Preparation and Properties of Nonionic Polyol Dispersion from Terpinene-Maleic Ester-Type Epoxy Resin

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ABSTRACT: A nonionic epoxy-based polyol (NTP) which can be used in place of the commonly used polyol dispersions to prepare two-component waterborne polyurethanes was synthesized with terpinene-maleic ester-type epoxy resin (TME), polyethylene glycol (PEG), and trimethylopropane (TMP) in the presence of sulfuric acid as catalyst. The synthesis process was tracked with gel permeation chromatography (GPC) and differential scanning calorimetry (DSC) by investigating the changes of molecular weight and glass transition temperature (T_g) of the product. FTIR was used to characterize the chemical structure of NTP. Major technical parameters of NTP were as follows: hydroxyl value 100 mg/g, hydroxyl group content 3.04%, T_g 4.03°C, and viscosity 150 mPa s (40% solid content). Effect of molecular weights and dosages of PEG on stability of NTP dispersion was examined by particle size analyses. It was found that stable dispersion was obtained when using PEG6000 as hydrophilic chain and its dosage $\geq$8% by the weight of TME. The average particle size of the prepared dispersion was about 200 nm from particles size and TEM analyses. The NTP dispersion showed characteristic of shear thinning, which indicated it was a pseudoplastic fluid. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 579–585, 2011

Key words: polyurethanes; resins; water-soluble polymers

INTRODUCTION

Polyurethanes are well known for anticorrosive properties, adhesion, and abrasion resistance.[1–5] They can also be designed for high tensile and impact strength, along with excellent low-temperature flexibility and are utilized in coatings and adhesives extensively. The increasing need to reduce volatile organic compounds (VOCs) and hazardous air pollutants (HAPs) emissions has led to increased efforts to formulate waterborne systems. Two-component waterborne polyurethane (2K-WPU) which combines high performance of two-component thermosetting systems and environmental friendliness, safety of waterborne systems together, has grown commercially application in coating and adhesive fields over the last decade.[6–12] 2K-WPU generally comprises polyisocyanates that are hydrophilically modified or unmodified and polyol dispersions that play an important role in the properties of the 2K-WPU systems. The commonly used polyol dispersions are acrylic polyol, polyester polyol, and polyurethane polyol dispersions which are complicated prepared and high cost.

Terpinene-maleic ester-type epoxy resin (TME) which is an alicyclolic epoxy resin with endocyclic structure are synthesized from the raw material turpentine which is a common biomass material in China.[13–16] Like the commonly used epoxy resin, TME has many excellent properties after cured, such as thermal and chemical stability, adhesion, mechanical and electrical properties, and could be widely utilized in the field of coatings, adhesives, composite materials, etc.

In this study, a novel nonionic TME-based polyol (NTP) dispersion is synthesized with TME, polyethylene glycol (PEG), and trimethylolpropane (TMP), which can be used in place of the commonly used polyol dispersions to prepare two-component waterborne polyurethanes. TME-based polyol with endocyclic structure which leads to good mechanical and thermal properties could form epoxy/polyurethane polymer after cured with polyisocyanate.[17] The purpose of this study is to provide new approach for the application of the renewable resource of forest products on preparation for environmental friendly special polymers.
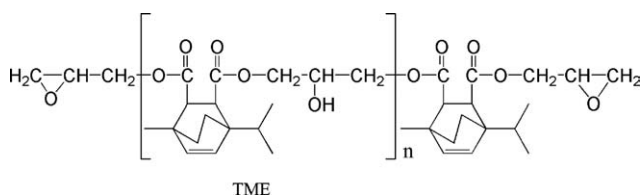
EXPERIMENTAL

Materials

The base material is an epoxy resin (TME) with endocyclic structure (Fig. 1) and epoxy value of 0.36

Figure 1 Chemical structure of TME.

mol/100 g, which was synthesized with terpinene-maleic anhydride and epichlorohydrin, as was reported elsewhere[14]; PEG2000, PEG4000, PEG6000, and PEG10000 were chemically pure, supplied by Guangdong Xilong Chemical Co., Ltd. (Shantou, China) trimethylolpropane (TMP) was chemically pure, purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) the major technical parameters of PEG and TMP were shown in Table I; dehydrating these polyol compounds with decompressing at 100°C for 1 h when using them. Sulfuric acid was analytical reagent, supplied by Hubao Chemical Reagent (Yangzhou, China).

