

Synthesis of High-Solid Content Sulfonate-Type Polyurethane Dispersion by Pellet Process

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ABSTRACT: A novel method to prepare polyurethane dispersions (PUDs) is introduced in this article. Water dispersible polyurethane ionomer pellets were synthesized without solvent; these pellets were then dissolved in acetone and dispersed in water. Then PUDs were obtained after acetone was distilled off. Polyurethane ionomers were synthesized from polyether diol containing sulfonate as hydrophilic monomer and poly(1,4-butylene adipate glycol) with an average molecular weight of 3000 as soft segments, isophorone diisocyanate and 1,4-butanediol as hard segments, and dibutyltin dilaurate as catalyst. The properties of PUDs were measured by Laser particle size analyzer, Brookfield viscosity, and TEM analysis. High-solid content and low viscosity PUDs were obtained. Meanwhile, PUDs exhibited excellent stability and polydispersity according to the above analysis. Tensile tests and dynamic mechanical analysis showed good mechanical and thermodynamic properties of PUD films. Some typical characteristics of crystalline polymers were revealed in the tensile stress–strain curves of PUD films. Peel strength test (PVC/PVC) yielded a maximum initial peel strength value of 6 N/mm and T-peel strength value of 10 N/mm. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Water dispersible polyurethane is dispensable in water due to the presence of ionic groups in its structure. By virtue of its versatile application and excellent properties, it has been used in a wide range of fields such as coating, adhesive, ink, biological materials, building materials, automotive, and textile.^{1–5} Extensive studies have shown different methods for synthesis of water dispersible polyurethane,^{6–10} and the most widely used methods are acetone process, prepolymer process, melt dispersion process, and cetimine-cetazine process. The most commonly used methods are the two processes that were mentioned initially. Acetone process has a homogenous polyurethane reaction system and sample to operate. However, there are so large amount of organic solvent to be used that make the cost of production go up and reduce production efficiency and security. Although a small amount of organic solvent was used in prepolymer process compared with acetone process, chain extension carried out in nonhomogeneous system, which will bring about difficult to control the degree of chain extension. Finally, poor reproducibility will appear in results. All the methods mentioned above belonged to batch reaction, and their common drawbacks include large energy consumption, low efficiency, and difficult in controlling the stability between batches.

In view of this, some continuous dispersion processes to prepare polyurethane dispersion (PUD)^{11–13} were introduced. Both the neutralization and chain extension were conducted in continuous mode, thereby reducing the amount of organic solvent and increasing the production efficiency are advantages of continuous dispersion process to prepare PUD. However, more energy is consumed when the prepolymer in viscous state disperses in water. Continuous dispersion processes as a new technology in the initial stage are not mature enough, and the poor reproducibility of the products is the major shortcoming.

All the products obtained through the traditional methods are PUD that contains more than 50% water, the weak point appeared immediately. If the temperature conditions are not well controlled during transportation and storage, the presence of water may cause loss of stability of the polyurethane owing to hydrolysis. The dispersions that contain more than 50% water will greatly enhance storage and transport costs.

In this article, a new method to prepare polyurethane ionomer pellets was introduced. It can be obtained in solid form and have higher production efficiency than the tradition methods. Pellets can be easier to handle and store. Besides, it can also reduce the costs. In further study, this pellet process is

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conducted by a twin screw extruder with the shape of a reactor, provided with higher temperature, so production efficiency will be improved largely by this continuous pellet process. High-solid content sulfonate-based PUDs were prepared by pellet process. Different variables on the properties of polyurethane were extensively investigated such as hydrophilic group content (HGC), the hard segment content (HSC, wt %), and total NCO/OH molar ratio (R). This article can provide valuable information in applications of waterborne polyurethanes in industrial adhesives.

EXPERIMENTAL

Materials

Isophorone diisocyanate (IPDI) was purchased from Bayer (Germany). Poly(1,4-butylene adipate glycol) (PBA) with an average molecular weight of 3000 was obtained from Dong Guan HonTex Chemical Co. Ltd. (China). Polyether diol containing sulfonate (SPPG) was purchased from Taiwai Po Chiun Company (China). 1,4-butanediol (BD) was obtained from Tian Jin JinBin Chemical Company (China). dibutyltin dilaurate (DBTDL) was purchased from Tianjin Chemical Reagents Factory (China). Acetone was purchased from Tianjin Chemical Reagents Factory (China). All these materials were used without further purification.

Testing Equipment and Analytical Methods

The structure of polyurethane was investigated through Tensor 27 Fourier transform infrared spectrometer (Bruker, Germany).

