

# The Preparation and Properties of Polyurethane/Nano-CeO<sub>2</sub> Hybrid Aqueous Coating<sup>1</sup>

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**Abstract**—To improve the ultraviolet resistance and thermal stability of waterborne polyurethane, stable waterborne polyurethane/nano-cerium oxide hybrid dispersions were obtained by adding nano-cerium colloids to previously synthesized waterborne polyurethane dispersions. The dried ceria colloid was characterized by X-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM). The XRD results indicated the prepared CeO<sub>2</sub> was a face-centered cubic structure. The prepared polyurethane/CeO<sub>2</sub> dispersions were studied by dynamic light scattering (DLS), transmission electron microscopy (TEM), UV–Vis spectroscopy and accelerated weathering test. The dried polyurethane/CeO<sub>2</sub> films were characterized using thermogravimetric analysis (TGA). The DLS analysis indicated the particles average diameter of hybrids emulsion was bigger than that of the pure waterborne polyurethane dispersion. TG analysis and accelerated weathering test suggested the hybrid latex films had better thermal stability and mechanical properties than those of the pure waterborne polyurethane. The UV–Vis absorption capacity of the dispersions prepared was increasing with the amount of CeO<sub>2</sub> colloid increased.

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## INTRODUCTION

Waterborne polyurethanes (WPU) are known to be environment-friendly materials with good adhesion, toughness, flexibility, etc. Therefore, WPU have attracted particular attention in some fields such as textile coatings, foams, elastomers, coatings, adhesives and sealants [1–3]. However, some properties of waterborne polyurethanes such as low mechanical strength, thermal stability and weather resistance need to be improved further [4].

CeO<sub>2</sub> nanoparticles have received much interest over the past decade concerning their potential use as an inorganic UV filter in coatings, due to their absorption properties in UV range combined with low photocatalytic activity [5–9]. However, nanoparticles tend to aggregate and show very poor dispersion in polymers. Therefore, one of the major difficulties of incorporating inorganic nanoparticles in such matrices is to avoid their agglomeration which can often lead to loss of the desired properties.

In this paper, the CeO<sub>2</sub> colloids were prepared from cerium nitrate under the catalysis of ammonia at 60°C by using polyvinyl alcohol (PVA) as colloid stabilizer. The influence of nanocerium oxide particles on UV absorbance and thermal stability of water-base poly-

urethane coatings have been researched. In the current study, the chemical composition and properties of polyurethane hybrid latex particles were determined by dynamic light scattering (DLS), UV–Vis spectroscopy, accelerated weathering test, transmission electron microscopy (TEM) and thermogravimetry analysis (TGA). The emphasis was put on the property comparison of PU and PU/CeO<sub>2</sub> with content variation of nano CeO<sub>2</sub>.

## EXPERIMENTAL

### Materials

Polytetramethylene ether glycol (PTMG,  $M_n = 1000$  g/mol) was dried at 60°C under vacuum before use, isophoronediiisocyanate (IPDI), dimethylolpropionic acid (DMPA), 1,4-butanediol (BDO), trimethylolpropane (TMP) were of analytical grade and used without further purification, and DMPA was dried at 40°C for 24 h in vacuum oven. triethylamine (TEA) was treated with 0.4 Å molecular sieves for 24 h before use, ammonia water, Polyvinyl alcohol 1799 (PVA, polymerization degree = 1700, alcoholysis degree = 99%), Cerium nitrate (Ce(NO<sub>3</sub>)<sub>3</sub> · 6H<sub>2</sub>O) and urea were all of analytical reagent grade, for all experiments, deionized water was used.

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**Table 1.** Recipes of the WPU

	IPDI, g	PTMG, g	DMPA, g	TMP, g	TEA, g	DBTDL, g	NMP, g	BDO, g	DI water, g
PU	11.1	10.0	3.76	0.31	2.8	0.02	8.0	0.02	75.5

#### *Preparation of CeO<sub>2</sub> Colloid*

The synthesis process was described as follows: 8.0 g PVA was dissolved into 92.0 g deionized water at 95°C several to form homogeneous solution, 3.0 g solid raw materials of cerium nitrate Ce(NO<sub>3</sub>)<sub>3</sub> · 6H<sub>2</sub>O and urea 1.0 g CO(NH<sub>2</sub>)<sub>2</sub> were dropped into the PVA solution when the temperature of the solution reduced to 60°C, the raw solutions were stirred for 1 hour to be homogeneous, then a certain amount of ammonia was added into the solutions for 5 h, and the pale yellow CeO<sub>2</sub> colloid was obtained finally without further treatment.