Preparation of NTP and NTP dispersion

A 500 mL four-necked flask equipped with stirrer, dropping funnel, thermometer, condenser, and heating mantle was charged with 80.1 g TME, 6.4 g PEG6000, and 7.4 g TMP. Then, 1.2 g sulfuric acid diluted in 5.6 g acetone was added drop by drop in about 1 min with constant stirring when the temperature was raised to 90°C. The reaction was continued for 1 h at 110–120°C, and a yellow transparent product (NTP) was obtained. This product with PEG chain segment was dispersed with 141 g distilled water directly by churning at 500–1000 rpm, at 70–90°C (The water was added drop by drop in about 30 min and then continued churning for 30 min.). A milk-white dispersion (NTP dispersion) with 40% solid content was prepared after diluted with water. Technical parameters of product were shown in Table II.

Measurements

Epoxy value and Hydroxyl value of the product were obtained by chemical analysis in terms of

TABLE I
Technical Parameters of PEG and TMP

Items	Molecular weight range (g/mol)	Average hydroxyl value (mg/g)	Average hydroxyl group content (%)
PEG2000	1800–2400	56.5	1.71
PEG4000	3400–4600	28.6	0.87
PEG6000	5400–7800	17.5	0.53
PEG10000	8500–11,500	11.1	0.34
TMP	134	1239.4	37.55

TABLE II
Technical Parameters of NTP

NTP (solid resin)	Appearance	Yellow transparent solid (room temperature)
	Hydroxyl value(mg/g)	100
	Hydroxyl group content (%)	3.04
	Softening point (°C)	71
	T_g (°C)	4.03
Dispersion of NTP	Appearance	Milk-white
	Solid content (%)	40
	pH	2
	Viscosity(mPa s, 25°C)	150

standard methods GB/T 13657-1992 and GB/T 7383-2007, respectively.[18,19]

Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) equipped with a Waters 1515 pump and Waters 2414 (Milford, Massachusetts) differential refractive index detector using THF as eluent after calibration with polystyrene standards.

Differential scanning calorimetry (DSC) thermograms were recorded with a PerkinElmer Diamond (Fremont, CA) differential scanning calorimeter at a heating rate of 20°C/min under a nitrogen gas flow of 20 mL/min.

The FTIR spectra were recorded in solid state using KBr pellet. A MAGNA-IR 550 (Nicolet Instrument Co., Madison, Wisconsin, USA) was used to record the spectra in the range of 400–4000 cm^{-1}.

Particle size analyses were carried out on a Nano-ZS ZEN3600 Zetasizer from Malvern Instruments (Malvern, UK), and the NTP dispersion was diluted with distilled water to 0.5% solid content.

Viscosity was measured by NDJ-8S digital display rotational viscosimeter (Shanghai Precision Scientific Instrument Co., Ltd., Shanghai, China) with different shear rates at 25°C.

The morphologies of the dispersion particles were studied by transmission electron microscopy (TEM) performed on a JEM-200CX (JEOL, Tokyo, Japan). To prepare TEM sample, the NTP dispersion was diluted with distilled water to 2% solid content.

RESULTS AND DISCUSSION

Dynamic track of NTP synthetic process

NTP was synthesized by the reaction between epoxy groups of TME and hydroxyl groups of PEG and TMP in the presence of sulfuric acid as catalyst (Scheme 1). It was a chain extension process. GPC and DSC were used to track this synthetic process. The investigated reaction conditions were as follows: molar ratio of hydroxyl group/epoxy group 0.6 : 1
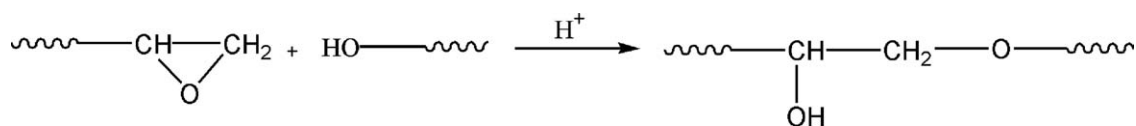
Scheme 1 Reaction between epoxy group and hydroxyl group.

