and tailorable compatibility, make them possible candidates to be used in aqueous dispersions. Nowadays, many studies about linear waterborne PU are being published, but there is no information about their use in UV curable waterborne coatings. More recently, a series of novel UV curable waterborne hyperbranched polyesters (WBHPs) and UV curable waterborne hyperbranched polyurethane dispersions (WHPUDs) consisting of a multihydroxy functional hyperbranched aliphatic polyester core were synthesized to explore their possible applications as UV/EB curable oligomers for coatings in our lab [12–14].

UV curable WHPUDs can be prepared by modifying some of the hydroxyl groups of Boltorn™ H20 as a polyol to acidic groups and tipping the remaining OH-groups with diisocyanate and acrylic functionality such as isophorone diisocyanate and hydroxy ethylacrylate, respectively [14]. They are different from conventional waterborne urethane acrylate ionomers that have 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 oligomer.

It is essential to have the hard segment formed from IPDI to get WHPUDs, which is a scope of the present study. Moreover, hyperbranched polymer is ready to impart a wide range of structural fine tuning by modifying the end functional groups of IPDI-HEA and salt-like moiety, which play a significant role in affecting physical and chemical properties. The effects of hard segments have shown that the IPDI system possesses superior dynamic mechanical and mechanical properties as compared to the water-soluble hyperbranched polymers as reported earlier [13].

In this article, we report the photopolymerization kinetics of WHPUDs, as the nature of the resultant cured films, which is very important to their applications, depends not only on the properties of prepolymer but also on the photopolymerization kinetics, that is, the photopolymerization rate (R_p) and final unsaturation conversion (P^f). Moreover, the influences of carboxylate anion content and degree of neutralization on the dynamic mechanical thermal properties, tensile properties and hardness of the cured WHPUD films have been studied.

Experimental

Materials

The hyperbranched aliphatic polyester Boltorn™ H20 was used as a principal polyol for aqueous dispersions and was supplied by Perstorp AB, Perstorp, Sweden. The detailed synthesis and characterization of WHPUD-10.6, WHPUD-8.8, WHPUD-6.10 were described elsewhere [14]. In WHPUD-10.6, ten end groups of Boltorn™ H20 have been modified by IPDI-HEA segment and six with salt-like moiety. The ideal molecular formula of Boltorn™ H20 and the schematic outline of the synthesis for WHPUDs are shown in Fig. 1. The dispersion was prepared at 40% solid content. From the preliminary experiments, it was found that 40% neutralization was a minimum value for forming a stable dispersion. Therefore, the degree of neutralization was varied from 40 to 100% in this study.

2-Hydroxy-4(−2-hydroxyethoxy)-2-methylpropionphenone (Irgacure 2959) (supplied by Ciba-Geigy, Switzerland) was used as a photoinitiator for UV curing. The commercial waterborne resin, EB 2002 (of functionality 2), was supplied by UCB Co., Belgium.

UV curing

The UV cured WHPUD films were formed by casting the formulations with 1.5 wt% Irgacure 2959 onto a glass plate. Film formation was carried out at room temperature. Water was then allowed to evaporate at temperatures between 25 and 80 °C in an oven. Then, it was exposed to a UV lamp (80 W cm^{-1}, made by Lantian Co., Beijing, China) at a variable conveyer speed.

