Available online at www.sciencedirect.com
SCIENCE DIRECT®

Polymer 46 (2005) 11066–11078

polymer

www.elsevier.com/locate/polymer

Physical and thermal properties of UV curable waterborne polyurethane dispersions incorporating hyperbranched aliphatic polyester of varying generation number☆

Anila Asif[a], Wenfang Shi[a,*], Xiaofeng Shen[b], Kangming Nie[b]

[a] *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*
[b] *Institute of Chemical Engineering, Anhui University, Hefei, Anhui 230039, People's Republic of China*

Received 24 June 2005; received in revised form 17 August 2005; accepted 13 September 2005
Available online 28 September 2005

Abstract

Three series of novel waterborne hyperbranched polyurethane acrylates for UV curable aqueous dispersions (WHPUD) based on hydroxy-functionalized hyperbranched aliphatic polyesters Boltorn™ of varying generation number were investigated. The effects of the overall composition, including acidic and acrylate groups, and functionality of hyperbranched polyester were studied in terms of particle size, rheology, photopolymerization kinetics, dynamic mechanical thermal as well as thermal degradation behaviors of WHPUDs. The average particle sizes of aqueous dispersions, 43–134 nm, were determined by laser light scattering. The stability and particle size were dependent on the amount of carboxylic acid groups, degree of neutralization, and molecular structure. The rheological features have revealed that all dispersions belong to pseudoplastic fluids. The shear thinning behavior of WHPUDs is more pronounced for lower generation of hyperbranched polyester. The photopolymerization rates of the resins under UV irradiation in the presence of a photoinitiator showed an increasing trend with higher functionality of acrylate. The glass transition temperature (T_g) of UV cured films evaluated by dynamic mechanical thermal analysis (DMTA) showed that the influence of end capping by hard segment consisting of IPDI–HEA is remarkable due to the increase of crosslink density. The T_g, storage modulus and loss modulus increased with increasing generation number from the second to the fourth. The results of TGA for cured WHPUD films indicated good thermal stability with no appreciable weight loss until 200 °C, and that an increase in the hard segment content provoked the increases in thermal degradation temperature. This behavior is rationalized by relating crosslink density dependence of chain end concentration and the generation number of hyperbranched polyester.

Keywords: UV curable waterborne dispersion; Hyperbranched polyurethane acrylate; Structure–property relationship

1. Introduction

Ultraviolet (UV) radiation is a well-accepted technology for the fast curing of polymeric materials, [1] whereas waterborne coatings are new safe materials that can reduce environmental pollution. Water-based UV-curable resins have started to gain commercial significance over the past few years [2,3] and their development has resulted in a wide variety of technical approaches in industrial applications, mainly as fast drying protective coatings, printing inks, and adhesives.

Polyurethanes have been found in wide applications such as coatings and adhesives due to their unique properties, and great efforts have been made in chemistry and physics [4–7]. Water-borne polyurethanes (PUs) represent a major trend of PU development because of increasing concern about environmental pollution, health and safety risks [8]. Polyurethane ionomers are one of the most rapidly developing and active branches of polyurethane chemistry due to their ability to form water dispersions [9,10]. Aqueous polyurethane dispersions are of three types, nonionic, cationic and anionic depending upon the type of hydrophilic segments present in PU backbone. Water-borne PUs are PU ionomers consisting of PU backbones with a minority of pendant acid or tertiary nitrogen groups, which are completely or partially neutralized or quaternized, respectively, to form salts [11,12].

The structure–property relationships of aqueous dispersions containing a fraction of ionic repeat units have been

---

☆ Supported by the grant (No. 50233030) from the National Natural Science Foundation of China, and NKBRSF project, No. 2001CB409600.

* Corresponding author. Tel.: +86 551 3606084; fax: +86 551 3606630.
E-mail address: wfshi@ustc.edu.cn (W. Shi).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.09.046

the subjects of numerous articles and reviews [13]. The unique properties of an aqueous PU dispersion are obtained from the structures and compositions of components, preparation method and microphase separation of incompatible soft and hard segments. In addition the interaction between ions and their counterions is also responsible to effect on its properties. Both the degree of neutralization and content of ionic component contribute significantly to the properties of ionomers [14]. Hourston et al. reported the influence of degree of neutralization and ionic moiety on the properties of waterborne dispersions [15]. In this respect, waterbased UV curable systems appear as a promising supplement by eliminating the use of acrylate monomers, and water being used as the only diluent.

Macromolecular architecture has been recognized as an important tool to obtain a polymer with tailored properties. Due to this, the interplay between molecular architecture and macroscopic properties has rendered increasing interest in recent years [16,17]. One group of highly branched polymers is dendritic (tree-like) polymers, comprising hyperbranched polymers and dendrimers [18]. Even though hyperbranched polymers are polydisperse and not fully branched, they still exhibit very different properties compared to their linear counterparts [19]. It is generally accepted that dendritic macromolecules have unusual properties such as (1) less flexibility, (2) lower entanglement degree, and (3) a significant chain end effect. It is also ready to impart a wide range of structural fine-tuning by the adjustment of degree of branching and/or modification of end functional groups to chemically suitable moieties, which play a significant role in affecting the melt processability and the final physical properties [20]. The structural control confers many unique properties to dendritic macromolecules, such as viscosity [21] and thermal behavior, [22] and provides synthetic opportunities for producing new polymer-like materials.

Hyperbranched polymers have also been described in several applications, ranging from processing additives to thermoset system components [23,24]. Now-a-days, many studies about waterborne polyurethane have been published but there is little information about the use of hyperbranched polymers in UV curable waterborne coatings. Hyperbranched polymers studied in this work are aliphatic polyesters using ethoxylated pentaerythritol as central cores and 2,2-bis(methylol)propionic acid (bis-MPA) as dendritic units. They are supplied by Perstorp, Sweden, under the tradename as Boltorn Hn series hyperbranched polymers where $n=20$, 30, 40. Boltorn™ H20 indicates that it statistically contains two generations of bis-MPA, whilst Boltorn™ H30 and H40 are third and fourth generation of the hyperbranched polymer, respectively. Moreover, theoretically the number of hydroxyl groups per molecule (x) for Boltorn™ H20, H30, and H40 are 16, 32 and 64, respectively. Their details can be found elsewhere [25]. In preceding articles, we dealt with a series of novel UV curable waterborne hyperbranched polyesters (WBHP) and UV curable waterborne dispersions (WHPUDs) consisting of a multi-hydroxy functional hyperbranched aliphatic polyester core [26–29]. The obtained results were discussed to deepen the understanding of the structure–property relationships of aqueous dispersions containing a variable fraction of ionic repeat units, and to explore their possible applications as UV/EB curable oligomers for coatings. The UV curable waterborne dispersions can be prepared by modifying some of hydroxyl groups (x) of Boltorn™ Hn to acidic groups (z) and tipping remaining OH-groups with isophorone diisocyanate–hydroxy ethylacrylate (IPDI–HEA) i.e. hard segment (y). The procedure to obtain WHPUDs was reported in our previous publication [28]. They are different from conventional waterborne urethane acrylate ionomers having only one ionic site in the center or at the end of a molecule. In order to give an overall view, this paper systematically examines the properties to evaluate the effects in terms of particle size, viscosity and photopolymerization kinetics of the dispersions, as well as dynamic mechanical and thermal degradation behaviors of their corresponding cured films.

2. Experimental

2.1. Materials

The hyperbranched polyesters were kindly supplied by Perstorp AB, Sweden, and used as received. The polymers are denoted as H20, H30, and H40 with the reference to hydroxyl terminal groups and generation number (g), from the second (H20) to the fourth (H40). Their hydroxyl number, molecular weight and polydispersity of the Boltorn polymers from the data sheets provided by Perstorp are listed in Table 1. Boltorn™ H20, H30, H40 were used as principal polyols for aqueous dispersions. The sample designation and stochiometric ratio of hard segment (HEA–IPDI) to salt like moiety for the preparation of WHPUD2, WHPUD3 and WHPUD4 are listed in Table 2. The detailed synthesis and characterization of WHPUD2-a, WHPUD2-b, WHPUD2-c were described elsewhere [28]. WHPUD3 and WHPUD4 have been prepared by the same procedure. The ideal molecular formula of Boltorn™ H30 and the schematic outline of the synthesis for WHPUDs are shown in Fig. 1. Deionized water was used as the dispersion medium. The dispersion was prepared at 40% solid content. 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.