The viscosity of PU solution before dispersion was measured in a digital viscometer (NDJ-8S, from Shanghai Precision & Scientific Instrument Co., Ltd., Shanghai City, China) by using the spindle No. 2 at 0.6 rpm at 25°C. The viscosities of PUD were measured by using the spindle No.1 at 60 rpm, No.2 at 60 rpm, No.1 at 30 rpm and No.2 at 30 rpm.

The mean particle diameters and the distribution of the PUD (PSD) were measured by Zeta Potential Analyzer, Zetaplus, from BROOKHAVEN at 25°C. The dispersions were diluted to around 0.1% with deionized water before the measurement.

The morphology of dispersions was observed through TEM micrographs, which were investigated by transmission electron microscopy (TEM; TECNAI G² 12, from FEI Optonics Co., Ltd., The Netherlands). The samples were stained with phosphotungstic acid.

The mechanical properties of the cast films were measured at room temperature using an Instron 5566 testing machine (USA), according to the ASTM D-412 specifications, with the crosshead speed of 200 mm/min.

Dynamic mechanical thermal analysis (DMA) was carried out on a DMA 242 (Netzsch, Germany) in the temperature ranging from -100 to 150°C at a frequency of 10 Hz and with a heating rate of 5 K min⁻¹. The specimens were prepared as 17 × 4 × 0.8 mm³ in size.

Initial peel strength was measured by BaoDa Model PT-1030 tensile testing machine (Jiangsu, China) at 25°C. The dispersions were brushed on fiber-intensified polyvinyl chloride (PVC) with 130 × 25 mm² in size by a brush. The two pieces

of PVC joint together after dried at 70°C, which is the activation temperature for 5–7 min. After the water was evaporated, Pressure Machine was used to give more pressure (≥ 1.2 mPa) for 5 ~ 6 s to avoid mismatch and bubble, which can decrease the peel strength. Five minutes after the joints were compressed, the tests started by the tensile testing machine by the speed of 200 mm/min, and it was finished until 70 mm stripe was peeled at least. Twenty-four hours later, T-peel strength was tested by the same way as initial peel strength.

Synthesis of Water Dispersible Polyurethanes Ionomer Pellets

Poly(1,4-butylene adipate glycol) (PBA), polyether diol containing sulfonate(SPPG), 1,4-butanediol (BD), Isophorone diisocyanate (IPDI), and a few drops dibutyltin dilaurate (DBTDL) catalyst were added into a 250 ml three-mouth flask equipped with a mechanical stirrer. These monomers were mixed at 50–60°C for a while to ensure sufficient mixing. The mixture was quickly transferred to molds, and these molds were put in blast oven at 110°C. Hereafter, the temperature was increased to 160°C gradually. The reaction was completed in 4–5 h. Products were removed from the oven and cooled to room temperature. Polyurethane ionomer was obtained, stored as solid form, and cut into small pellets.

Preparation of Polyurethane Dispersions

The pellets obtained from aforementioned method were put into a 1000 ml three-mouth flask equipped with a mechanical stirrer and a reflux condenser. Then an amount of acetone (twice the quality of polyurethane) was added to dissolve the solid polyurethanes. When the pellets dissolved completely, specified quantity of water was added to disperse the polyurethanes ionomer solution. High-solid content (around 50%) PUDs were obtained after the acetone was distilled. Codes and parameter of PUD were described in Table I.

RESULTS AND DISCUSSION

The production scheme of PUDs is expressed as Figure 1. Polyurethane ionomer pellets were synthesized with the absence of organic solvent in higher temperature and less time. When cut into pellets, it is more convenient to handle and store. Pellets were dissolved in acetone, then water was added to disperse solution, and PUDs were obtained after acetone was distilled off. The acetone used in this process can be reused without being reprocessed, because this is a process of physical change without the participation of reactive NCO groups.

Molecular Weight of PU

The relationship between R and the viscosity of the PU dissolves in acetone before dispersing is presented in Figure 2(a). According to the Mark-Houwink equation $[\eta] = KM^a$, higher viscosity means higher molecular weight of polyurethane was obtained, so molecular weight has the same trend as the viscosity accordingly. Viscosity increased up to near $R = 1.02$ with the increment of R , while it decreased therefore. This law conforms to the theoretical state of the molecular weight changes with different value of R , which is shown in Figure 2(b). In theory, the highest molecular weight is obtained when $R = 1$.¹⁴ However, high activity NCO group is prone to take side reactions, which cause results to deviate from theoretical value.