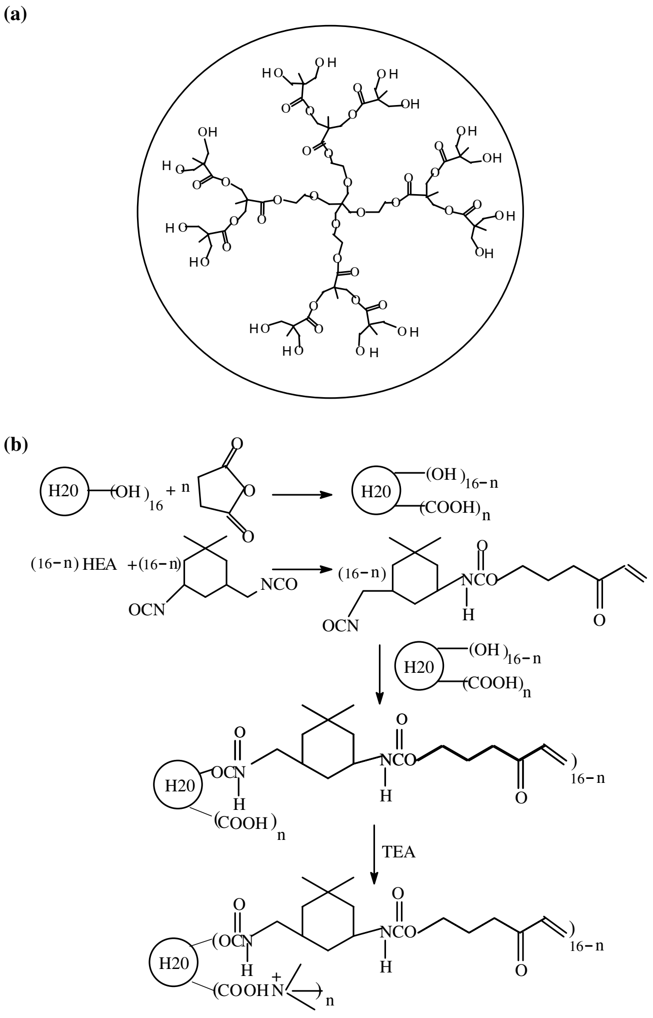

Fig. 1 **a** Idealized formula of Boltorn™ H20. **b** Schematic description of the synthesis for WHPUDs

Measurements

The gel content of the cured film was determined by the Soxhelt extraction method. After being irradiated, the samples were put into a basket made of 200 mesh stainless steel net. The gel content of a sample was determined by extracting the irradiated sample (w_o) in a basket for 48 h with boiling toluene. The solvent was renewed after the first 24 h of extraction. After the extraction, the basket was washed with acetone. The insoluble material (w) was dried under vacuum for about 2 days to constant weight, and weighed to determine the gel content. The gel contents in the cured films were determined from the difference in weight before and after extraction experiment as follows:

Gel content (%) = $w/w_o \times 100$, where w_o and w are the weight of samples before and after extraction, respectively. Several runs were made for each sample, and an average value was taken.

The photopolymerization kinetics was carried out on a modified CDR-1 DSC apparatus made by Shanghai Balance Instrument Co. The digitized data based on the traces on a strip chart recorder were analyzed by the software Origin 6.1 on a personal computer. A UV Spotcure System BHG-250 (Mejiro Precision Co., Japan) was used for irradiating the resins. The resin containing Irgacure 2959 (1.5 wt%) was heated in an oven at 60 °C for 1 h to obtain a homogeneous mixture, and placed in an aluminum DSC pan, carefully weighed, and then transferred to the sample holder in the photo-DSC instrument. The sample was purged with N_2 for 5 min to remove air before irradiation. Both the polymerization rate and unsaturation conversion were calculated as a function of irradiation time.

The final unsaturation conversion (P^f) was calculated by the following formula: $P^f = H_t/H_\infty$, where H_t is the heat effect within t seconds, H_∞ is the heat effect of 100% conversion of double bonds. The DSC curve was adjusted by the weight of the sample (g). The polymerization rate was defined by $\mathrm{mmol_{C=C}\ g^{-1}\ s^{-1}}$, namely, the variation of double bond concentration ($\mathrm{mmol\ g^{-1}}$) per second. For calculating the polymerization rate, the value of polymerization heat $\Delta H_o = 86\ \mathrm{J\ mmol^{-1}}$ per acrylic double bond was considered [15].

A dynamic mechanical thermal analyzer (DMTA; Rheome Tric SCI Apparatus Ltd., USA) was used to measure the tensile storage modulus (E'), tensile loss modulus (E'') and tensile loss factor (tan δ) of UV cured films at a frequency of 1 Hz and a heating rate of 2 °C $\mathrm{min^{-1}}$ in the range of −50 to 200 °C. The UV cured films were made on a glass plate with a special frame as a support (20×5×1 mm) under UV exposure. The sample chamber was kept dry by a stream of moisture-free nitrogen.

Tensile properties were measured at room temperature with a Universal Testing Machine (DCS-5000 Shimadzu Co., Japan). The dumb-bell shaped specimens were prepared according to ASTM D412-87. A cross-head speed of 25 mm $\mathrm{min^{-1}}$ was used throughout these investigations to determine the ultimate strength and elongation at break for all samples. The value quoted for each sample was the average of five measurements.

The pendulum hardness of the cured films was evaluated using a QBY Pendulum apparatus made by Tianjin Instrument Co., China. The sample was mixed with Irgacure 2959 (1.5 wt%) and applied on a glass plate (100×90×5 mm) by a coater with a 100 µm gap.

Results and discussion

Gel content

The properties of great importance are cure speed and extent of cure for a resin system. The rate of photopolymerization was found to increase with increased prepolymer unsaturation functionality. The gel content measurements of the cured films can be used to determine the amount of cross-linked polymer formed after UV irradiation. The inextractable parts in wt% as a function of cure time are shown in Fig. 2 in the cured WHPUD-10.6, WHPUD-8.8, WHPUD-6.10 and commercial EB 2002 films.