Table 1
Material characteristics of Boltorn™ hyperbranched polyesters

Generation number (g)	Sample	Hydroxyl number (mg KOH/g)	Molecular weight (g mol^{-1})	Polydispersity (M_w/M_n)
2	Boltorn™ H20	490–520	2100	1.3
3	Boltorn™ H30	480–510	3500	1.5
4	Boltorn™ H40	470–500	5100	1.8

Table 2
Sample designation and stochiometric ratio of HEA–IPDI and COOHNH$_3^+$ for the preparation of WHPUD2, WHPUD3 and WHPUD4

Samples	Stochiometric ratio of HEA–IPDI:COOHNH$_3^+$ $x=(y+z)$	
Boltorn™ H20 $x=$(16 OH groups per molecule)	y	z
WHPUD2-a	6	10
WHPUD2-b	8	8
WHPUD2-c	10	6
Boltorn™ H30 $x=$(32 OH groups per molecule)		
WHPUD3-a	12	20
WHPUD3-b	16	16
WHPUD3-c	20	12
Boltorn™ H40 $x=$(64 OH groups per molecule)		
WHPUD4-a	24	40
WHPUD4-b	30	34
WHPUD4-c	36	28

The commercial waterborne resin, EB 2002 (of functionality 2) was supplied by UCB Co., Belgium.

2.2. UV curing

The formulations with 1.5 wt% Irgacure 2959 were coated onto a glass plate at room temperature. Water was then allowed to evaporate at the temperature between 25 and 80 °C in an oven. Finally, the samples exposed to a UV lamp (80 W cm^{-1}, made by Lantian Co., Beijing, China) at a variable conveyer speed.

2.3. Measurements

The average particle sizes and their distribution of WHPUDs were measured by the laser light scattering method. A modified commercial light scattering spectrometer (ALV/SP-150 equipped with an ALV-5000 multi $-\tau$ digital time correlator) was used with a solid-state laser (ADLAS DPY 425 II, at $\lambda=632.8$ nm) as a light source at 25 °C. The particle concentration in the dispersion was adjusted to 0.1% using deionized water and stirred well to obtain a homogeneous dispersion.

The rheological behavior of final products was determined with a QNX Model Rotating Viscometer (Tianjin Instrument Co., China) with variable shear rates.

The photopolymerization kinetics was carried out on a modified CDR-1 DSC apparatus made by Shanghai Balance Instrument Co., under irradiation using a UV Spotcure System BHG-250 (Mejiro Precision Co., Japan). The digitized data based on the traces on a strip chart recorder were analyzed by the software Origin 6.1 on a personal computer. 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 [29]. The DSC curve was adjusted by the weight of sample (g). The polymerization rate was defined by $\text{mmol}_{C=C}\ g^{-1}\ s^{-1}$, namely the variation of double bond concentration (mmol g^{-1}) per second. For calculating the polymerization rate, the value of polymerization heat $\Delta H_o=86$ J mmol^{-1} per acrylic double bond was considered [30].

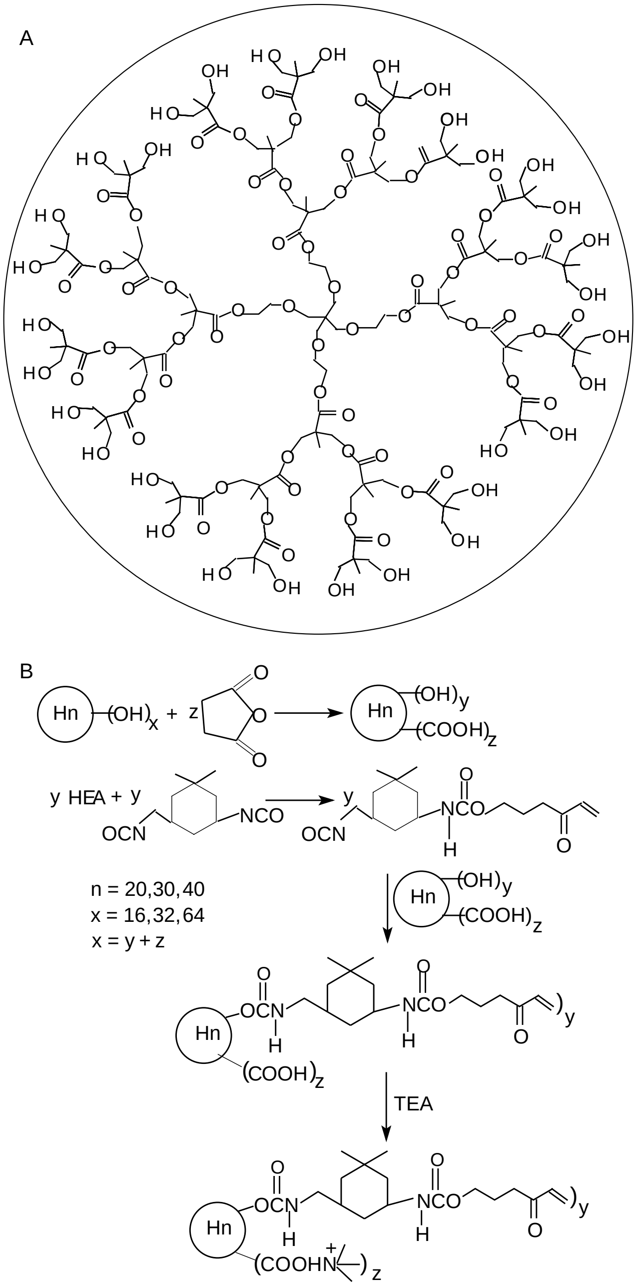

Fig. 1. (A) Idealized formula of Boltorn™ H30. (B) Schematic description of the synthesis for WHPUDs.

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 rate of 2 °C min^{-1} over a temperature range from -50 to 200 °C. The sample chamber was purged with high purity grade of nitrogen at a constant flow rate to prevent the sample from moisture. The UV cured films were made on a glass plate with a special frame as a support ($20\times5\times1$ mm) under UV exposure.

Thermogravimetric analysis (TGA) was carried out using a Shimadzu TG-50 instrument (Shimadzu Co., Japan). The cured samples ranging 8–10 mg were placed in a platinum sample pan and characterized by performing a scan from room temperature to 700 °C at a rate of 10 °C min^{-1} in nitrogen atmosphere. The degradation temperature of the cured sample was taken as the temperature at which 5% weight loss had occurred. No weight loss in the TGA curves in temperature range of 30–110 °C was used as a guideline for having achieved complete drying.

3. Results and discussion

3.1. Particle size

It is well known that all ion-containing polymers are not water dispersible and a minimum amount of ionic content is, therefore required for the formation of a stable dispersion. The dispersibility is governed by the hydrophilicity of the chains and the hydration of the neutralizing cations. Generally, increased hydrophilicity results in smaller particles. Therefore, it is important to be able to control the particle size via chemical composition. For example, relatively larger particles are preferred in surface coatings for rapid drying, and smaller ones are desirable when the deep penetration of dispersion into a substrate is an essential step.

3.1.1. Effect of acid content

Three series of WHPUDs with H20, H30 and H40 having different contents of carboxylate group were prepared in order to study the effect of ionic content (Table 2). The variations of the average particle sizes of WHPUDs to depict the effects of acid content and generation number of hyperbranched polyester are listed in Table 3. Smaller polymer particles are obtained at higher COOH content and degree of neutralization [31]. The aqueous dispersions obtained from three hyperbranched polyesters with particle sizes in the range of 43–134 nm. It can be seen in Table 3 that the particle sizes follow the same order for three series, i.e. WHPUD2-a < WHPUD2-b < WHPUD2-c (43.75–70.69 nm), WHPUD3-a < WHPUD3-b < WHPUD3-c (52.82–92.19 nm) and WHPUD4-a < WHPUD4-b < WHPUD4-c (69.65–99.36 nm) at 100% neutralization. It is further noted that the particle sizes at both 40 and 70% neutralization follow the consistent behavior as above. The WHPUD4 series have the largest particle sizes. In PU dispersions, the average particle sizes increase as the ionic group concentration per unit chain length of prepolymers decreases. The asymptotical decrease of particle size with increasing acid content is due to the stabilizing mechanism of ionomer dispersions.