(PEG calculated with their average hydroxyl value showed in Table I), dosage of PEG6000 8% by the weight of TME, temperature 115°C, dosage of sulfuric acid 1.5% by the weight of TME. Changes of the average molecular weight of the product with increased reaction time were studied by GPC, and the result was shown in Figure 2. Average molecular weight of the product increased with the polymeric reaction taking place and its weight-average molecular weight grew from 1639D when reaction time was 15 min to 9053D when reaction time prolonged to 75 min. Molecular weight distribution of the product also changed from broad distribution at the beginning of the reaction to relatively narrow and large molecular weight distribution after the prepolymeric reaction. At the beginning of the reaction, an epoxy group of TME which had two epoxy groups reacted with a hydroxyl group of PEG which had two hydroxyl groups or a hydroxyl group of TMP which had three hydroxyl groups and formed different intermediate products which still had at least two functional groups. So, in the GPC curve, there was a broad peak representing the molecular weight distribution of all kinds of intermediate products and original reactants. Prolonging reaction time, these in-

termediate products can react with each other or the residual TME, TMP, and PEG to form new intermediate products and went on. At the end of the reaction, they formed relatively narrow and large molecular weight distribution prepolymers.

Glass transition temperature (T_g) of the product increased with its molecular weight as shown in Figure 3. According to the free volume theory, larger free volume of the polymer results to lower T_g.[20] End chain segments which can move easily have larger free volume than the other segments in the chain. Low-molecular-weight polymers have higher proportion of end chain segments than high-molecular-weight polymers, which leads to their lower T_g. So, the increase of T_g of the products could also indicate chain extension of this reaction.

Characterizations of NTP

Technical parameters of NTP

The major technical parameters of the solid resin NTP and the dispersion of NTP prepared under optimal conditions, including hydroxyl value, hydroxyl group content, softening point, T_g of the solid resin NTP and solid content, pH, viscosity of
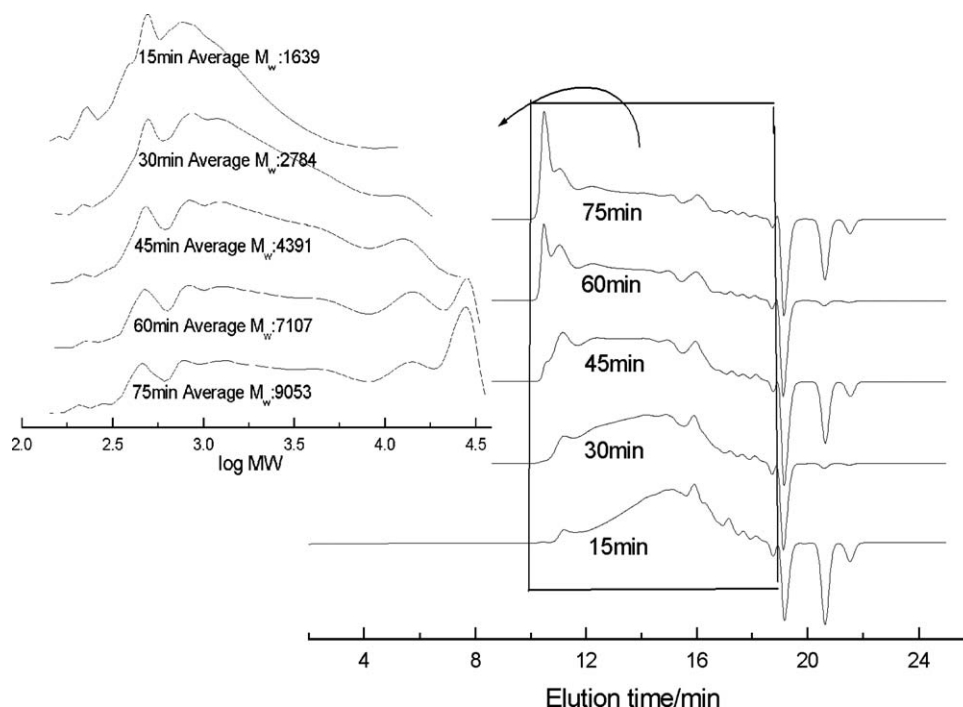
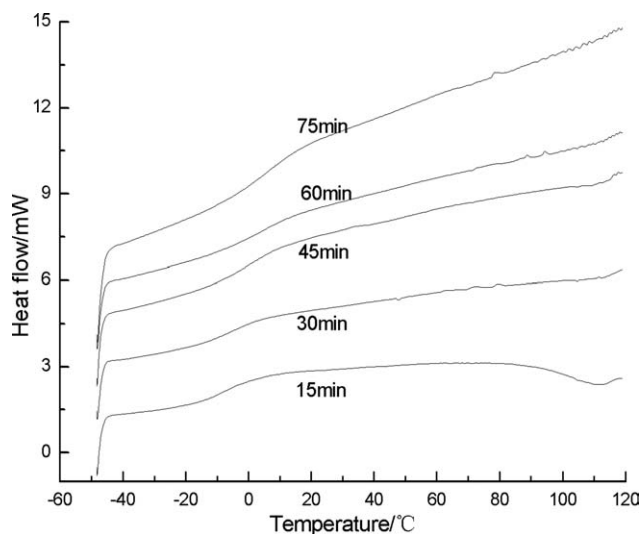**Figure 2** GPC curves of the synthetic process.