The gel contents of all samples exhibit a similar behavior that increases quickly at the beginning of irradiation due to the high concentration of radicals presented in the formulations, as irradiation time increased. As the mobility of reactive functional groups reduced, the functional groups become less and less reactive so that reaction stops while forming the cross-linked polymers. Therefore, the constant values of gel contents have been obtained by extending irradiation time to 17.5 s for all samples. The maximum weight loss after 20 s irradiation time was 12% for EB 2002 resin. This can be speculated to be due to the lower unsaturation functionality in EB 2002 resin, resulting in less insoluble cross-linked polymers. However, at the irradiation time of 15 s, the gel fractions approaching 95.5, 93 and 92% for WHPUD-10.6, WHPUD-8.8 and WHPUD-6.10 are obtained respectively. This indicates that the samples were highly cross-linked. The high cross-linking of hyperbranched prepolymer indicates

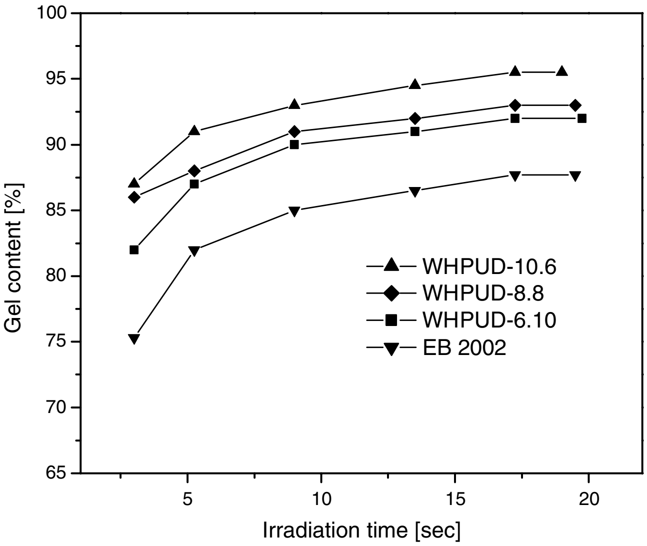

Fig. 2 Gel content in the cured films of WHPUDs and EB 2002 as a function of irradiation time

that the end groups were highly accessible for polymerization and not trapped in the network. It also means that the loss of mobility of the reactive groups during the curing effectively limited the degree of conversion, even though essentially all of the low molecular weight species have been incorporated into the network.

Photopolymerization kinetics

UV radiation curing has been successfully used to induce photopolymerization in telechelic prepolymers, which will develop in three dimensions to yield strongly cross-linked polymer networks. Figure 3 shows the time dependencies of photopolymerization rates (R_ps) for the waterborne hyperbranched polyurethane dispersions (WHPUDs) compared with EB 2002. In general, polymerization reaction rate profiles of UV curable prepolymers exhibit several typical features, which are autoacceleration, autodeceleration, structural heterogeneity and unequal functional group reactivity. Some of these features are illustrated in Fig. 3. The high peak polymerization rates (R_p^{max}s) are observed for WHPUD-10.6, WHPUD-8.8 and WHPUD-6.10 compared to EB 2002 under the same conditions. The differences observed in R_p^{max}s can be ascribed to the differences in concentration of unsaturation and viscosity of formulations. The observed high rates can be accounted for the hydrogen bonding preassociation in these systems. This is in accordance with the work done by Jansen et al. [16], where the acrylated prepolymers capable of hydrogen bonding exhibited 3–6 times higher polymerization rates than their nonhydrogen bonding counterparts. It can be observed that the R_p^{max} values for WHPUD-10.6, WHPUD-8.8, WHPUD-6.10 and EB 2002 are 0.29, 0.23, 0.20 and 0.05 $\text{mmol}_{C=C}\ g^{-1}\ s^{-1}$, respectively. Thsese values indicate that the high concentration of acrylic end groups located at the outer layer of the sphere-like structure leads to a high value of R_p^{max}. The initial portions of curves involve a rapid increase in rates, whereas the second phases of polymerization involve a less rapid increase and have generally been referred to as autoacceleration, that is, the polymerization rate increases despite the consumption of prepolymers. During the autoacceleration, the mobility of radicals decreases dramatically, which leads to the reduction of the termination rate, as the termination mechanism becomes reaction diffusion controlled. Finally, the polymerization reaction attains a maximum rate and then begins to decrease. This region has generally been referred to as autodeceleration where the vitrification cross-linking restricts and eventually stops the propagation. In these polymers, the bulk mobility of radicals is severely hindered, leading to a diffusion limited termination mechanism. It is speculated that HEA radicals undergo a bimolecular termination process. The termination process may deviate from recombination or disproportion by the formation of inhomogeneties in the pre gel stage and trapping of free radicals in inaccessible positions.