Table 3
Effects of carboxyl content and degree of neutralization on the average particle sizes of WHPUDs

Sample	Average particle size (nm) Degree of neutralization		
	100%	70%	40%
WHPUD2-a	43.75	81.40	99.74
WHPUD2-b	59.83	89.63	113.82
WHPUD2-c	70.69	97.58	125.02
WHPUD3-a	52.82	86.96	98.18
WHPUD3-b	73.98	94.26	105.61
WHPUD3-c	92.19	101.76	129.57
WHPUD4-a	69.65	94.36	105.61
WHPUD4-b	91.86	102.84	113.80
WHPUD4-c	99.36	111.77	134.30

It is clearly seen that the ionic groups are located predominantly on the surfaces of particles, whereas the chain segments form the interior of the particle. At the interface between particles and water a double layer is formed by the dissociation of ionic groups. So the electrical double layer stabilizes these dispersions in water. As the particle size reduced, the number of dispersed particles and viscosity increased. It is important to mention for this comparative study of three series that we obtained WHPUD2 and WHPUD3 with the same mole ratio of HEA–IPDI:COOH content but was not feasible for WHPUD4 as the higher content of unsaturated segment leads to crosslinking during the preparation.

On the other hand, the effect of the generation number and molecular weight on particle size is controversial, whereas in the literature [32] it is generally reported that smaller particles can be produced by the dispersion of polyurethane with longer (more flexible) soft segments. On the contrary, in our case it is very clear that higher generations of WHPUDs have larger particle sizes although H20 and H30 are thought to have more extended molecular conformation, whilst the longer chains of H40 are more flexible. Table 1 implies that the lower generation materials have the higher concentration of salt-like units due to higher hydroxyl number. Furthermore, it is likely that as the generation number increases, the dendritic arms become more flexible and fold back into the hyperbranched molecules, and thus less polar end groups will be exposed to other molecules. Presumably, these intermediate sizes of WHPUD3 and WHPUD4 are believed to be the result of competition between the higher molecular weight of third and fourth generation of hyperbranched polyester and acid content of resulting dispersion. The presence of more hydrogen bonding may result in the aggregation between PU molecules. In general, ionic content is inversely proportional and molecular weight is directly proportional to particle size. In our case there is an increase in molecular weight as well as ionic content when WHPUD2-a, WHPUD3-a and WHPUD4-a have been considered. Hence, it is interesting to see the dual effects, if the ionic content plays a major role, the particle size is expected to decrease with increasing COOH groups, whereas the particle size is expected to increase with higher generation (larger molecular weight). So the comparable sizes of dispersions related to different series are born out quantitatively as a result of above discussed factors.

3.1.2. Effect of degree of neutralization of ionic groups

The degree of neutralization has a direct effect on the particle sizes of dispersions, i.e. WHPUD2, WHPUD3 and WHPUD4, as listed in Table 3. It is clear that the particle sizes are 52.82, 86.96 and 98.18 nm for WHPUD3-a, and 69.65, 94.36 and 105.61 nm for WHPUD4-a at the degree of neutralization of 100, 70 and 40%, respectively. It is inevitable

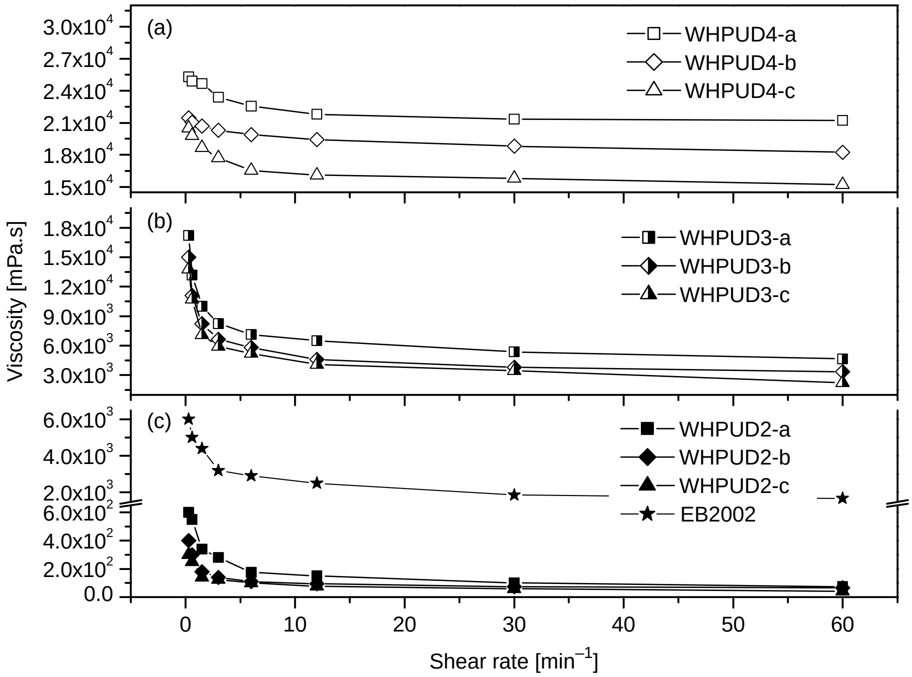

Fig. 2. Dependence of viscosity on shear rate for WHPUD2, WHPUD3, WHPUD4 and EB 2002 at 30 °C.

that the average particle sizes of WHPUDs decrease as the mole ratio of TEA to COOH varies from 0.4 to 1.0 for these dispersions. This result is ascribed to the variation of the content of carboxylic group that can be neutralized by TEA and responsible for reduction in particle sizes of aqueous dispersions.

In waterborne dispersions, the degree of dissociation depends on the degree of neutralization. Consequently, with increasing the degree of neutralization, the surface charge density increases. Moreover, the properties of PU dispersions, such as their ability to release hydrophobic species, depend on the degree of neutralization of carboxyl groups.

3.2. Rheological behaviors

The rheological property is a very important factor determining the processibility and end-use property of a polymer material. The chain structure and topology of a polymer determine its rheological properties [33]. The viscosity arises from the interactions among the particles in dispersion. 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. It is assumed that hyperbranched molecular structures disrupt the local entanglement network and thus reduce the entanglement density of molecular chains due to their relatively compact, globular structures and resulting in a rather lower viscosity. Despite this importance, some recent studies on the melt rheology of certain commercial aliphatic hyperbranched polyester indicates that such materials with lower generations may exhibit shear-thinning behavior due to the interactions between the functional groups on the molecular periphery, whilst Newtonian behavior was observed for materials with larger molecular weight (higher generations) [34,35]. Non-Newtonian phenomena with supermolecular interdendrimer hydrogen bonding have also been reported recently by Uppuliri et al. [36].

The rheological data at a variable shear rate are plotted in Fig. 2 to underscore the difference in behavior exhibited by WHPUDs having different acid contents and based on various generations of hyperbranched polyesters. In the first approach the viscosity of WHPUDs and EB 2002 as a function of shear rate at 40% solid content was monitored. Fig. 2 reflects clearly that at each shear rate the viscosity of commercial waterbased resin EB 2002 (linear structure) is higher than those of WHPUD2 series implying less entanglement in hyperbranched structure.