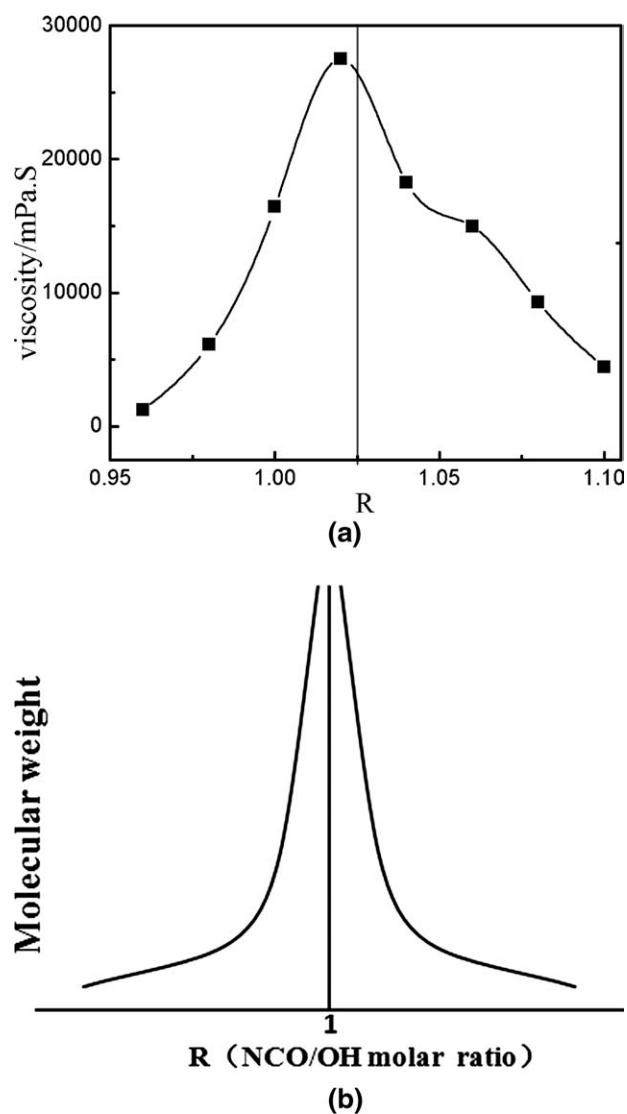


Figure 2. Effect of R on (a) the viscosity of the PU dissolves in acetone before dispersing and (b) molecular weight of PU.

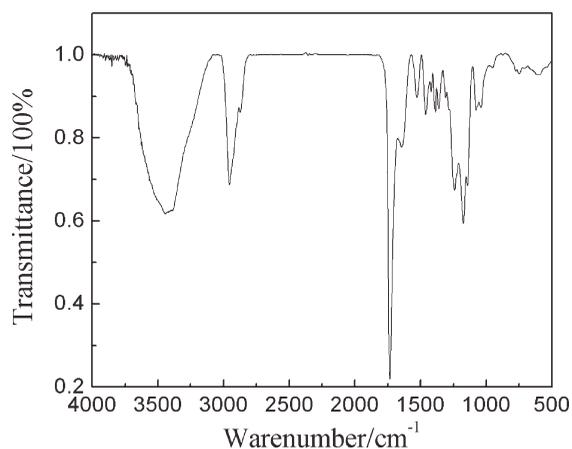


Figure 3. FTIR spectra of PUDs film.