As shown in Fig. 4, the final unsaturation conversion P^f over 80% is obtained after a longer irradiation time for three WHPUD resins. The highest conversion is observed for WHPUD-10.6, followed in order by WHPUD-8.8 and WHPUD-6.10. Overall conversions are 80, 78 and 74% for WHPUD-10.6, WHPUD-8.8 and WHPUD-6.10, respectively, compared to 65% for

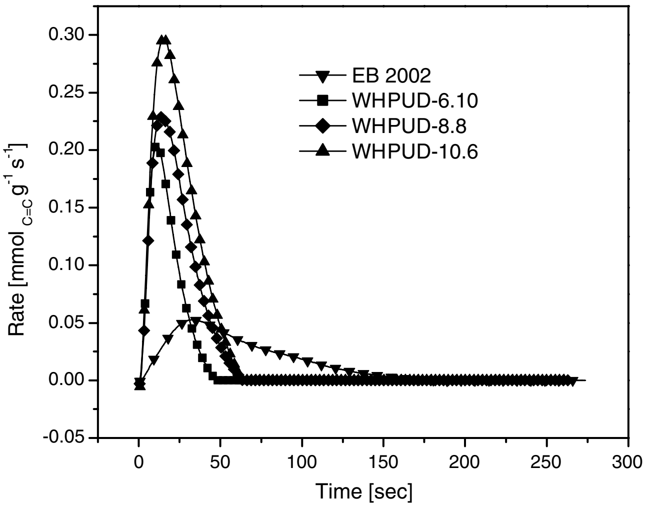

Fig. 3 Photopolymerization rate comparison of WHPUDs and EB 2002 using 1.5% Irgacure 2959

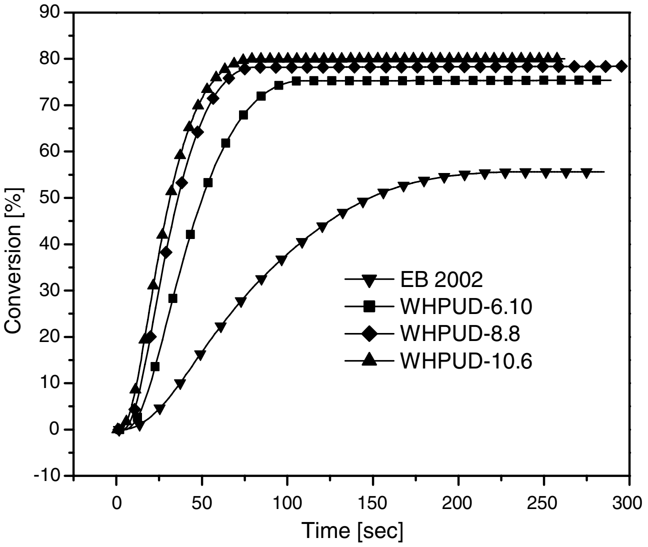

Fig. 4 Unsaturation conversion comparison of WHPUDs and EB 2002 using 1.5% Irgacure 2959

EB 2002. The amount of carboxylic acid introduced into the aliphatic hyperbranched polyester structures to make them dispersible in water may affect the curing kinetics by influencing the viscoelastic properties. Figure 4 illustrates the effect of carboxyl content on the curing kinetics of WHPUDs. It is clear from these curves that the higher the ionic content, the lower the unsaturation conversion. For WHPUD-10.6 and WHPUD-8.8 resin, the P^{f} is much higher than that for WHPUD-6.10 before 50 s irradiation because of the higher concentration of acrylic end groups for the formers. This is also due to the fact that as the ionic group content (carboxylic group neutralized with triethylamine) in waterborne hyperbranched polyester increased, the strengthened electrostatic repulsion among the ionic centers made the chain propagation reaction difficult. The rate of chain termination also decreased to a certain extent [17].