The viscosity increases for the three series in the order of WHPUD2 < WHPUD3 < WHPUD4. It has been observed that the viscosity for WHPUD3 and WHPUD2 dispersions decrease drastically when the shear rate increases from 0.3 to 6 min^{-1}, whereas decreases gradually from 6 to 60 min^{-1}, while the viscosity of WHPUD4 does not drop sharply. 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. However, in our case this observation holds well within a series, when the rheological behavior of WHPUD2 could be observed from the shear stress for the dispersions as a function of shear rate, given in Fig. 2(a). The viscosity of aqueous dispersions in this study decreases in the order of WHPUD2-a > WHPUD2-b > WHPUD2-c. Moreover, the same behaviors have been observed for WPUD3 and WHPUD4 series. Also, the WHPUD2 and WHPUD3 have significantly lower viscosity than WHPUD4 analogs at comparable weight fraction due to

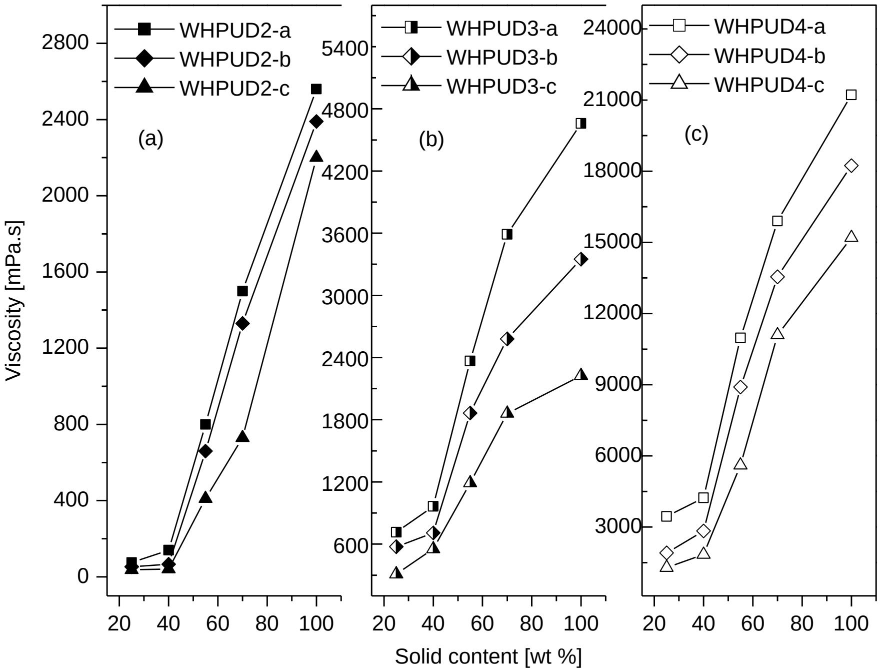

Fig. 3. Dependence of viscosity on solid content of WHPUD2, WHPUD3 and WHPUD4 at 30 °C.

the difference in molecular weights. As the ionic group concentration in the prepolymer increases, the mutual repulsion of the same charges causes the expansion of chains, which may result in increasing the viscosity of dispersions.

The hard segment in a prepolymer also plays an important role in determining the viscosity of dispersions. It seems from the results illustrated in Fig. 2 that the IPDI-based dispersions exhibit pronounced deviation from Newtonian flow behavior. The chain entanglements and hydrogen bonding between urethano and urea linkages can be more rapidly formed in the IPDI-based prepolymers because of the flexibility of the chains.

Although the literature regarding melt viscosity of hyperbranched polymers to date suggest that, H20 and H30 demonstrate shear thinning, whilst H40 is Newtonian. The similar rheological findings can also be observed for waterborne dispersions having parent polymer H20 and H30. Fig. 2(c) depicts the shear thinning for dispersions based on H40 as the viscosity of WHPUD4-a, WHPUD4-b and WHPUD4-c decreases monotonically. The cause of this phenomenon is not fully understood. As this is believed to be the first study on such dispersions, no directly related literature is available to offer an insight towards this observation. However, it has been reported that the lack of entanglement in dendritic polymers leads to their Newtonian behavior [22]. It is apparently not the case here for WHPUD2 and WHPUD3, since they are smaller molecules as compared with WHPUD4 and thus likely to have more entanglements than WHPUD4, so shear thinning behavior could be due to the polar interactions among molecules resulting from the numerous peripheral polar groups. Moreover, it is expected that greater shear rates may help to reduce the polar influence on the temperature dependence of steady shear viscosity, as the molecules have to undergo greater scale of realignment to cope with the more vigorous deformation applied.

In addition, the rheology of a water dispersible system can be easily controlled by the addition of water. It is important to measure the viscosity of dispersions as a function of solid content, because in the case of UV curable aqueous resins, water must be evaporated before UV irradiation. Thus, a higher solid content with the same viscosity is beneficial in terms of energy efficiency. Fig. 3 shows the viscosity profiles of WHPUD2, WHPUD3 and WHPUD4 as a function of solid content at a shear rate of 60 min^{-1}. The viscosity of all the WHPUDs was found to reduce drastically with the addition of water. In all systems, the viscosity dropped with the addition of 30% water by weight and continued to drop as more water was added (Fig. 3). For instance, in WHPUD4-a, WHPUD4-b and WHPUD4-c the viscosity dropped approximately 25% with the initial addition of 30% water and dropped significantly, i.e. almost 70–85% at 25% solid content of these dispersions. The viscosity measurements of WHPUD2 and WHPUD3 also reveal the consistent results as above.

It is clear that for all samples the decrease in the solid contents cause their viscosity to decrease. It is important to noteworthy that the decreased solid content leads to the orientation of prepolymeric molecular chains, thus destroying the associated structures such as hydrogen bonding and chain entanglements. As a result, the flow resistance decreases and the viscosity reduces.

3.3. Photopolymerization kinetics

Photopolymerization offers many advantages, such as rapid curing, high-energy efficiency and low volatile organic content (VOC), and has been an ongoing focus of coating research.

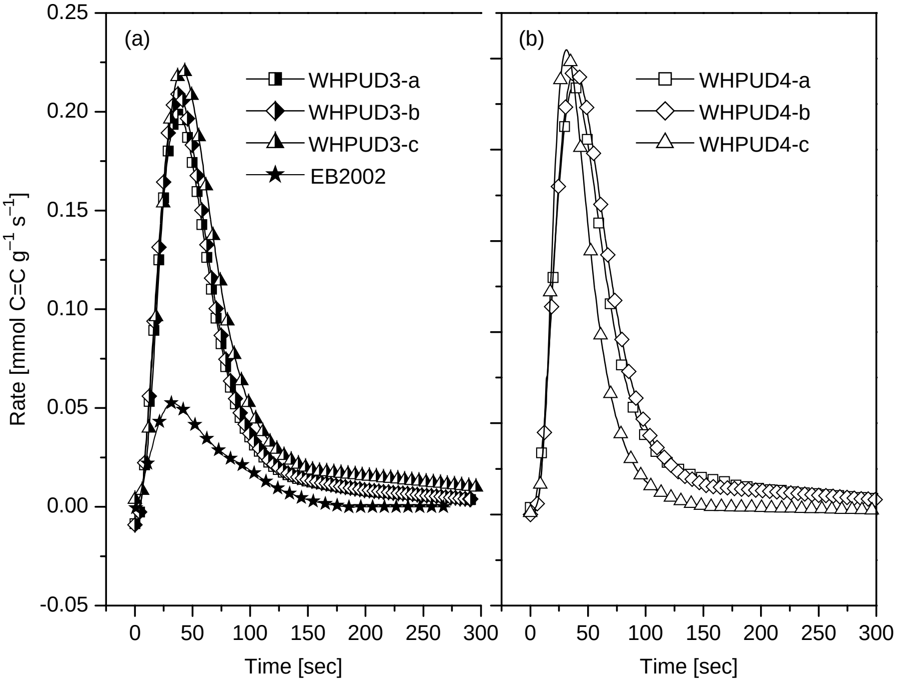

Fig. 4. Photopolymerization rate comparison of WHPUD3, WHPUD4 and EB 2002 using 1.5% Irgacure 2959.

The photoinitiated polymerization of acrylates and methacrylates is one of the most efficient processes for the rapid production of polymeric crosslinked materials with defined properties. The most important parameters characterizing the curing kinetics of an oligomer are the rate at the peak maximum R_p^{max} and the final degree of double bond conversion (P^f).

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 shown in Fig. 4. 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.