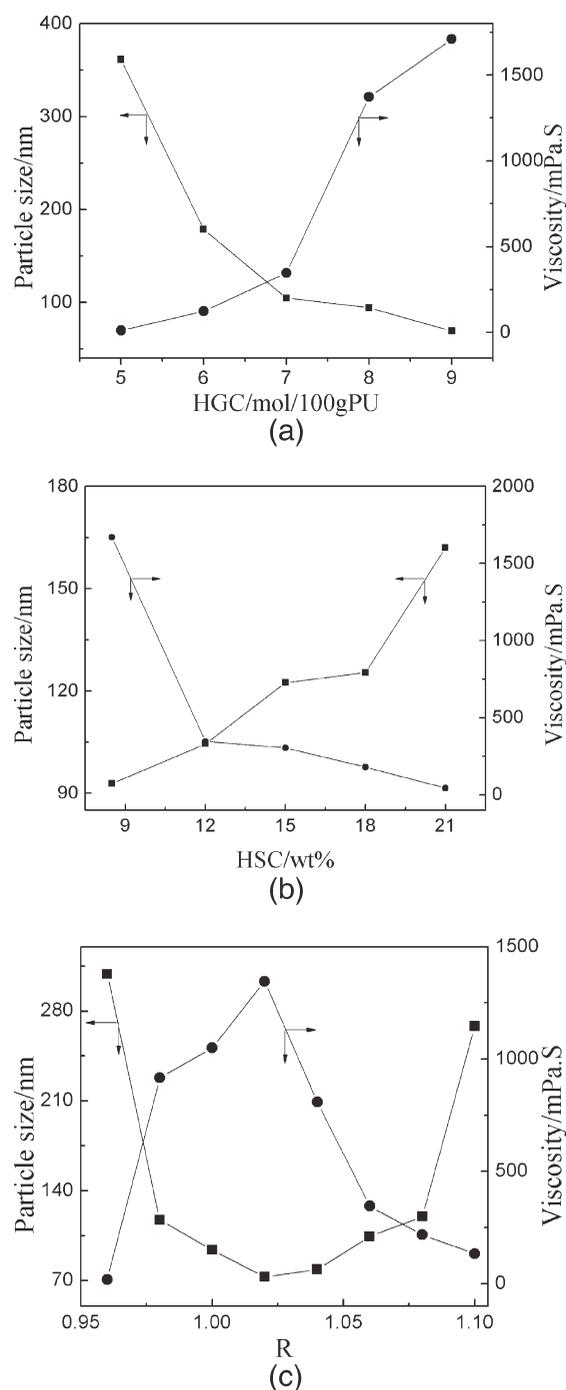


Figure 4. The effect of (a) HGC on particle size and viscosity of PUDs, (b) HSC on particle size and viscosity of PUDs, and (c) R on particle size and viscosity of PUDs.

increases. This agrees very well with the previous result that broadening the particle size distribution can increase the maximum packing fraction of a monodisperse system and give a lower viscosity.²¹

TEM Analysis

TEM micrographs for PUDs are shown in Figure 6. As shown in Figure 6, the particles of PUDs exhibit irregular spheroid.