Dynamic mechanical thermal analysis (DMTA)

Dynamic mechanical thermal analysis was utilized to investigate the mechanical properties of WHPUDs in an effort to further understand the structure/property relationships of these UV cured films. The softening point (T_s) is defined as the extrapolated onset of the drop of log (E'). E' is a measurement of material stiffness and can be used to provide the information regarding polymer molecular weight, degree of cure and cross-link density [18]. The temperature associated with the peak magnitude of tan (δ) is defined as the glass transition temperature (T_g). The T_s/T_g ratio expresses the width of the tan (δ) peak; it is a rule that a higher T_s/T_g ratio leads to a narrow tan (δ) peak and more homogeneous film but broader tan (δ) transition suggests the greater degree of heterogeneity of cross-links. Moreover, dynamic mechanical analysis is a quick and direct method for the determination of cross-link density of highly cross-linked thermoset coatings from modulus measurements [19]. This method provides the modulus values with very small deformation of highly cross-linked networks. This is because the network chains can respond to these small deformations by undergoing changes in conformation that require only rotation of bonds in the network chains. If bond angle bending and bond breakage are eliminated by using small deformations, and if entanglements are also avoided, the relationship between rubbery plateau modulus and cross-link density is very simple,

$$V_e = E'/3RT$$

where V_e is the cross-link density, i.e., the molar number of elastically effective network chains per cubic centimeter of a sample, E' is the tensile storage modulus, R is the gas constant and T is the temperature in Kelvin. The earlier works showed that the type and content of the hydrophilic segment largely influenced mechanical, dynamic mechanical and tensile-stress properties [20–22]. The mechanical and dynamic mechanical properties of UV cured WHPUDs and EB 2002 are listed in Table 1. The dynamic mechanical thermal behaviors of the WHPUD-10.6, WHPUD-8.8, WHPUD-6.10 and EB 2002, and the temperature versus (E'), tan (δ) and (E'') plots are shown in Fig. 5a–c, respectively.

Table 1 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 (s)
WHPUD-10.6	20	72	0.849	2.32	265
WHPUD-8.8	18	63	0.866	2.14	204
WHPUD-6.10	14	58	0.867	1.34	187
EB 2002	7	40	0.895	1.09	128

The distinct glass transition peak was observed from Fig. 5b for WHPUD-10.6, WHPUD-8.8, WHPUD-6.10 and EB 2002 at around 72, 63, 58 and 40°C, respectively. As shown in Fig. 5a–c, E' and E'' values exhibit the same behavior, a result consistent with T_g values. Moreover, the tan (δ) peak temperature moves toward higher temperature, and the peak becomes broader as the hard segment content (IPDI-HEA) increases. The broadening of the loss peak may indicate that the relaxation is not a single one and comprises several consecutive ones. The increased peak temperature would mean that the relaxation occurs at high temperature, indicative of high film rigidity. The single tan (δ) peaks of WHPUDs are ascribed to the phase mixing behavior and the overall effect would hinder the motion of segments and broaden the distribution of their relaxation times. This implies that the hard and soft segment miscibility increased, perhaps owing to the increased cohesions within hard segments via hydrogen bonding. When the phase mixing is relatively complete, the backbone mobility is greatly restricted by the hard segments, which are solubilized by the soft segments. In general, polyester soft segment was found to contribute to phase mixing by hydrogen bonding between oxygen of the soft segment and NH group of the hard segment [23]. The hard segment consisting of IPDI-HEA unit has a direct influence on T_gs of WHPUDs. It seems that the heterogeneity of the network structure increases. Moreover, the heterogeneity is directly related to the cross-linking density of the polymer. Higher cross-linking of the resins enhanced the T_g of the cured films as reported by Li et al. [24]. Consequently, these results were also observed in the loss modulus (E'') versus temperature curves as shown in Fig. 5c. E'' values increase monotonically for WHPUDs with increasing the hard segment content, implying that the phase mixed morphology is maintained, while EB 2002 shows the drastically low values that is mainly due to the lower cross-linking density. The higher values of E'' suggest the greater mobility of the polymer chains associated with dissipation of energy when the polymer is subjected to deformation. The broad E'' and tan (δ) transition suggest the nonuniformity of cross-links. It is speculated that the nonuniformity during film formation may introduce voids in the polymer matrix. Moreover, as no significant reactions occur, it is an indication of physical cross-links through coulombic forces and hydrogen bonding. The overall effect would be to hinder the motion of different segments and broaden the distribution of their relaxation times.

