Preparation and Characterization of Colloidal Carbon Sphere/Rigid Polyurethane Foam Composites

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ABSTRACT: Sucrose decomposed under hydrothermal conditions, generating colloidal carbon spheres (CCSs) with a perfectly spherical morphology. X-ray diffraction indicated that the main component of the CCSs was disordered carbon, and massive hydroxyl groups existed on the surface, as confirmed by Fourier transform infrared spectroscopy. CCSs were first introduced into polyurethane foams (PUFs), and CCS-reinforced PUF (PUF/CCS) composites were synthesized. The introduction of CCSs did not increase the viscosity of polyol/CCS blends significantly. The good dispersion of CCSs and the compatibility between CCSs and polyurethane were confirmed by transmission electron microscopy measurements. The results of mechanical testing showed that PUF/CCS composites exhibited greatly improved mechanical properties in comparison with neat PUFs, and this could be ascribed to the finer cell structure of the PUF/CCS composites, which was inspected with scanning electron microscopy. Thermogravimetric analysis indicated that the effects of CCSs on the thermal stability of the foams were slight. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 3863–3869, 2009

Key words: composites; fillers; polyurethanes

INTRODUCTION

Polyurethane foams (PUFs) are usually produced by the reaction of a polyisocyanate with a polyol or other reactants containing reactive groups with isocyanate. As a hydroxyl-containing component, which is usually used as a reactive material with polyisocyanate, can have a wide range of molecular weights, functionalities, and types (ether and ester) and polyisocyanate is also variable in its structure (e.g., aromatic, aliphatic, or polycyclic),[1] a variety of rigid PUFs can be produced with excellent characteristics, such as heat insulation, sound absorption, lightness, and shock proofing, and they are widely used in applications such as building insulation, appliances, transportation, and furniture.[2,3] However, the biggest disadvantages of PUFs when they are used as structural or semistructural materials are their low mechanical strengths (e.g., compressive strength and tensile strength), which are key physical properties of materials for withstanding strain during use.[4] Common methods for improving the mechanical properties of rigid PUFs are to increase the density and to use reinforcing agents.[2]

In past decades, rigid PUFs reinforced with particles such as hollow glass spheres,[5,6] clay,[7] garnet,[1] and microsilica and nanosilica[8] and with fibers such as glass fibers[9] and lignin[10] have been prepared and studied. In recent years, carbonaceous materials have attracted research interest, and several have been introduced into PUFs. Kabir et al.[11] prepared carbon nanofiber/PUF composites and found that the yield strength was improved by 20% with a 1.5 wt % concentration of carbon nanofibers. A dynamic mechanical analysis of PUF reinforced with carbon black indicated that the addition of carbon black resulted in a shift to higher temperatures for the loss tangent (tan δ) and a reduction of the peak height.[12] Polyurethane (PU)-infiltrated carbon foams were synthesized by Bunning et al.,[13] and both the thermal and mechanical properties were improved significantly. Shi et al.[14] obtained rigid PUF/expandable graphite (EG) composites with good flame retardancy.

In our work, colloidal carbon spheres (CCSs), a carbonaceous material, were prepared and introduced into PUFs, and this was the first approach to synthesizing rigid, CCS-reinforced PUF (PUF/CCS) composites. Then, by means of a series of characterization methods, including transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, and thermogravimetric analysis (TGA), the microstructures and mechanical and thermal properties of these novel PUF/CCS composites were measured and analyzed.

EXPERIMENTAL

Materials

Polymethylene polyphenylisocyanate (PAPI), polyether polyol (GR-4110G; [OH] = 420 mg of KOH/g), a surfactant (H-310A), and a catalyst [dimethyl cyclohexane (DMCHA)] were all supplied by Shanghai Plastics Co. (Shanghai, China). *N*-Pentane, which was used as a blowing agent, was analytical-grade. Sucrose was purchased from Shanghai Fine Chemicals Co., Ltd. (Shanghai, China). Deionized water was prepared with an ion exchanger by us.

CCS preparation

In this work, sucrose was selected as the precursor. An aqueous sucrose solution (0.2 mol/L) was poured into a stainless steel autoclave with a fill rate of 80%. After 4 h of a hydrothermal treatment at 175°C, the black powder was separated from the obtained liquid centrifugally and was washed with deionized water and ethanol three times.

Preparation of the PUF and PUF/CCS composites

The CCSs were dried in an oven at 60°C for 2 h and were then dispersed in a polyol with a mechanical stirrer at 1000 rpm for 10 min and ultrasonically treated for 15 min. Then, the catalysts, surfactant, and blowing agent were added to the mixture and stirred at 2500 rpm for 5 min. After this, PAPI was added and stirred strongly at 4000 rpm for about 30 s, and finally, the system was cured in a mold at 40°C for 40 min. The formulation for PUF (PUF/CCS) is listed in Table I, in which the mass fractions of the other components are all based on the polyol. The density of the foams was controlled at 55 ± 2 kg/m^3.

Characterization and measurement

FTIR spectra

FTIR spectroscopy studies were carried out to characterize CCS functional groups with a Nicolet (Madison, WI) 550 FTIR spectrometer; the KBr pellets were made on a hand press from a mixture of the sample and KBr powder.