#### *Synthesis of Waterborne Polyurethane*

The synthesis of the polyurethane dispersions was carried out in a four-necked glass reactor equipped with a mechanical stirrer, a thermometer, a nitrogen inlet and a condenser with a CaCl<sub>2</sub> drying tube. Polyurethane prepolymer based on IPDI, PTMG, DMPA and TMP was prepared with NMP as the solvent and DBTDL as the catalyst. The reaction was carried out at 80°C in a water bath under a nitrogen atmosphere for 2 h. Then, BDO was added dropwise while controlling the temperature at 80°C, the reaction was continued for 30 min. After the prepolymer temperature dropped to room temperature, the prepolymer was neutralized by TEA for 15 min and the degree of neutralization was 100%. The PU dispersions with solid content of 27 wt % were obtained by adding an adequate amount of distilled water. Table 1 is the recipes of the WPU.

#### *Preparation of Polyurethane/Nano-CeO<sub>2</sub> Hybrids*

The CeO<sub>2</sub> colloid was added to PU dispersions at room temperature with stirring for 30 minutes. A homogeneous colloid dispersion with 0.2, 0.4, 0.8 and 1.0 wt % based on the WPU dispersions content was obtained.

#### *Preparation of Polyurethane/Nano-CeO<sub>2</sub> Hybrid Films and Dried Ceria Colloids Films*

The films were made by solvent evaporation method. Cast the hybrids emulsion onto the level polytetrafluoroethylene (PTFE) templates and removed water inside at room temperature for 48 h, annealed at 50°C for another 12 h, and finally the films were kept into a desiccator to avoid moisture.

#### *Characterization of CeO<sub>2</sub> Colloid, PU Dispersions and Films*

The dried ceria colloid films were characterized by X-ray diffraction (XRD) (Rigaku, Japan D/max-2200PC).

The dried ceria colloid films were characterized by H-600 transmission electron microscope equipped with high-resolution (Hitachi Company, Japan).

The particle size and its distribution of the synthesized latex were measured by Nano-ZS particle sizer (Malvern Instruments Company, UK). The samples were diluted with distilled water into an appropriate concentration as indicated by the instrument. The particle size was characterized by z-average diameter  $D_z$  and the particle size distribution was characterized by polydispersity index (PDI). They were automatically calculated by the computer connected to the machine.

Transmission electron microscopy (TEM) micrographs of the PU and PU/nano-CeO<sub>2</sub> particles were taken with H-600 transmission electron microscope (Hitachi Company, Japan) with an acceleration voltage of 200 kV. The samples were stained with 2% phosphotungstic acid (PTA) solution.

Thermogravimetry analysis (TGA) was performed on a Q500 thermogravimeter (TA Instruments Company, USA) under the nitrogen atmosphere at a heating rate of 10 grad/min from 30 to 550°C.

UV-Vis characterization was conducted with a UV-Vis spectrophotometer (UV-2550, Shimadzu, Japan).

Accelerated weathering test was simulated by a system of UVB radiation sources in the 280–320 nm range with a constant irradiation at a power of 0.50 W/m<sup>2</sup> (Xenon lamp, ATLAS, American). The specimens were exposed to a UVB radiation cycle at 60°C for 8 h, followed by exposure to 4 h of condensing water vapor at 50°C and (70 ± 10)% humidity. The specimens were removed for 15 days.

A GT-U5 universal tensile testing machine (GOTECH Testing Machines Inc, Taiwan, China) at a crosshead speed of 300 mm/min was used. Three identical dumbbell-shaped specimens were tested respectively and their average mechanical properties were reported.