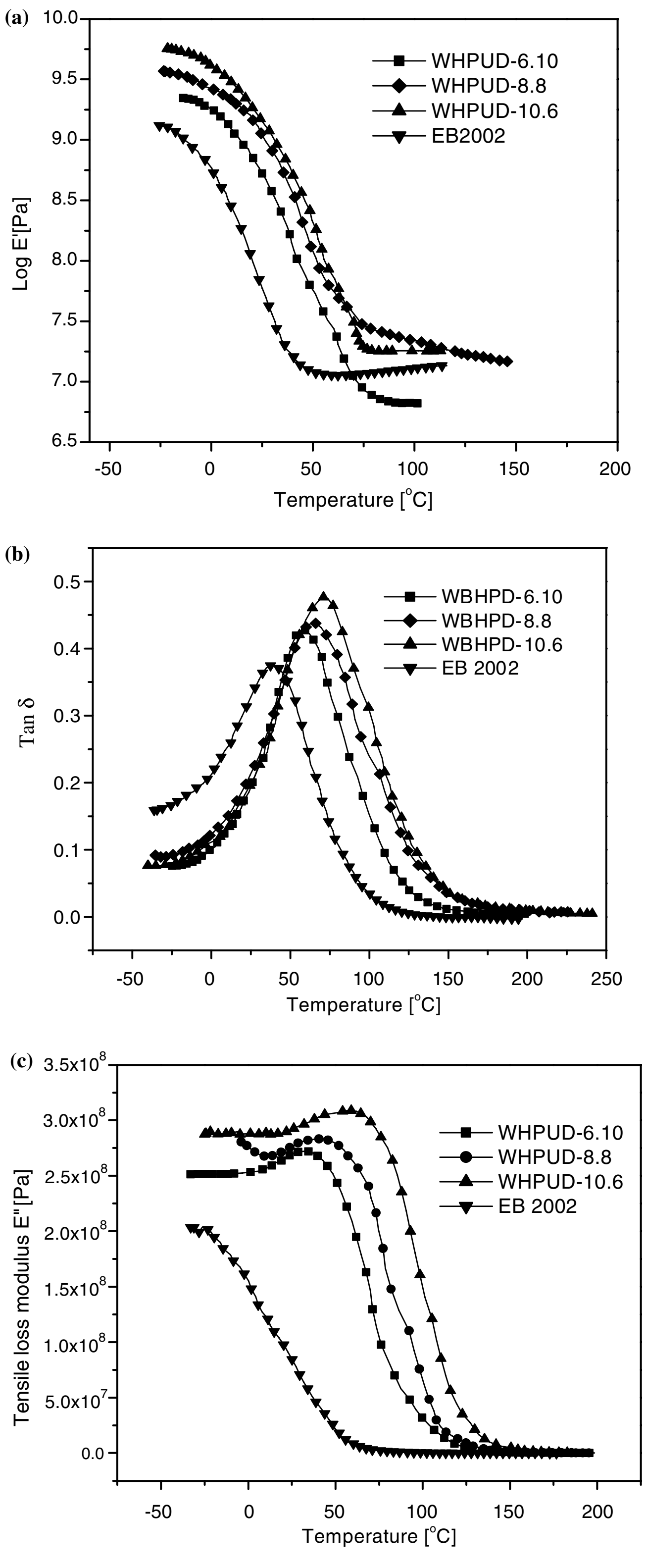

Fig. 5 **a** Tensile storage modulus E', **b** tensile loss factor (tan δ), and **c** tensile loss modulus E'' versus temperature of WHPUDs and EB2002

The effect of the degree of neutralization of ionic groups

Generally, ionic sites in the hard segments will lead to the increase of the incompatibility between the hard and soft segment in a PU ionomer, thus forming cohesion within hard segments. However, the effect of ionic sites is additional to an already present strong interaction between urethane groups. Due to the energetically preferred bond between ionic and urethane groups, the ionic site may at least partially destroy the highly ordered interactions, thus decreasing segregation. An increase in the number of ionic sites may then cause a new order. In general, the T_gs of TEA-neutralized polymers are lower than those of the polymers containing no TEA. It is inevitable that the neutralization decreases hydrogen bonded NH groups, leading to a slight decrease in the order of rigid segment regions and giving phase mixing. It seems that TEA works as a plasticizer. This behavior must be associated with hydrogen bond concentration in the polymer chains.

The degree of neutralization was varied from 40 to 100% for WHPUDs. The storage modulus E' and tan (δ) profiles of WHPUD-10.6 versus temperature are shown in Fig. 6a, b. The storage modulus and T_g both decrease with increasing the degree of neutralization. The T_gs are 72.0, 76.1 and 78.3 °C as the degree of neutralization varied from 100, 70 and 40%, respectively. These results indicate that the neutralization can lead to a decrease in the order of rigid hard segment regions and give phase mixing because of the reduction of hydrogen bonds by neutralizing. This means that some $C=O$ groups previously bonded to the NH of the urethane groups may be switched to bond with $^{+}NR_3H$.