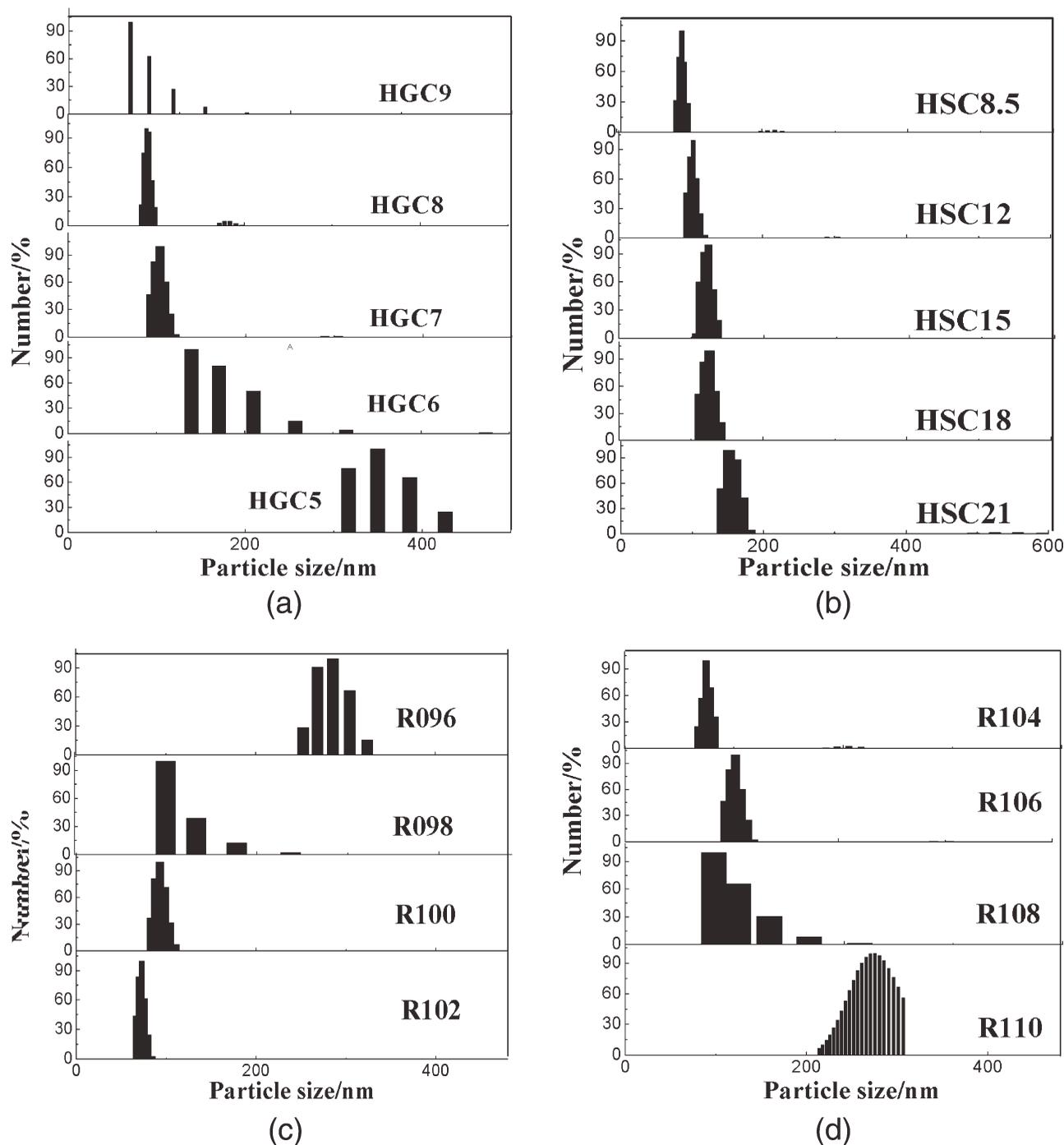


Figure 5. Effect of (a) HGC on PSD of PUDs, (b) HSC on PSD of PUDs, (c) R on PSD of PUDs, and (d) R on PSD of PUDs.

Bigger particle size and broader PSD were obtained when HGC is low. With the increase of HGC, the particles of PUD turn to regular spheroid, smaller particle size, and narrower PSD, which is consistent with the above discussion.

Mechanical Properties

Figure 7 shows the tensile stress–strain curves obtained for the various PUDs films. Tensile stress–strain curves exhibit typical crystalline polymer tensile properties with a yield point

observed,²² and all the samples show similar stress–strain behavior.

As shown in Figure 7(a), bigger tensile stress and smaller elongation at break were obtained with the increase of hard segments content. More —NH—COO— groups and hydrogen bonds²³ were introduced into polyurethane molecular chain due to the increment of HSC and led to cohesive energy increase.²⁴ As a result, the tensile stress increases and elongation at break decreases.