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 crosslinking restricts and eventually stops the propagation. The high R_p^{max} s of 0.235, 0.243 and 0.255 mmol$_{C=C}$ g^{-1} s^{-1} are observed for WHPUD4-a, WHPUD4-b and WHPUD4-c, respectively, compared to 0.199, 0.208 and 0.221 mmol$_{C=C}$ g^{-1} s^{-1}, respectively, for WHPUD3 series under the same conditions. These values indicate that the high concentration of acrylic end group located at the outer layer of the sphere-like structure leads to a high value of R_p^{max}.

The observed high rates can be accounted for the hydrogen bonding pre-association in these systems. This is in accordance with the work done by Jansen et al, where the acrylated prepolymers capable of hydrogen bonding exhibited 3–6 times higher polymerization rates than their non-hydrogen bonding counterparts [37].

It must be stated here that lowest R_p^{max} value for EB 2002 has been observed among all series. The difference observed in R_p^{max} s can be ascribed to the variation in the concentration of unsaturation, chemical structure and the viscosity of formulations. Moreover, it has been observed that WHPUD2-a, WHPUD2-b and WHPUD2-c are 0.20, 0.23, and 0.29 mmol$_{C=C}$ g^{-1} s^{-1}, respectively, and its rate profiles are not shown to avoid repetition.

This is already evident that in WHPUD4 the higher soft segment content leads to crosslinked coatings that are elastomeric, where the mobility restriction is expected to be less pronounced than those in WHPUD2 and WHPUD3. Although, based on the preliminary information about degree of unsaturation, we tentatively believe that higher generation based dispersions have higher R_p^{max} but actually lower generation materials have the higher concentration of double bond unit as compared to the soft segment content. The viscosity data elucidated why WHPUD2-b had a comparable R_p^{max} compared with WHPUD3-b. For instance, the WHPUD2-b formulation with about theoretically eight double bonds while WHPUD3-b has sixteen double bonds per prepolymer molecule, exhibited a comparable curing speed with lower viscosity. As mentioned in previous section, the viscosity of aqueous dispersions in this study decrease in order of WHPUD4 > WHPUD3 > WHPUD2. Here, the combination of viscosity and concentration of unsaturation provides the clear evidence that polymerization rates are not simply predictable.

Conversion profiles (Fig. 5) indicate that up to 84 and 78% acrylate groups have polymerized in WHPUD3-c and WHPUD4-c after a 250 s UV exposure, respectively, a quite remarkable feature for a polymerization carried out at ambient temperature. The highest conversion is observed for

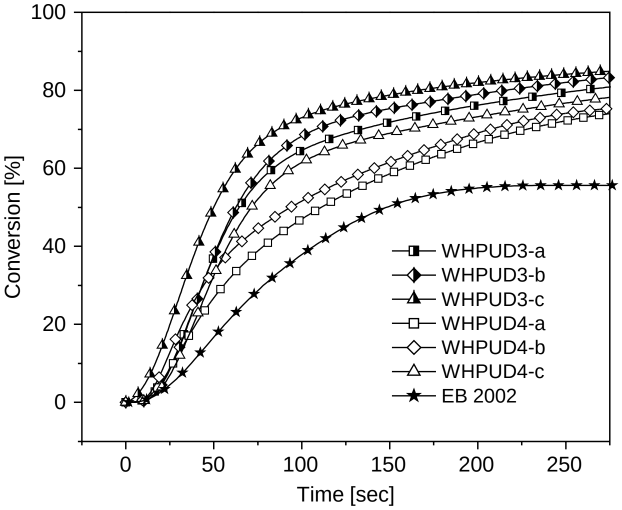

Fig. 5. Unsaturation conversion comparison of WHPUD3, WHPUD4 and EB 2002 using 1.5% Irgacure 2959.

WHPUD3-c, followed in order by WHPUD3-b and WHPUD3-a. These results suggest that the molecular mobility and the accessibility of the acrylate double bonds are superior in WHPUD3 due to the lower viscosity. As shown in Fig. 5, the final unsaturation conversion P^f for all samples of WHPUD4 and WHPUD3 continues to increase slightly up to 300 s. This may be interpreted that the network with lower crosslink density can easily release the polymeric radicals for further photopolymerization. The amount of carboxylic acid introduced into WHPUDs to make them dispersible in water may affect the curing kinetics by acting on the viscoelastic properties, which is also shown in Fig. 5. It can be seen that the final conversion decreases as the acid content increases. This is also due to the fact that as the ionic group content (carboxylic group neutralized with triethylamine) in water-borne 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.

3.4. Dynamic mechanical thermal analysis (DMTA)

DMTA was utilized to investigate the thermal mechanical properties of UV cured WHPUD films in an effort to further understand the structure/property relationships. The temperature associated with the peak magnitude of loss factor (tan δ) is defined as the glass transition temperature (T_g). The softening point (T_s) is defined as the extrapolated onset of the drop of log storage modulus (E'). E' is a measurement of material stiffness and can be used to provide the information regarding the molecular weight of a polymer, degree of cure and crosslink density [38]. 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 film is more homogeneous, whereas broader tan (δ) transition suggests the greater degree of heterogeneity of crosslinks [39].

Table 4
Dynamic mechanical properties of WHPUD2, WHPUD3, WHPUD4 and EB 2002

Sample	T_s (°C)	T_g (°C)	T_s/T_g	V_e (mmol ml^{-1})
WHPUD2-a	14.0	58.0	0.867	1.34
WHPUD2-b	18.0	63.0	0.866	2.14
WHPUD2-c	20.0	72.0	0.849	2.32
WHPUD3-a	22.1	61.6	0.881	1.78
WHPUD3-b	31.8	68.9	0.891	2.09
WHPUD3-c	36.3	74.8	0.889	2.34
WHPUD4-a	23.8	64.2	0.880	2.02
WHPUD4-b	32.9	69.4	0.893	2.45
WHPUD4-c	37.2	77.1	0.886	2.59
EB 2002	7	40	0.895	1.09

This method provides the modulus values with very small deformation of highly crosslinked networks. This is because the network chains can respond to these small deformations by undergoing changes in conformation that requires only rotation of bonds in the network chains. If bond angle bending and bond breakage are eliminated by using small deformation, and if entanglements are also avoided, the relationship between rubbery plateau modulus and crosslink density is very simple,

$$V_e = \frac{E'}{3RT}.$$

Where V_e is the crosslink density, i.e. the molar number of elastically effective network chains per cubic centimeter, E' is the tensile storage modulus, R is the gas constant, and T is the temperature in Kelvin. The dynamic mechanical thermal properties of WHPUD2, WHPUD3, WHPUD4 and EB 2002 are summarized in Table 4. The tan (δ), E', and E'' are plotted as a function of temperature for WHPUD3 WHPUD4 and EB 2002 in Figs. 6–8, respectively.

The data in Table 4 indicate that the T_g increases with increasing the generation number from the second to the fourth of hyperbranched polyester and the concentrations of hard segment. This is in a good agreement with theoretical predication for highly branched (hyperbranched and dendritic) polymers and is analogous to linear polymers, [40], i.e. longer arms yield higher glass relaxation temperatures.