Elongation at break was measured during the measure of tensile strength. When the specimen was extended, the distance between the two standard lines was recorded.

$$X = (L_1 - L) / L \times 100\%$$

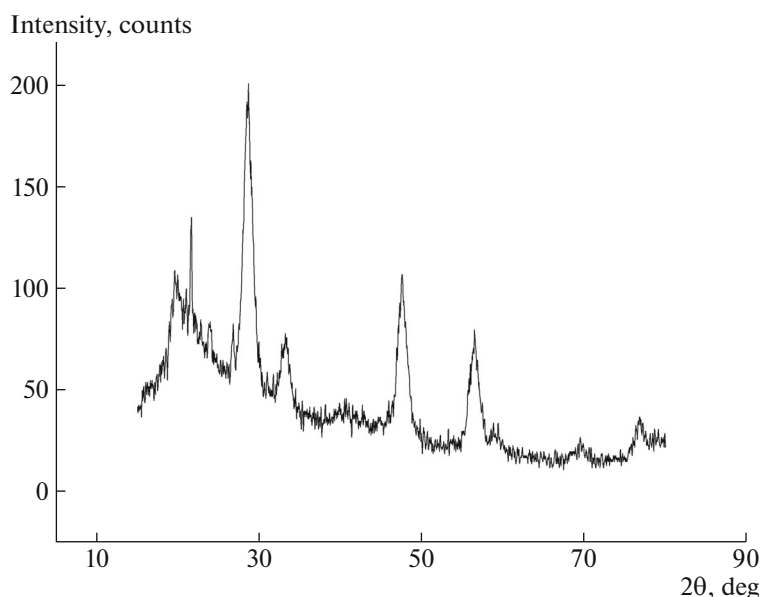


Fig. 1. X-ray diffraction pattern of the dried ceria colloids.

where  $X$  is the elongation at break (%),  $L_1$  is the distance between the midline of specimen at break (mm) and  $L$  is the distance between the midline of the former samples (mm).

## RESULTS AND DISCUSSION

### *XRD Patterns of Dried Ceria Colloid*

Figure 1 showed the XRD patterns of the dried ceria colloid. The main peaks were  $2\theta = 28.8, 33.1, 48.1, 56.8$ , which showed a good match with literature data (JCPDS no. 34-0394). The main Bragg peaks with Miller indices (111), (200), (311) and (220) could be identified clearly, which was indicative of a face-centered cubic structure. The result means that the pure crystallized ceria particles have been synthesized in PVA solution at near room temperature.

### *TEM of Dried Ceria Colloid*

The HRTEM images in Fig. 2 showed the morphologies of the CeO<sub>2</sub>. Three well-resolved planes with fringe spacing between two adjacent lattice planes of approximately 0.32, 0.27, and 0.20 nm were observed. The  $d$ -spacing of 0.32, 0.27, and 0.20 nm agreed well with the lattice spacing of (111), (200) and (220) planes in CeO<sub>2</sub>. The observed HRTEM results were in good agreement with the XRD results.

### *Latex Particle Size and Morphology*

Figure 3 showed the  $D_z$  and PDI of WPU and WPU/CeO<sub>2</sub> emulsions with different CeO<sub>2</sub> colloid content. As seen from Fig. 3, the average particle sizes

of WPU, and WPU/CeO<sub>2</sub> (0.4 wt % ceria colloid) emulsions were 39.92 and 61.29 nm respectively. The average particle size increased with the increment content of CeO<sub>2</sub> colloid. The more the amount of CeO<sub>2</sub> colloid is, the bigger the  $D_z$  and PDI of the composite emulsions are. But even the dosage of ceria colloid was 0.8 wt %. The average particle size was 72.80 nm. This can be explained as followed: the prepared of CeO<sub>2</sub> colloid was water dispersion, and the PU was also water dispersion.