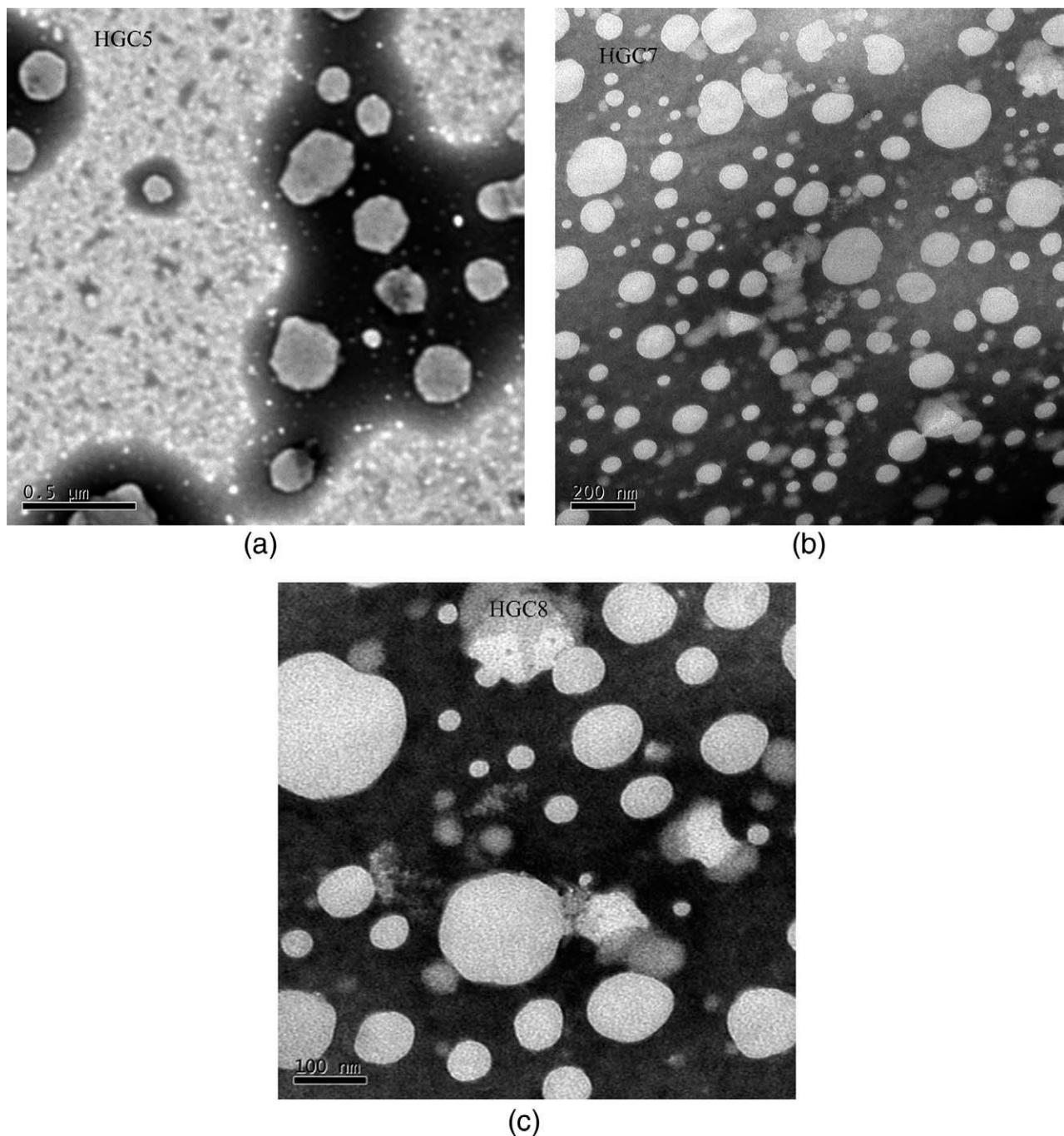


Figure 6. TEM micrographs for PUDs prepared from the control of (a) HGC, HGC5, $\times 9300$; (b) HGC, HGC7, $\times 13,000$; and (c) HGC, HGC8, $\times 30,000$.

As expected, an increment of the molecular weight provoked an increase of tensile stress and elongation at break as shown in Figure 7(b). This was attributed to the better flexibility of molecular, and bigger cohesive energy was obtained as the increase of molecular weight.

Dynamic Mechanical Thermal Analysis

DMA results of the PUD films with different hard segment content are shown in Figure 8. Only one glass transition peak at around -30°C (T_g) as shown in Figure 8(a, c) in all specimens.

It suggests that there is good compatibility between soft and hard segment attribute to low hard segment content in PUDs films.²⁵ However, when the temperature is above 70°C , soft segment as the crystalline phase in polyurethane has melted absolutely.

Figure 8(b, c) shows the variation of storage modulus (E') and loss modulus (E'') as a function of the temperature for the PUDs film. Storage modulus (E') decreased suddenly after T_g and shifted to rubbery plateau. Loss modulus (E'') has a peak at about -30°C , which is glass transition temperature. Both storage

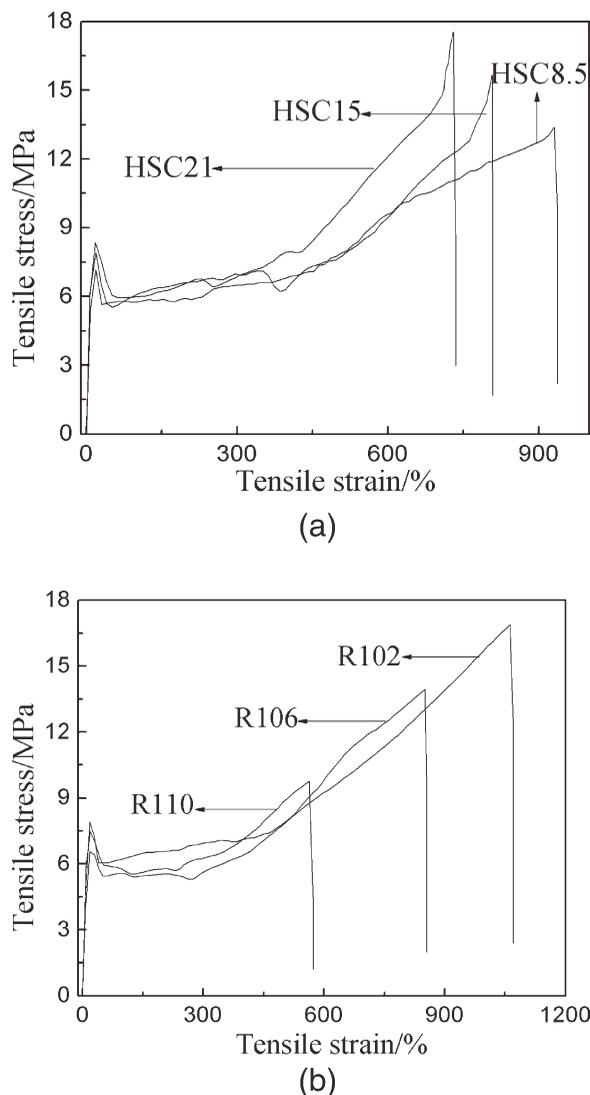


Figure 7. Tensile stress–strain curves of PUDs films.

modules (E') and loss modulus (E'') increase with increasing HSC. This is in agreement of previous studies.^{26,27} This is because that the increase in HSC will introduce more —NH—COO— groups into molecular chain that can form hydrogen bonds with ester units of the soft segment,²⁸ As a consequence, storage modulus (E') and loss modulus (E'') increased accordingly.