Fig. 6 shows the loss tangent curves for WHPUD3, EB 2002 and WHPUD4 as a function of temperature. The glass-transition temperature increased about 5–14 °C for an increase in the hard segment concentration for WHPUD2-a to WHPUD2-c. Similarly, the T_g's for WHPUD3-a, WHPUD3-b and WHPUD3-c are 61.6, 68.9 and 74.8 °C, while for WHPUD4-a, WHPUD4-b and WHPUD4-c are 64.2, 69.4 and 77.1 °C, respectively. The linear structure EB 2002 shows the low values of T_g, E' and E'' that is mainly due to the lower cross-linking density. The higher crosslink density affects the loss tangent curves in two different ways. First, the loss tangent peaks shift to higher temperatures. This occurs because the samples with higher crosslink density have higher glass-transition temperatures. Second, the loss tangent peaks become broader. The broadening of the loss peak may indicate that

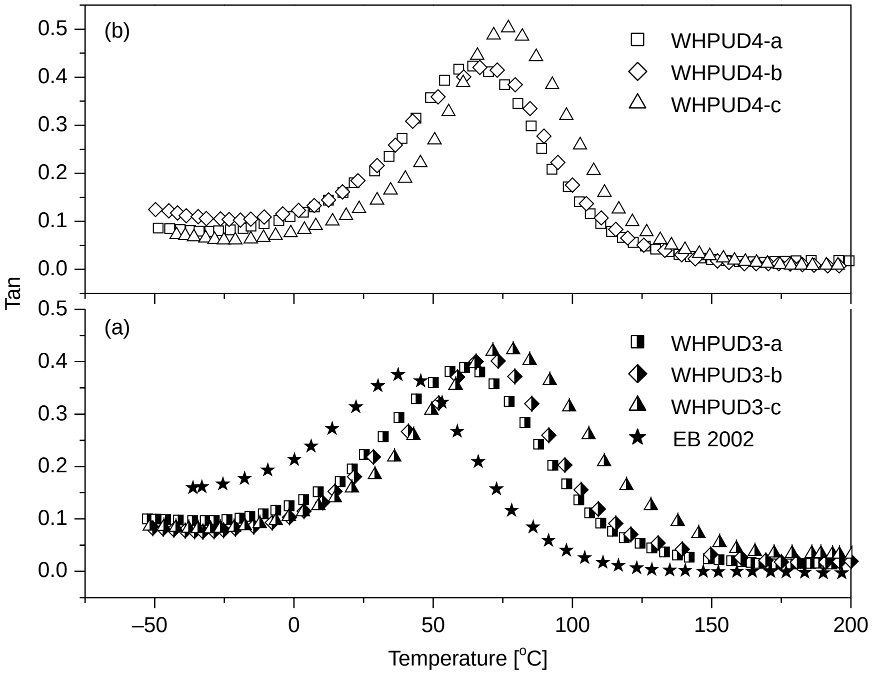

Fig. 6. Tensile loss factor (tan δ) as a function of temperature for (a) WHPUD3, EB 2002 and (b) WHPUD4.

the relaxation is not single one and comprises of several consecutive ones. This broadening is attributed to an increase in the distribution of molecular weight between crosslinks or an increase in the heterogeneity of the network structure.

Of more importance is the observation of single glass transitions in all of the dispersion systems cited. This implies that the hard and soft segment miscibility increased, perhaps owing to the increased cohesions within the hard segments via hydrogen bonding. When the phase mixing is relatively complete, the backbone mobility is greatly restricted by the hard segments.

As shown in Figs. 7 and 8, E' and E'' values of WHPUD3 and WHPUD4 exhibit the same behavior, a result consistent with T_g values. Once the glass-transition temperature is reached, the elastic modulus decreases rapidly as the polymer chains begin to move. The elastic modulus continues to decrease until it plateaus at around 98 °C. At this point, the chemical crosslinks prevent the polymer from flowing.

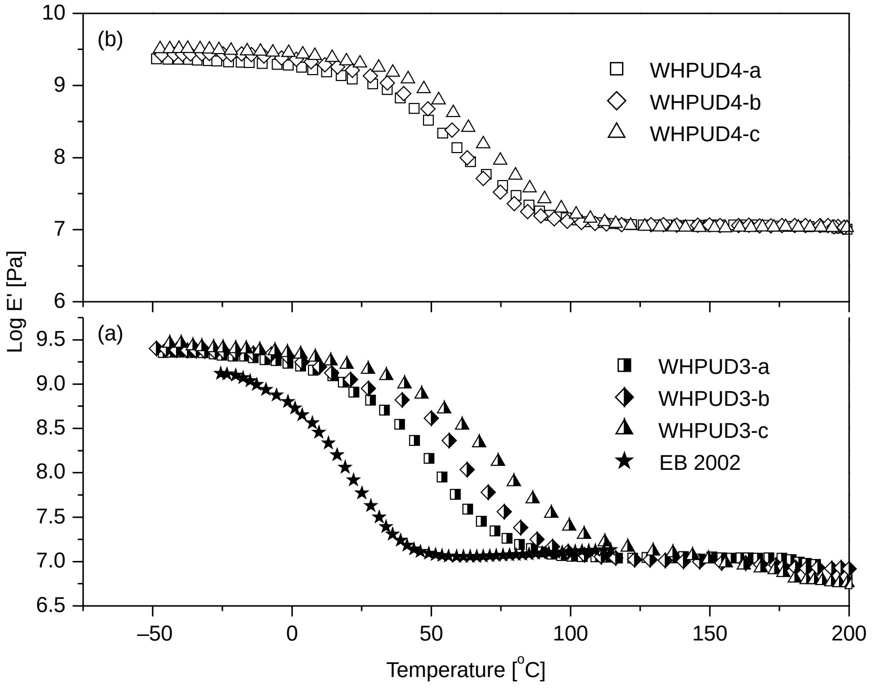

Fig. 7. Tensile storage modulus E' as a function of temperature for (a) WHPUD3, EB2002 and (b) WHPUD4.

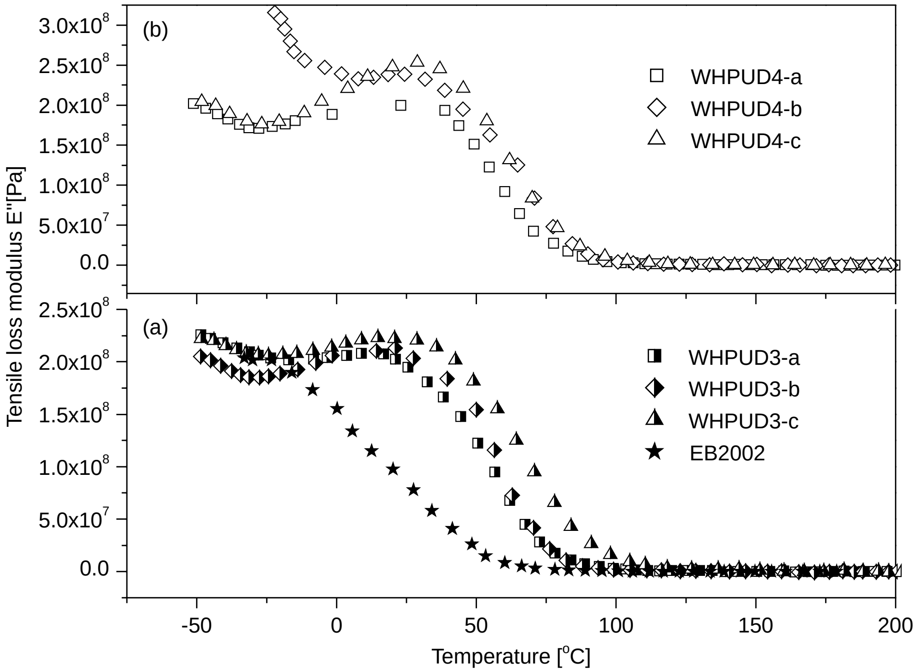

Fig. 8. Tensile loss modulus E'' as a function of temperature for (a) WHPUD3, EB 2002 and (b) WHPUD4.

The modulus for samples with lower crosslink density decreases at a lower temperature and at a faster rate than the samples with higher crosslink density. The elastic modulus curves follow the same trends for WHPUD4 as those shown in Fig. 7(b). It can be seen from Tables 1and 2, that the concentration of hard segment per molecule decreases with increasing generation number. The higher concentration of the end groups for lower generation polymer implies a greater possibility of molecular interactions between branches. Presumably, the shorter arms of H20 macromolecules are relatively stiff and the back folding of segments hardly occurs and the end groups in H20 reside at the molecular periphery. With increasing generation number, the branch flexibility, especially chain end mobility, increases and the inward folding of the molecules is more likely [41].

Consequently, these results were also observed in the loss modulus (E'') versus temperature curves as shown in Fig. 8. The hard segment consisting of IPDI–HEA unit also has a direct influence on E'' values of WHPUDs. E'' values increase monotonically for WHPUDs with increasing the hard segment content, implying that the phase mixed morphology is maintained. The higher values of E'' suggest the greater mobility of the polymer chains associated with the dissipation of energy when the polymer is subjected to deformation. The overall effect would be to hinder the motion of different segments and broaden the distribution of their relaxation times.