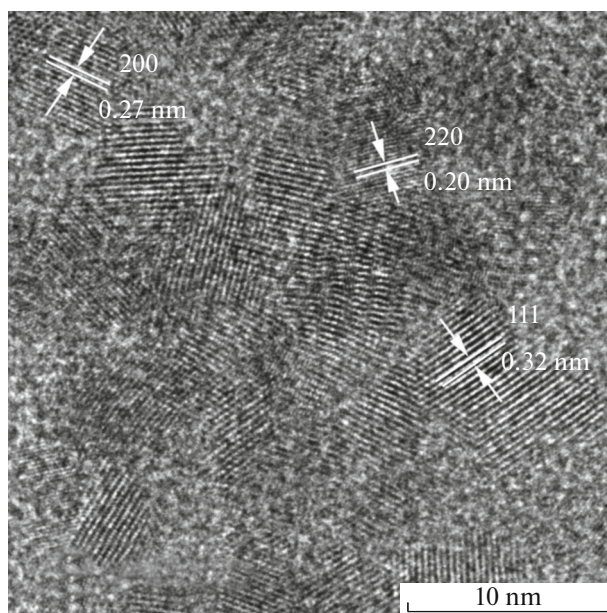
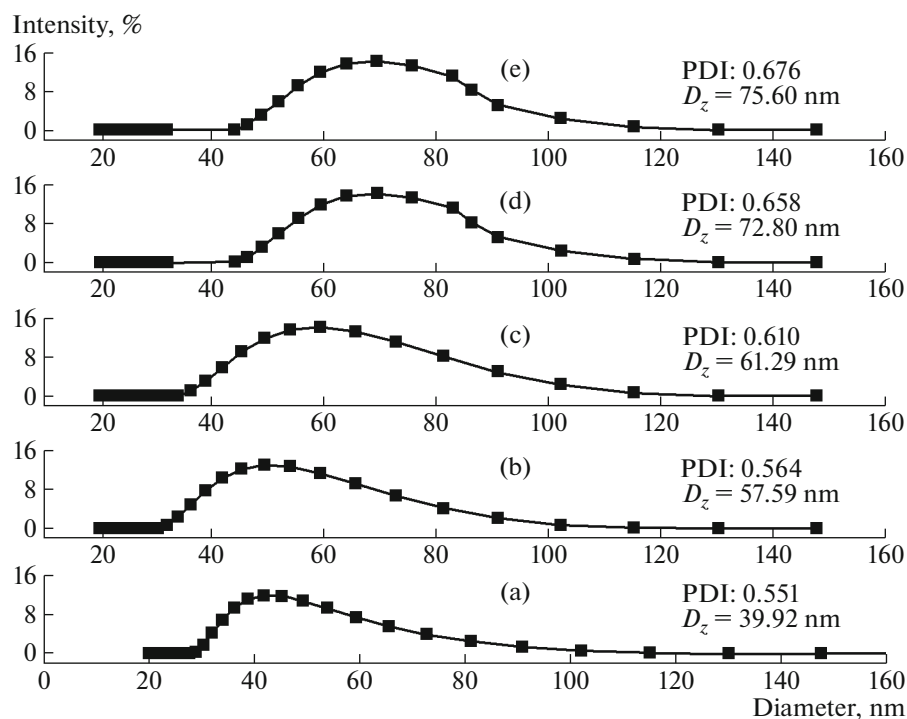
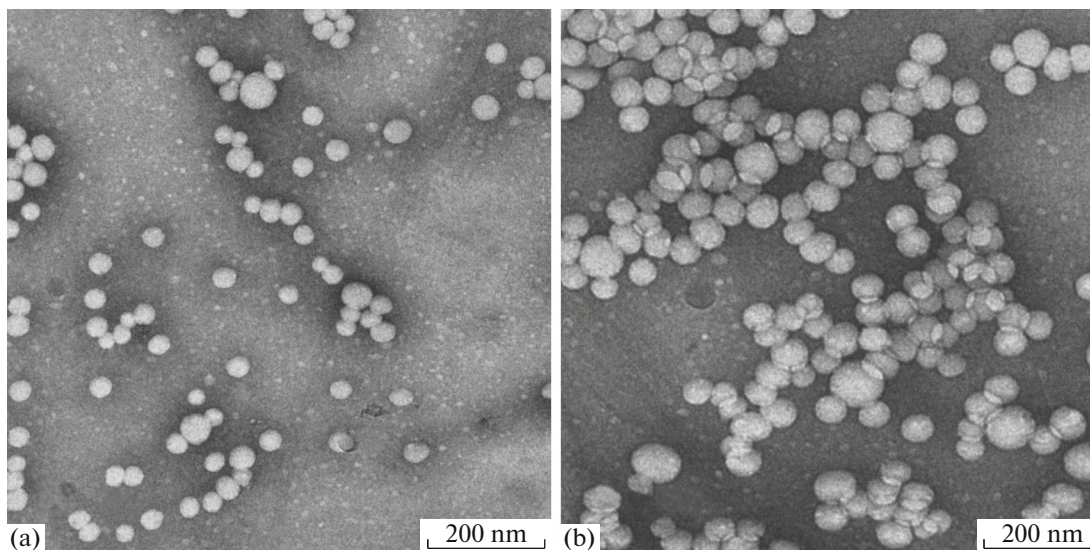


Fig. 2. High resolution transmission electron microscopy (HRTEM) images.