Figure 3 DSC curves of the synthetic process.

the dispersion of NTP, were obtained by chemical analysis and instrumental analysis according to standard methods and showed in Table II. The pH of the dispersion of NTP was about 2 because of the using of sulfuric acid as catalyst.

FTIR analysis

Compared with the FTIR spectrum of TME in Figure 4, the characteristic absorption peak of epoxy groups at 908 cm^{-1} in the spectra of NTP was disappeared, and the characteristic absorption peak of OH at 3131–3570 cm^{-1} was strengthened evidently. This result suggested that the reaction of epoxy groups with OH groups took place expectably. After the reaction, epoxy groups and the original OH groups were consumed, and new OH groups were generated after the ring open of epoxy group (Scheme 1). It was also found that the C—O—C bond stretch absorption peaks at 1020–1075 cm^{-1} and —CH$_2$— characteristic absorption peak at 2875 cm^{-1} appeared in the FTIR spectra of NTP were all strengthened because of the introduce of PEG to NTP structure as hydrophilic chain.

Stability of NTP dispersion

According to Stokes Law, separating rate of the dispersion particles is directly proportional to the density difference of oil phase and water phase, the viscosity of continuous phase, and the size of the particles.[21] When the density difference of oil phase and water phase and the viscosity of continuous phase are invariableness, the size of the particles can compare the stability of waterborne dispersion. Effect of molecular weights and dosages of PEG on

stability of the dispersion was examined by particle size analyses.