Adhesive Properties

Effect of f HGC, HSC, and R on adhesion properties of PUDs are shown in Figure 9. The data in Figure 9(a) show that initial peel strength, and T-peel strength improved up to HGC = 7 mmol/100 gPU as hydrophilic group in the polyurethane ionomer increased, while it decreased slightly thereafter. Because more Coulomb attraction between the ionic center sites was available and better adhesion was obtained with increment of ionic content under the activation temperature.²² However, there are too much ionic groups in the molecular chain, which can raise activation temperature of PUDs adhesive. Peel strength decreased eventually because it could not reach the real activation temperature.

As shown in Figure 9(b, c), initial peel strength and T-peel strength decrease with increasing HSC and decreasing molecular weight. This is because initial peel strength associated with the flexibility of molecular chain and the cohesion of molecules, and

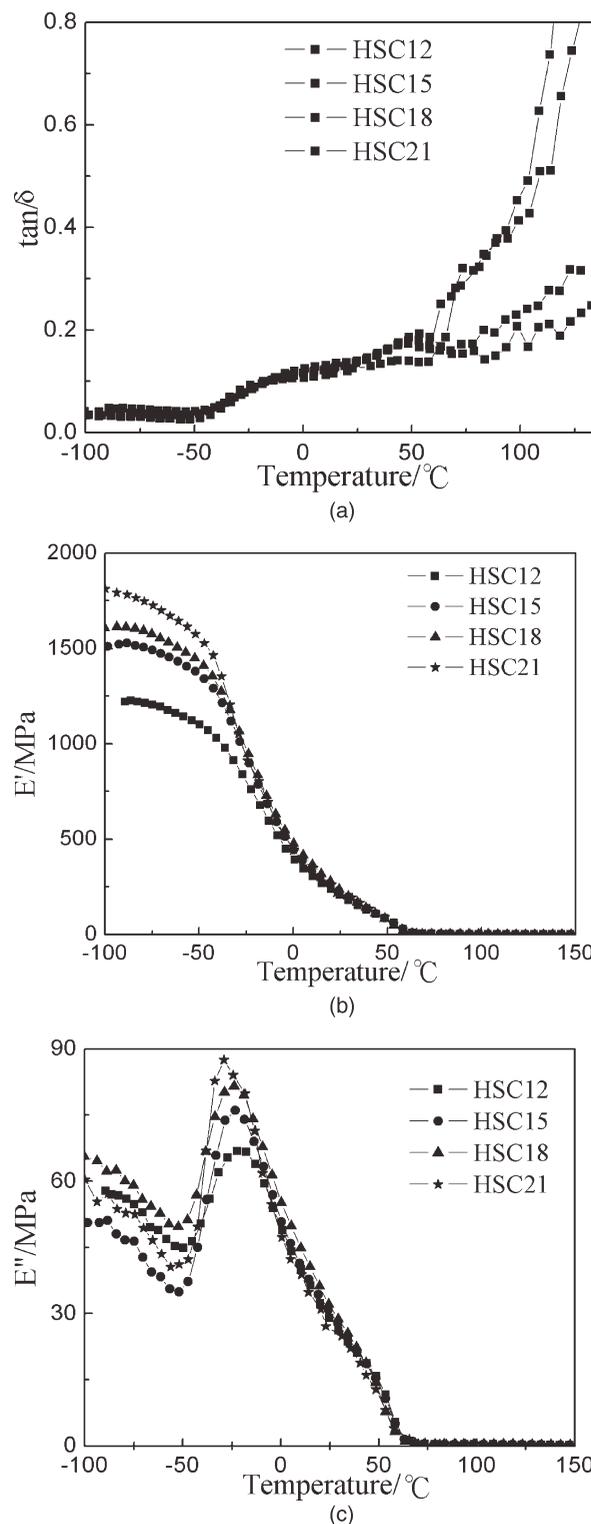


Figure 8. Effect of HSC on (a) $\tan \delta$ of PUD films, (b) storage modulus (E') of PUD films, and (c) storage loss modulus (E'') of PUD films.