**Fig. 3.** Particle distribution of polymer emulsions: (a) WPU and WPU/CeO<sub>2</sub> with (b) 0.2, (c) 0.4, (d) 0.8, and (e) 1.0 wt % ceria colloid.



**Fig. 4.** TEM photograph of (a) WPU and (b) WPU/CeO<sub>2</sub> (0.4 wt % ceria colloid).

The morphologies of WPU and WPU/CeO<sub>2</sub> (0.4 wt % ceria colloid) particles were observed by TEM in Fig. 4. It was found that the particles were spherical. The observed emulsion size was consistent with the results measured by particle size distribution analysis of WPU and WPU/CeO<sub>2</sub> (0.4 wt % ceria colloid). It could be seen there were some nanoceria colloid particles inserted inside of polyurethane particles.

This could be concluded that the hybrid emulsion had been successfully obtained by mixing waterborne polyurethane and CeO<sub>2</sub> colloid.

#### *Thermogravimetric Analysis (TGA)*

To investigate the influence of CeO<sub>2</sub> colloid on the thermal stability of waterborne polyurethane films,

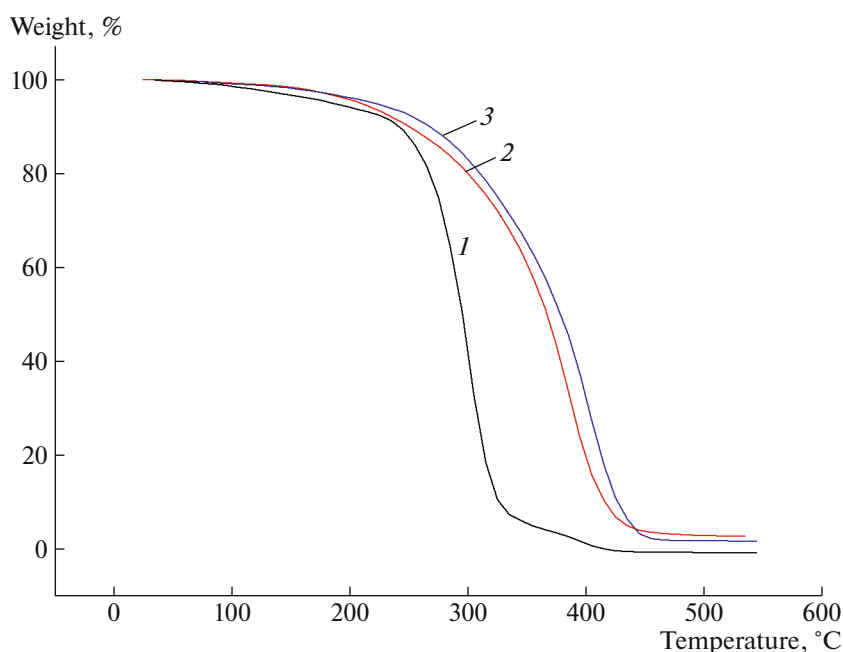


Fig. 5. (Color online) The TGA curves of the latex films of (1) WPU and WPU/CeO<sub>2</sub> with (2) 0.4 and (3) 1.0 wt % ceria colloid.

the pure WPU film, WPU/CeO<sub>2</sub> (0.4 wt % ceria colloid) and WPU/CeO<sub>2</sub> (1.0 wt % ceria colloid) hybrids films were analyzed by TGA. Figure 5 showed the TGA curves of pure WPU film, WPU/CeO<sub>2</sub> (0.4 wt % ceria colloid) and WPU/CeO<sub>2</sub> (1.0 wt % ceria colloid) hybrid film. Temperatures of the 10, 30 and 50% loss were shown respectively in Table 2.

All of the films were very stable until the temperature was reached up to 150°C, the initial decomposition temperature of all films was almost the same. The decomposition temperature of WPU/CeO<sub>2</sub> membrane was much higher than that of the pure WPU membrane when the temperature ranged from 200 to 400°C. As shown in Table 2, The  $T_{50}$  value increased from 295 to 379°C, and the  $T_d$  values of these films increased with increasing cerium colloid content in the films matrix. Which indicated that these prepared films containing nano-CeO<sub>2</sub> particles could endure relatively high temperature, the incorporation of nano-CeO<sub>2</sub> into WPU did improve the decomposition temperature. The diagram of interaction between WPU and ceria colloid was described as Fig. 6, the nano CeO<sub>2</sub> particles were embedded in the polymer matrix uniformly, the interfacial interaction between the nano CeO<sub>2</sub> particles and the polymer could improve the thermal properties of hybrids films.