Effect of PEG molecular weights

The nonionic dispersion particles can be dispersed stably in water depends on the formation of a strong interface layer which is composed of hydrated hydrophilic chains and covers on the surface of the particle. So, chain length (molecular weight) and dosage of PEG which served as hydrophilic chain directly affected the stability of dispersion of NTP. Remaining the dosage of PEG unchanged, 8% by the weight of TME, the effect of molecular weight of PEG on stability of dispersion was investigated. The result was shown in Figure 6. PEG6000 had the best dispersing efficiency compared with PEG2000, PEG4000, and PEG10000. The Z-average particle size of dispersion prepared with PEG6000 was 194 nm, and Z-average particle size of dispersion prepared with PEG10000 and PEG4000 were bigger, 642 nm and 1763 nm, respectively, (Fig. 5). The polyol prepared with PEG2000 could not be dispersed with water. It was because when the dosages of PEG remained unchanged, higher molecular weight PEG with longer chain had fewer number of chains. The hydrophilic chains of PEG10000 were long enough to from strong interface layer but the number of chains was not enough to cover the surface of particles effectively when forming small size particles with big total surface area. Therefore, the particle size of dispersion prepared with PEG10000 was little big to reduce the total surface area of particles and make the number of hydrophilic chains enough to cover the surface of particles effectively. When using the same weight of PEG2000, the number of chains was enough to cover the surface of particles, but the chain length was too short to form strong interface
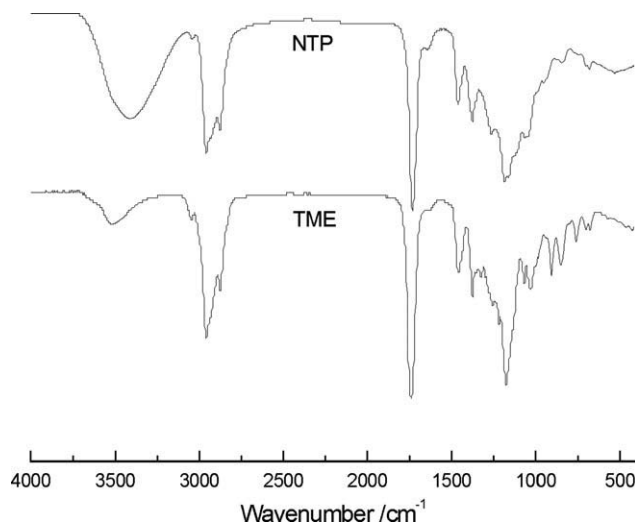

Figure 4 FTIR spectra of TME and NTP.

Size Distribution by Intensity

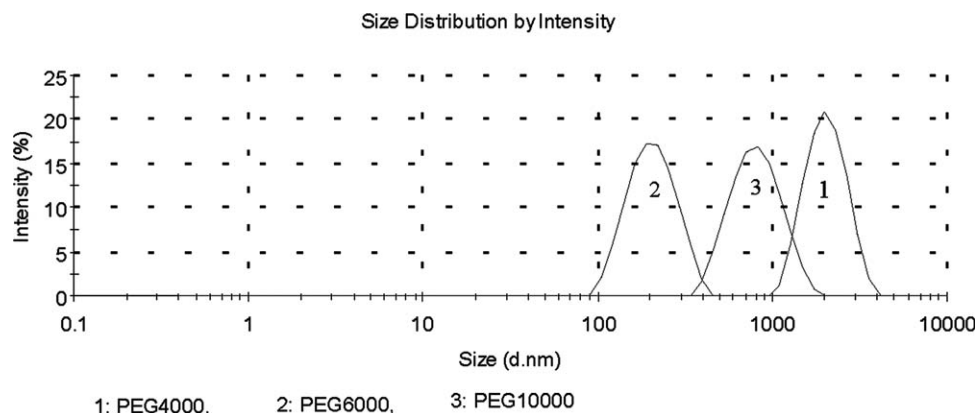1: PEG4000,   2: PEG6000,   3: PEG10000

Figure 5 Effect of PEG molecular weights on particle size of NTP dispersion.

layer. Then, the polyol prepared with PEG2000 could not be dispersed in water stably. PEG6000 which had a fit molecular weight could provide enough number and enough length of hydrophilic chain, and it had the best dispersing efficiency.