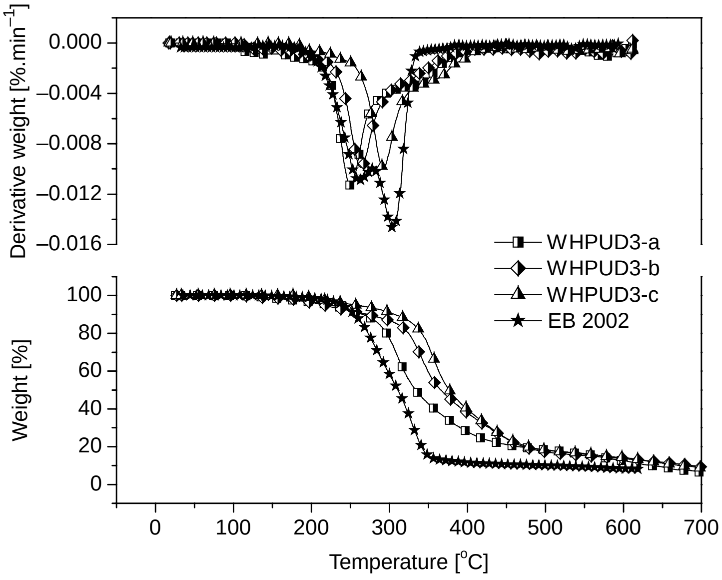

Fig. 9. TGA and DTGA curves of UV cured WHPUD3 and EB 2002 films in N_2 at a heating rate of 10 °C min^{-1}.

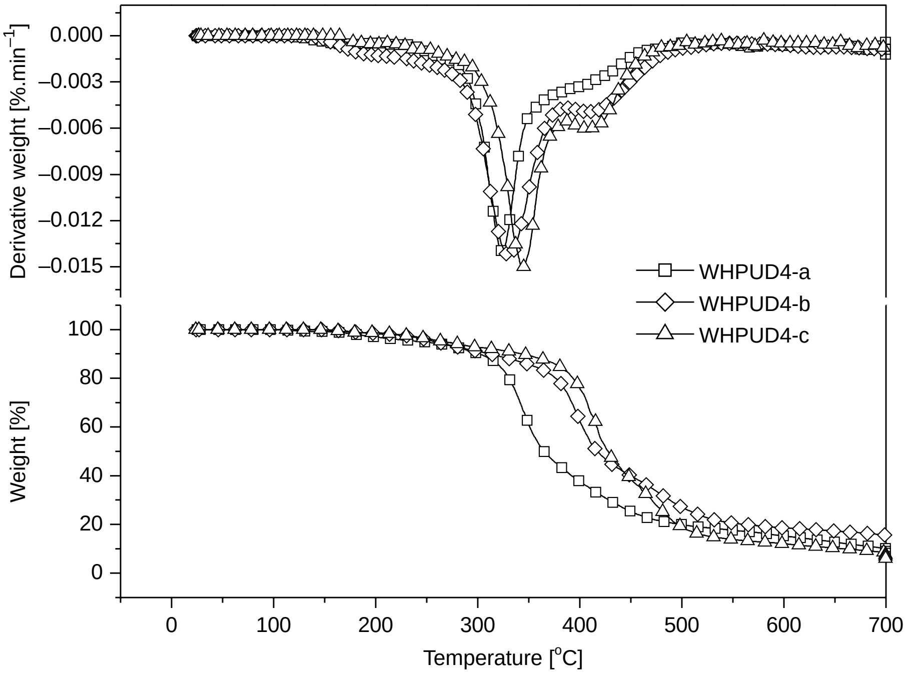

Fig. 10. TGA and DTGA curves of UV cured WHPUD4 films in N_2 at a heating rate of 10 °C min^{-1}.

3.5. Thermal behavior

The thermal degradation investigation of polymers allows the determination of proper conditions for manipulating and processing, and for obtaining high-performance products that are stable and free of undesirable by-products. Besides that, TG provides a method for accelerating the lifetime testing of polymers so that short-term experiments can be used to predict in-use lifetime. The onset degradation temperature (T_{on}) of WHPUDs was defined as the initial temperature of degradation, corresponding to the intersection of tangent drawn at the intersection point of decomposition step with the horizontal zero-line of the TG curve.

Figs. 9 and 10 show the degradation profiles of WHPUD3 and WHPUD4, respectively, with variation of hard, soft segment content ratio and generation number in a nitrogen atmosphere. Table 5 shows the TG parameters obtained for all three series, i.e. WHPUD2, WHPUD3, WHPUD-4 and EB 2002. EB 2002 has values of T_{1on}, T_{1max}, T_{2max} and E_a 233, 303, 344 °C and 176 J mol^{-1}, respectively. The qualitative characterization of degradation process is illustrated by the onset and maximum peak temperature of the first step, T_{1on} and T_{1max}, along with the same for second step, T_{2on} and T_{2max}. However, due to the phase mixed structure of the UV cured WHPUD the second peak is diffused one. It is in the hard segment that the initial degradation happens, thus the first observable weight loss occurs through the degradation of urethane groups.

It is clear that all TGA curves display a slower initial and then a rapid degradation process. It was found that the degradation was comparatively slow in polymers having more hard segment content (HEA–IPDI). In many cases, polymers lose their desirable properties during few percent of weight loss. The T_{1max} temperatures for WHPUD2 and WHPUD3 are ranged from 290–321 °C and, 293–340 °C while the T_{2max} fall in the range of 316–376 °C and 376–409 °C, respectively.

Table 5
TGA data of UV cured WHPUD2, WHPUD3, WHPUD4 and EB 2002 films

Sample	T_{1on} (°C)	T_{1max} (°C)	T_{2max} (°C)	Residue at 550 °C	Thermal degradation temperature T_d[a] (°C)
WHPUD2-a	206	290	316	12.3	211
WHPUD2-b	218	303	333	14.5	234
WHPUD2-c	242	321	376	19	256
WHPUD3-a	199	293	376	16.0	215
WHPUD3-b	210	304	372	15.3	223
WHPUD3-c	240	340	409	16.3	256
WHPUD4-a	235	323	401	17.6	244
WHPUD4-b	242	332	413	20.5	258
WHPUD4-c	248	341	416	13.8	266
EB 2002	233	303	344	9.2	176

[a] Temperature taken at which 5 wt% weight loss.

It can be found that for WHPUD2 and WHPUD3, there was not a significant difference for $T_{1\max}$ values. On the other hand, the difference is much more when WHPUD4 has been considered. It is presumably due to the concentration of hard and soft segments that results in comparable crosslink density for lower generation as compared with higher ones. As a result, the slightly lower starting temperatures and shorter decomposition temperature ranges were observed for the lower generation polymer as listed in Table 5.

The strength should mainly be governed by the hard fraction and crosslink density; that is, the more urethane linkages are formed to enhance hard fraction, together with an increased chance of hydrogen bonding formation. Therefore, the increase in degradation temperature may be attributed to the higher heterogeneous rigid region.

Figs. 9 and 10 also depict the differential thermogravimetric (DTG) curves for WHPUD3, EB 2002 and WHPUD4 samples. The curves show that the hard segment content have a strong influence on the thermal profile of samples as a whole. It can be seen that the thermal stability decreases in the order of WHPUD3-c > WHPUD3-b > WHPUD3-a and similarly WHPUD4-c > WHPUD4-b > WHPUD4-a. It is clear that EB 2002 has lowest thermal stability among all series.

This implies that the increase of hard segment content increases the columbic forces and crosslink density, which are responsible for the improved thermal stability. Soft–hard segment phase separation was most pronounced when the hard segment has increased irrespective of generation number. As expected, the hard segment decreases; the second peak becomes less pronounced, leading to phase mixing. This implies that the intermolecular hydrogen bonding is more effective as compared to the intramolecular one. In general, polyester soft segments were found to contribute to phase mixing by hydrogen bonding between the oxygen in the soft segment and NH group in the hard segment. However, it is not easy to interpret the trend of the degradation behavior for PUA ionomers with increasing hard–soft segment mole ratio and generation number because of the complicated morphology of the samples.