#### UV-Vis Absorption of WPU/CeO<sub>2</sub> Hybrids Emulsion

The UV-Vis absorption capacity of the WPU/CeO<sub>2</sub> hybrids emulsion with different CeO<sub>2</sub> content was measured. As shown in Fig. 7, UV-Vis

absorption of the emulsion increased monotonically with cerium colloid content. There were two possible reasons for this. One was that CeO<sub>2</sub> had 4f valence electrons and had resourceful electronic transition levels, the band gap  $E_g$  was 3.1 eV, the valence band electron was excited when UV irradiated. The electronic transition levels could absorb ultraviolet light UVB (290–320 nm) and UVA (320–400 nm). The other possible reason was that the CeO<sub>2</sub> nano-particles in the emulsion imparts a very efficient UV scattering because of the large refractive index of CeO<sub>2</sub> nanoparticles. Maybe the interaction between the crystallite surface of CeO<sub>2</sub> and organic molecule, the size dispersion as well as interaction with the nano-trapping levels, played an important role in the red shift. Table 3 demonstrates the mechanical properties of hybrids with various dosages of CeO<sub>2</sub> colloid before and after UV illumination. The tensile and elongation at break of the composite before and after illumination both increased at first and then decreased as the con-

Table 2. The thermal lost weight temperature of the latex film of WPU, WPU/CeO<sub>2</sub>

Sample	$T_{10}$ , °C	$T_{30}$ , °C	$T_{50}$ , °C
WPU	175	281	295
WPU/CeO <sub>2</sub> (0.4 wt %)	208	327	369
WPU/CeO <sub>2</sub> (1.0 wt %)	223	340	379

$T_{10}$ ,  $T_{30}$ , and  $T_{50}$  respectively refer to the decomposition temperature of WPU and WPU/CeO<sub>2</sub> film sat mass loss of 10, 30, and 50%.

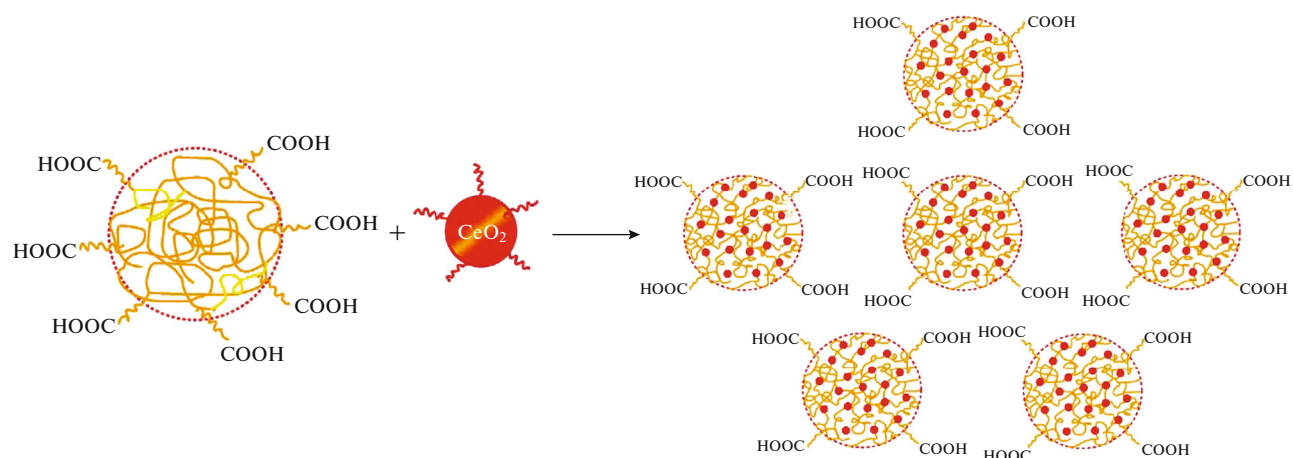


Fig. 6. (Color online) The interaction between WPU and ceria colloid.