Effect of PEG dosages

PEG provided hydrophilic chain to disperse the polyol, whose dosage was important to the stability of the NTP dispersion. If its dosage was too small, there were too few hydrophilic chains to cover the surface of particles effectively when forming small size particles with big total surface area. The ineffective covered particles could coalesce with each other forming big particles, which made the dispersion unstable. It was shown that the prepared NTP could not be dispersed in water stably when the dosage of PEG6000 was less than 8% by the weight of TME. It was also found that the prepared dispersion particle size became two-peak distribution, a small small-size peak and a big large-size peak, when increasing the dosage of PEG6000 (Fig. 6). The main reason for this result was that there were two types of configuration of PEG chain when covering the surface of

particles, straight configuration and crimp configuration.[22] Increasing the dosage of PEG, there were more PEG chains crowding on the particle surface, and some crimp configuration chains would become straight, which enlarged the particle size. Smaller size particles were gained to enlarge the total surface of particles and relax the crowding.

Rheology behavior of NTP dispersion

Rheology behavior is important for the using and storage of a dispersion when used as coatings and adhesives. If the dispersion is a pseudoplastic fluid whose apparent viscosity decreases with increasing the shear rate, its characteristic of shear thinning is beneficial to the using and storage of the dispersion.[23]

Rheology behavior of dispersions can be characterized by power-law equation as follows:

$$\tau = K\gamma^n \ \text{ or } \ \eta_\alpha = K\gamma^{n-1}$$

where τ is shear stress, K is viscosity coefficient, γ is shear rate, n is flow behavior index ($n = 1$ for

Size Distribution by Intensity

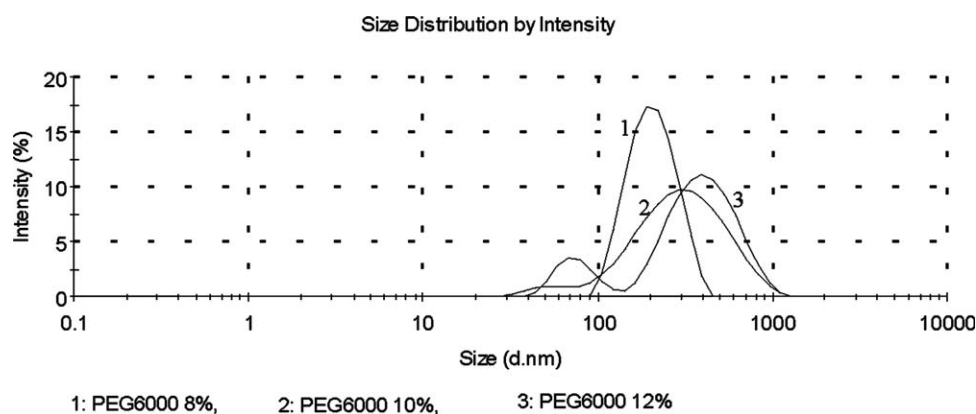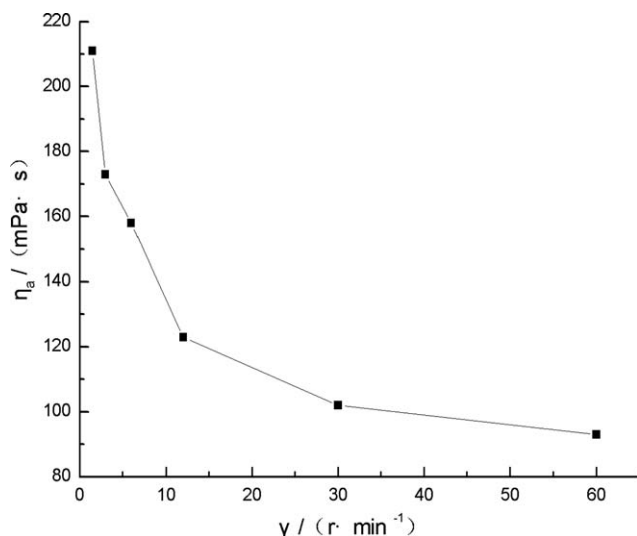1: PEG6000 8%,   2: PEG6000 10%,   3: PEG6000 12%

Figure 6 Effect of PEG dosages on particle size of NTP dispersion.

Figure 7 Rheological curves of NTP dispersions.

Newtonian fluid, and $n < 1$ for pseudoplastic fluid), and η_∞ is apparent viscosity.