The neutralizing cation has a profound effect on the dispersion and mechanical properties of ionomers. The dispersion properties of PU ionomers such as dispersibility, the particles size and dispersion stability has been overlooked [25]. It is well recognized that the metal cations produce smaller particles than the corresponding

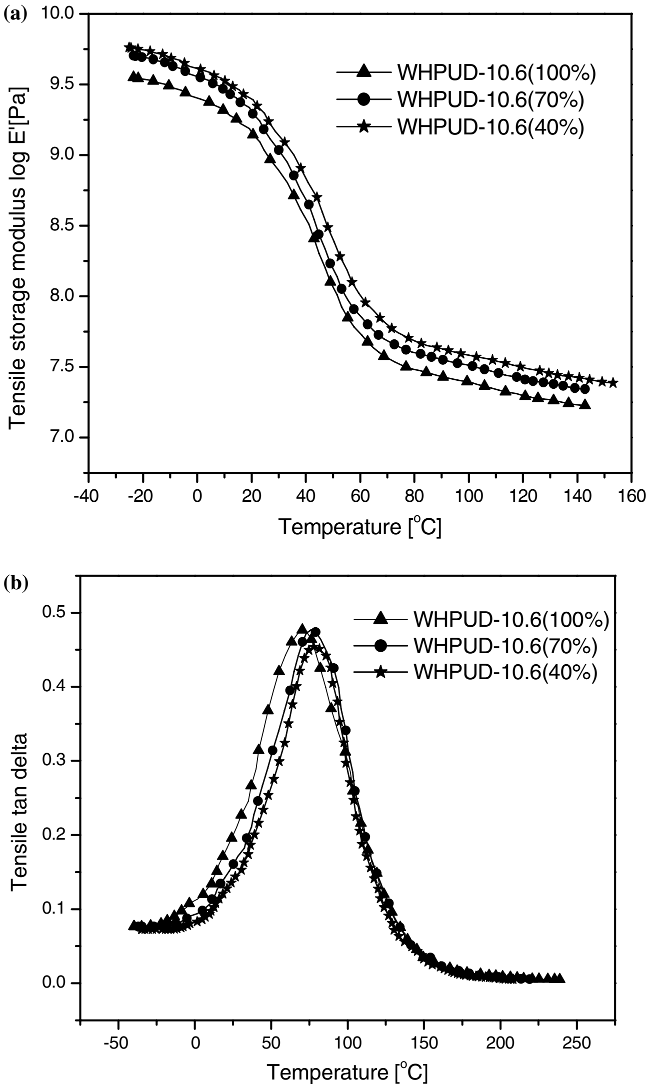

Fig. 6 Effect of the degree of neutralization of WHPUD-10.6 on **a** tensile storage modulus *E′* and **b** tensile tan *δ*

ammonium cations. This is due to the ease of hydration during the addition of water. Generally, primary particle sizes are smaller for metal cations in the order of Li < Na < K. The presence of metal cations is not desirable for dispersions intended for use in coatings due to nonvolatility during curing and thus water sensitivity [26]. However, it is reasonable to suppose that the effects of neutralizing agents (Li+, Na+, K+) are not useful for the present study.

Mechanical properties

The mechanical properties of the cured films are dependent on suitable UV curing conditions to achieve high cross-link density. Thus, to obtain the best physical and mechanical properties of the UV cured product, one must not only consider the material used but also the conditions under which the film was formed. These reaction conditions will completely control the polymerization and the conversion of double bond in the system. The conversion, in turn, will determine the mechanical and physical properties of the obtained material.

Tensile properties

Figure 7 shows the stress–strain curves for the UV cured films of WHPUDs and EB 2002. The tensile strength and modulus increase by increasing the hard segment, whereas the elongation at break decreases. In PU ionomers, the mechanical strength is governed mainly by the hard segments and the flexibility of soft segments. WHPUD-10.6, WHPUD-8.8, WHPUD-6.10 and EB 2002 have tensile strength values of 18, 19, 16.3 and 12 MPa, respectively, whereas the elongation values at break are 34, 47, 78 and 49%, respectively. The increase of tensile strength is due to the increased amount of urethane linkage and interchain ionic interaction. The decreased elongation at break can be explained by the increased chain rigidity and intermolecular interaction, such as, (a) electrostatic forces between ionic centers, (b) hydrogen bonding between urethane groups and (c) association of hydrophobic segments. The effects of the degree of neutralization on tensile properties are illustrated in Fig. 8. The degree of neutralization was varied from 40 to 100% for sample WHPUD-10.6. It is clear