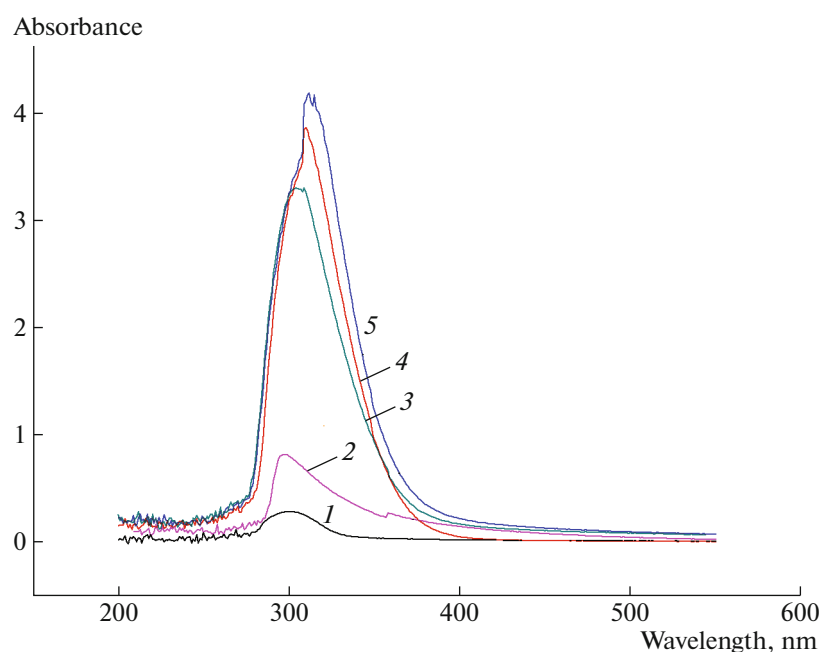


Fig. 7. (Color online) UV-Vis absorption of polymer emulsions: (1) WPU and WPU/CeO<sub>2</sub> with (2) 0.2, (3) 0.4, (4) 0.8, and (5) 1.0 wt % ceria colloid.

tent of CeO<sub>2</sub> colloid increased. Before illumination, the highest tensile and elongation at break were 43.9 MPa and 338%, respectively, at 0.4 wt % CeO<sub>2</sub> colloid.

After illumination, the tensile strength and elongation at break decreased to 41.8 MPa and 337%. However, the 0.4 wt % CeO<sub>2</sub> colloid sample had the highest ten-

Table 3. The mechanical properties of hybrids films with various dosage of CeO<sub>2</sub> colloid before and after UV illumination

Dosage of CeO <sub>2</sub> colloid, %	Tensile strength, MPa		Elongation at break, %	
	before illumination	after illumination	before illumination	after illumination
0	34.7	28.1	350	323
0.2	39.2	36.8	343	325
0.4	43.9	41.8	338	337
0.8	41.9	40.2	324	320
1.0	40.1	39.6	318	316

sile strengths among the specimens after illumination. For the pure WPU, the tensile and elongation at break decreased from 34.7 MPa and 350% before illumination to 28.1 MPa and 323% after illumination. After illumination, the tensile strength and elongation at break of the composite with 0.4 wt % CeO<sub>2</sub> colloid respectively increased by 48.8 and 4.3% compared with the pure WPU.

### CONCLUSIONS

In conclusion, a series of stable waterborne polyurethane/ceria dispersions containing 0.2, 0.4, 0.8, and 1.0 wt % ceria colloids were prepared. The structure and properties of polyurethane/ceria dispersions have been examined. Based on the results obtained, the following conclusions may be drawn:

(1) The stable nano-crystalline CeO<sub>2</sub> hydrosol was prepared at 60°C in PVA solution. The XRD results indicated the prepared CeO<sub>2</sub> was face-centered cubic structure.

(2) TEM images of the emulsion showed that CeO<sub>2</sub> was homogeneously distributed in the polyurethane emulsion.

(3) The polyurethane/ceria dispersions displayed strong UV shielding ability, which was drawn from the UV–Vis absorption of WPU/CeO<sub>2</sub> hybrids emulsion. The tensile strength and elongation at break of the composite with 0.4 wt % CeO<sub>2</sub> colloid increased by 48.8 and 4.3% compared with the pure WPU.

(4) WPU/CeO<sub>2</sub> hybrids exhibited a better thermal stability than pure WPU.

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