The logarithmic form of power-law equation can be written as follows,

$$\log \tau = \log K + n \log \gamma$$

The relation between $\log \tau$ and γ is linear, and the factor n can be evaluated graphically from the slope of the $\log \tau - \log \gamma$ line, and K from its intercept with $\log \gamma$ axis.

Figure 7 showed the rheological curve of NTP dispersion at 25°C, and correspondingly, Figure 8 showed the $\log \tau - \log \gamma$ line. The result indicated that the apparent viscosity of NTP dispersion decreased with the increasing of shear rate. The obtained $\log \tau$ had good linear correlation with $\log \gamma$, and the flow behavior index n of the dispersion
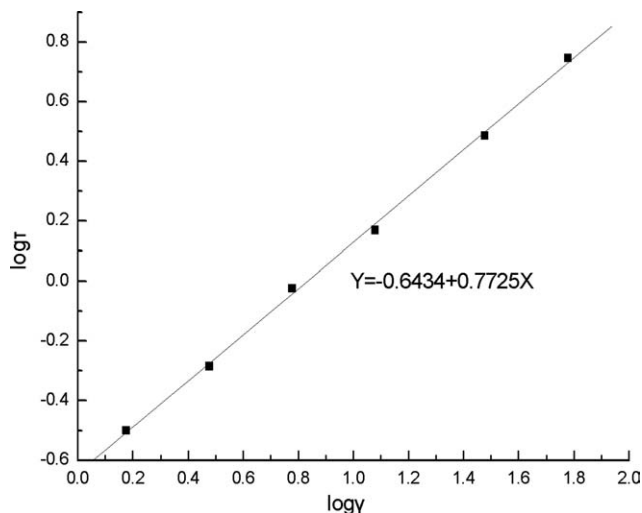
Figure 8 Relation between $\log \tau$ and $\log \gamma$.
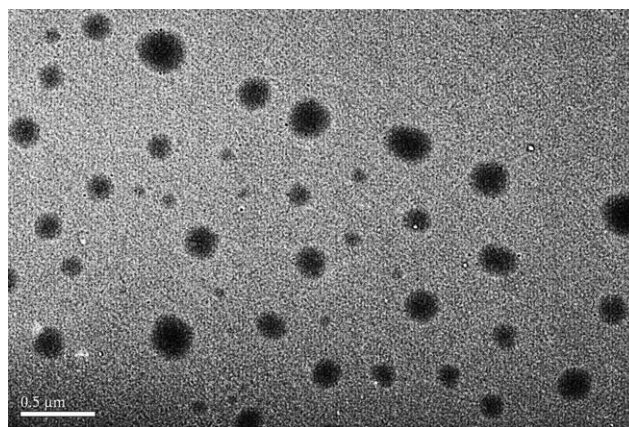
Figure 9 TEM micrograph of NTP dispersion particles.

was <1, which indicated the NTP dispersion was pseudoplastic fluid.

Micromorphological analysis of NTP dispersion

TEM micrograph of NTP dispersion was shown in Figure 9. The prepared particles had spherical shape, and their size distributed from 90 to 450 nm, most of them about 200 nm. This TEM result corresponded to the result from particles size measurement.

CONCLUSIONS

A novel biomass-based polyol(NTP) was synthesized to substitute the commonly used polyol dispersions to prepare two-component waterborne polyurethanes. GPC and DSC were used to track the synthetic process by investigating molecular weight and T_g changes of the product. Major technical parameters of NTP prepared under optimal conditions were as follows: hydroxyl value 100 mg/g, hydroxyl group content 3.04%, T_g 4.03°C, and viscosity 150 mPa s (40% solid content). PEG provided hydrophilic chain to NTP dispersion, and its molecular weight and dosage affected the stability of dispersion. It was found that stable dispersion was obtained when using PEG6000 as hydrophilic chain and its dosage $\geq 8\%$ by the weight of TME. The particles size of NTP dispersion distributed from 90 to 450 nm, and the average particle size was about 200 nm. The NTP dispersion showed characteristic of shear thinning, which was beneficial to the using and storage of dispersion.

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