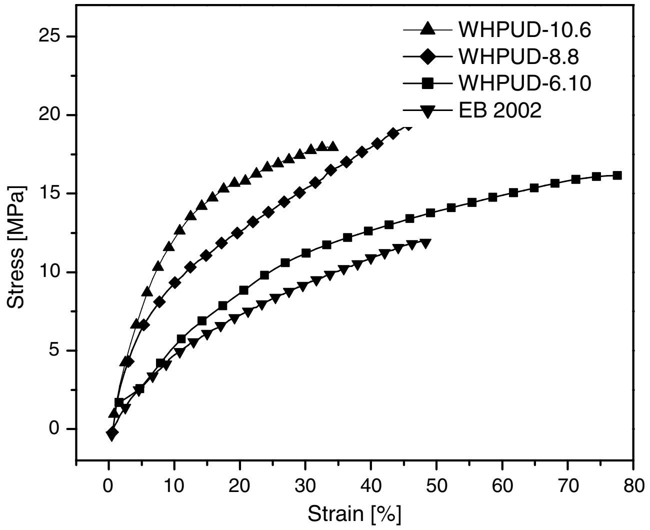

Fig. 7 Stress–strain curves for WHPUDs and EB 2002 with 100% neutralization

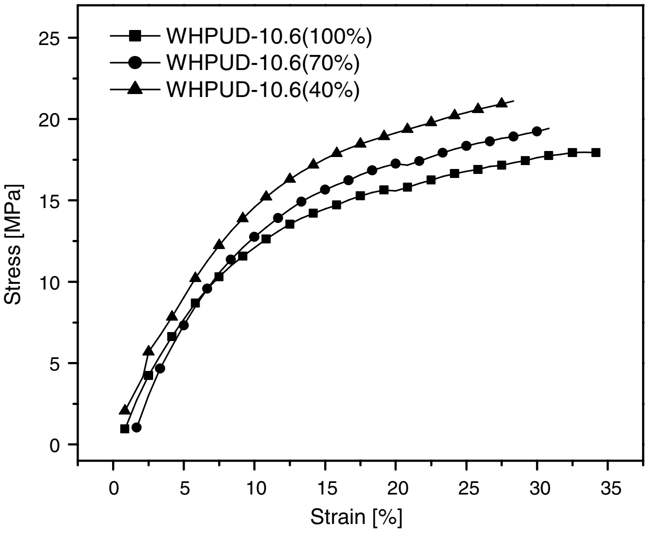

Fig. 8 Stress–strain curves for WHPUD-10.6 ionomer having different degrees of neutralization

from Fig. 8 that as the degree of neutralization increases, the tensile strength decreases, while the elongation at break increases. From these results, it is concluded that the mechanical properties may be related to the decreased structural order resulting from phase mixing because of the reduction of hydrogen bonding and columbic interactions.

Pendulum hardness

Pendulum hardness is one of the important physical properties of UV cured films that is taken into account for applications. It is well known that the pendulum hardness is related to the cross-linking network density, the conversion of double bonds and distinct interchain physical interactions within PU networks. Moreover, the high interchain interactions through hydrogen bonding can be enhanced via urethane and carboxyl groups by incorporating acrylate and acidic moiety. From Table 1, it can be seen that the pendulum hardness follows the order of WHPUD-10.6 > WHPUD-8.8 > WHPUD-6.10 > EB 2002. The fact that the pendulum hardness of WHPUDs is higher than EB 2002 can be explained as being due to just two double bonds per EB 2002 molecule. These results corroborate that increasing double bond concentration of the system leads to higher cross-link density of the UV cured films.

Conclusions

It is noteworthy that the versatility in designing a hyperbranched polymer for waterborne rad-cure applications makes it a unique tool for the structure/property relationship that allows it to have a unique combination of properties. A series of UV curable waterborne hyperbranched PU dispersions can polymerize rapidly in the presence of hydroxyphenyl ketone photoinitiator (Irgacure 2959). It was found that the presence of ionic groups in the network played an important role in determining the final properties of a prepolymer. The study of polymerization kinetics using Photo-DSC has revealed that WHPUDs can be polymerized rapidly under UV irradiation. Their R_p^{max} and P^f are in the order of WBHP-10.6 > WBHP-8.8 > WBHP-6.10. Furthermore, the final unsaturation conversion is also dependent upon the concentration of double bond accessible for polymerization and the acid content of waterborne coatings. With an increase in the hard segment content (consisting of IPDI-HEA), the glass transition temperature shifted to higher temperature, and the hardness, E', E'', and tensile strength also increased, but the elongation at break decreased mainly due to the increased cross-links. Moreover, the tensile strength, T_g and E', decreased with an increase in the degree of neutralization, presumably because the neutralization led to an increase in phase mixing.

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