4. Conclusions

This study is focused on the characterization of three series of novel waterborne hyperbranched polyurethane acrylates for aqueous dispersions (WHPUD) based on hydroxy-functionalized hyperbranched aliphatic polyesters Boltorn™ of varying generation number by particle size, rheology, photopolymerization kinetics, dynamic mechanical thermal as well as thermal degradation behaviors. 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 allowing reaching unique combination of properties. It has been shown that both hard and soft segment contents, in addition to the generation number of hyperbranched polyester, can have a significant effect on the physical and thermal properties of WHPUDs. It has been found that the particle sizes of WHPUDs are sensitive to the carboxyl content, degree of neutralization. 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. The unique rheological properties of these novel series of dispersions reveal that all dispersions belong to pseudoplastic fluids. The low generation WHPUD2 and WHPUD3 exhibit much pronounced non-Newtonian behavior while WHPUD4 show a slight decrease of viscosity by increasing shear rate. While all three systems were found to have shear thinning behavior, there was a large difference among the individual viscosity range of these systems due to their high molecular weights. The study of polymerization kinetics using Photo-DSC has revealed that the $R_p^{\max}$ and P^f of WHPUDs are mainly dependent upon the concentration of double bond accessible for polymerization and acid content of waterborne coatings. The observed trend may again be explained by the content of hard segment (consisting of IPDI–HEA) and molecular mobility considerations related to viscosity. The soft and hard segment of WHPUDs formed virtually phase mixed morphology based on the single tan (δ) peak and the peak temperature (T_g), E', and E'' moved toward higher temperature with increasing generation number and HEA–IPDI content. The increased T_g was interpreted in terms of increased hard segment and columbic forces between ionic centers. The thermal degradation behaviors illustrate that the thermal stability of UV-cured films of WHPUDs also improves with increasing hard–soft segment ratios and generation number.

From the results, it was deduced that molecular architecture appears to be the most important factor determining the nature of intermolecular interactions and consequently all these properties.

References

[1] Wicks ZW, Jones FN, Pappas SP. Organic coatings: science and technology. vol. 2. New York: Wiley; 1994.
[2] Decker C. Macromol Rapid Commun 2002;23:1067.
[3] Decker C, Masson F, Schwalm R. Macromol Mater Eng 2003;288:17.
[4] Oertel G, editor. Polyurethane handbook. New York: Hanser Publishers; 1985. p. 510–76.
[5] Nishio A, Mochizuki A, Sugiyama JI, Takeuchi K, Asai M, Yonetake K, et al. Polym Sci, Part A: Polym Chem 2001;39:416.
[6] Liu Y, Linblad MS, Ranucci E, Albertsson AC. J Polym Sci, Part A: Polym Chem 2001;39:630.
[7] Anžlovar A, Ž igon M. J Polym Sci, Part B: Polym Phys 2002;40:115.
[8] Dieterich D. Prog Org Coat 1981;9:281.
[9] Barrere M, Landfester K. Macromolecules 2003;36:5119.
[10] (a) Barni A, Levi M. J Appl Polym Sci 2003;88:716–23.
  (b) Kim BK, Shin JH. Colloid Polym Sci 2002;280:716.
  (c) Kwak YS, Park SW, Kim HD. Colloid Polym Sci 2003;281:957.
  (d) Cheong IW, Nomura M, Kim JH. Macromol Chem Phys 2000;201:2221.
[11] Hourston DJ, Williams GD, Satguru R, Padget JC, Pears D. J Appl Polym Sci 1998;67:1437.
[12] Kim BK. Colloid Polym Sci 1996;274:599.
[13] (a) Lee CY, Kim JW, Suh KD. J Appl Polym Sci 2000;78(11):1853.
  (b) Yang JW, Wang ZM, Zeng ZH, Chen YL. J Appl Polym Sci 2002;84(10):1818.
  (c) Yang JE, Kong JS, Park SW, Lee DJ, Kim HD. J Appl Polym Sci 2002;86(9):2375.

[14] Kim BK, Lee YM. Colloid Polym Sci 1994;270:956.

[15] Hourston DJ, Williams GD, Satguru R, Padget JC, Pears DJ. Appl Polym Sci 1999;74:556.

[16] (a) Fréchet JMJ, Tomalia DA. Dendrimers and other dendritic polymers. Weinheim: Wiley; 2001.
(b) Fujikawa M, Ano R, Nakao K, Shimizub R, Miki A. Bioorgan Med Chem 2005;13:4721.
(c) Ptiček A, Hrnjak MZ, Jelenčić J, Kovačić T. Polym Degrad Stab; in press.
(d) Wei ZC, Fan HH, Li N, Wang HZ, Zhong ZP. J Mol Struct 2005;748:1.

[17] Tomalia DA, Naylor AM, Goddard WA. Angew Chem Int Ed 1990;29:138.

[18] Inoue K. Prog Polym Sci 2000;25:453.

[19] Kim YH, Webster OW. J Am Chem Soc 1990;112:4592.

[20] Yanga S, Lua W, Chena N, Hu Q. J Mol Struct-Theochem 2005;719:119.

[21] (a) Magnusson H, Malmström E, Hult A, Johansson M. Polymer 2002;43:301.
(b) Luciani A, Plummer CJG, Nguyen T, Garamszegi L, Månson JAE. J Polym Sci, Part B: Polym Phys 2004;42:1218.

[22] Wooley KL, Hawker CJ, Pochan JM, Fre'chet JMJ. Macromolecules 1993;26:1514.

[23] Ziemer A, Azizi M, Pleul D, Simon F, Michel S, Kreitschmann M, et al. Langmuir 2004;20:8096.

[24] (a) Mulkern TJ, Beck Tan NC. Polymer 2000;41:3193.
(b) Xu G, Shi WF. Prog Org Coat 2005;52:110.

[25] (a) Perstorp AB. SE-284 80, Perstorp, Sweden.
(b) Malmstrtöm E, Johansson M, Hult A. Macromolecules 1995;28:1698.

[26] Asif A, Shi WF. Eur Polym J 2003;39:933.

[27] Asif A, Huang CY, Shi WF. Polym Adv Technol 2003;14(9):609.

[28] Asif A, Huang CY, Shi WF. Colloid Polym Sci 2004;283(2):200.

[29] Asif A, Huang CY, Shi WF. Colloid Polym Sci 2005;283(7):721.

[30] Andrzejewska E, Andrzejewski M. J Polym Sci, Part A: Polym Chem 1998;36:665.

[31] Kim YB, Kim HK, Yoo JK, Hong JW. Surf Coat Tech 2002;157:40.

[32] Kim BK, Lee JC. J Polym Sci, Part A: Polym Chem 1996;34:1095.

[33] (a) Sendijarevic I, McHugh AJ. Macromolecules 2000;33(2):590.
(b) Simões R, Cunha AM, Brostow W. Comp Mater Sci; in press.

[34] Hsieh TT, Tiu C, Siomon GP. Polymer 2001;42:1931.

[35] Hult A, Malmstrtöm E, Johansson M. Hyperbranched polyesters. In: Salamone JC, editor. Polymeric materials encyclopedia. Boca Raton: CRC Press LLC; 1996.

[36] Uppuluri S, Morrison FA, Dvornic PR. Macromolecules 2000;33:2551.

[37] Jansen JFGA, Dias AA, Dorschu M, Coussens B. Macromolecules 2003;36(11):3861.

[38] Neag M. ASTM manual. American society for testing and materials. vol. 17 1995 p. 841, [PA, USA].

[39] (a) Gillham JK. Polym Eng Sci 1986;26:1429.
(b) Chiou BS, Scheon PE. J Appl Polym Sci 2002;83:212.

[40] Zhu PW, Zheng S, Simon G. Macromol Chem Phys 2001;202:3008.

[41] Kao HM, Stefanescu AD, Wooley KL, Schaefer J. Macromolecules 2000;33:6214.