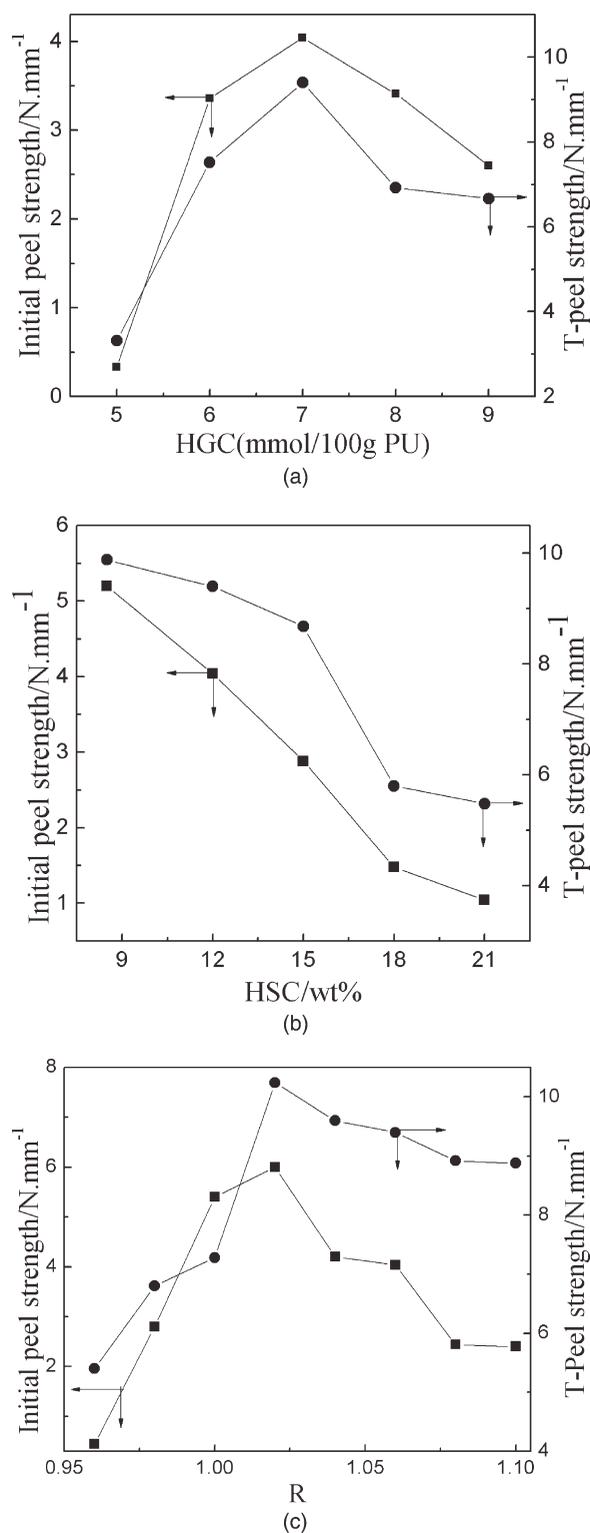


Figure 9. Effect of (a) HGC on adhesion properties of PUDs, (b) HSC on adhesion properties of PUDs, and (c) R on adhesion properties of PUDs.

crystallization degree of PUDs films plays a very important role on T-peel strength at activation temperature. Under a certain molecular weight, the increase of HSC will decrease the flexibility of molecular chain, which can make adhesive force to the sub-

strate decrease. Therefore, initial peel strength reduced accordingly. However, too much HSC probably hindered the crystallization of soft segment, leading to a reduction of T-peel strength. The bigger molecular weight may cause the greater cohesion of molecules when HSC was confirmed. Hence, initial peel strength and T-peel strength increase as molecular weight increased.

CONCLUSIONS

Polyurethane ionomer pellets were prepared by pellet process, PUDs with a solid content of 50% were obtained after pellets were dissolved in acetone, dispersed in water, and distilled acetone. The results of PUDs tests showed that particle size decrease with increasing of HGC and decreasing of HSC and molecular weight. TEM analysis indicated that particles of PUDs were regular spheroid and narrower PSD with increasing of HGC. Tensile stress-strain curves exhibit typical crystalline polymer tensile properties with a yield point observed; the increment of HSC led to stronger tensile stress and smaller elongation at break; and the stronger tensile stress and larger elongation at break were obtained with an increase of molecular weight. DMA showed good compatibility between soft and hard segment, and storage modulus (E') and loss modulus (E'') were increased as HSC increased. Peel strength (PVC/PVC) test results showed that peel strength improved up to HGC = 7 mmol/100 gPU as HGC increased, while it decreased slightly therefore. An increase in HSC could lead to peel strength decrease, and better adhesion was achieved by increasing of molecular weight.

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