TEM

TEM (S-529, Hitachi, USA) was employed to investigate the CCS morphology in ethanol and PU. CCSs were dispersed in ethanol ultrasonically, and then some were transferred to a 200-mesh, polymer-coated copper grid. Samples of PU with CCSs were prepared with an ultramicrotome (Ultracut UCT, Leica, Heerbrugg, Switzerland). Approximately 70–

TABLE I
Formulation for PPU-Filled Rigid PUF

Ingredient	Parts by weight
Component A	
Polyol	100
CCS	0, 2.3, 4.6, 6.8
Catalysts	3.0
Surfactant	5.0–6.0
Blowing agent	10
Component B	
PAPI	130

100-nm-thick films were cut with a freshly prepared glass knife. The thickness of the films was determined with the given color chart. One of the films was transferred to a 200-mesh, polymer-coated copper grid.

Wide-angle X-ray spectra

Wide-angle X-ray spectra were recorded with a Ricon (Tokyo, Japan) D/max-rB 12-kW diffractometer; and the X-ray beam was nickel-filtered Cu Kα radiation ($\lambda = 0.1542$ nm) at 40 kV and 100 mA, whereas corresponding data were recorded from 2.5 to 50° at a scanning rate of 8°/min.

Viscosity

A Sanse (Suzhou City, Jiangsu Province, China) rotary viscosimeter was employed to determine the viscosity of the polyol and CCS blends according to GB/T 12008.8-92.[15]

Hydroxyl value

The CCS hydroxyl value was determined by the reaction of hydroxyl groups with phthalic anhydride and by an alkaline titrimetric method to determine the residual content of phthalic anhydride according to GB12008.3-89.[16] The hydroxyl value was calculated with the following equation:

$$x = \frac{(V_1 - V_2) \times c \times 56.1}{m} \qquad (1)$$

where x is the hydroxyl value; V_1 and V_2 are the mean consumption of the NaOH solution in the blank test and in the test in which CCSs reacted with phthalic anhydride, respectively; c is the molar concentration of the NaOH solution; and m is the CCS weight.

SEM

The microstructure of the foams was examined with SEM (S-529, Hitachi). The average cell chord lengths of different samples were measured from SEM micrographs via the counting of the cell amounts on
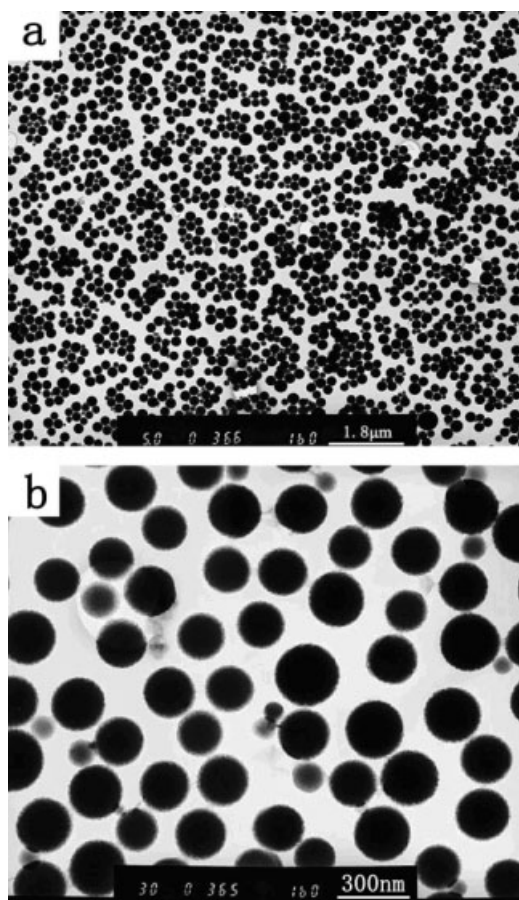
Figure 1 TEM micrographs showing the CCS morphology at (a) 5000 and (b) 30,000×.

several lines. The average cell diameters were obtained with the following equation:

$$D = L/0.616 \quad (2)$$

where D and L are the average cell chord length and average cell diameter, respectively.

Compressive testing

The compressive strength and modulus of the foams with and without CCSs were determined on a universal testing machine (CMT6104, Sans, Shenzhen, Guangdong Province, China) at room temperature according to the GB/T 8813-88 test standard.[17] Measurements were performed perpendicularly to the foam rise direction. The crosshead speed was set at 2 mm/min, and the foams were pressed up to 15% deflection.

TGA

The thermal stability of the foams with and without CCSs was determined with a Shimadzu (Kyoto, Japan) DTG-60H thermogravimetric analyzer between 25 and 600°C under a nitrogen atmosphere at a rate of 10°C/min.

RESULTS AND DISCUSSION

CCSs

According to Wang et al.,[18] under hydrothermal conditions, sucrose molecules dehydrate and polymerize together, forming a kind of amphiphilic compound with a larger hydrophobic alkyl and a hydrophilic hydroxyl. With the polymerization of sucrose molecules, as the concentration reaches the critical micelle concentration, the amphiphilic compound forms spherical micelles, with the hydrophobic groups making up of the core of the micelles and the hydrophilic hydroxyls occupying the surface; this is followed by the growth of the spherical micelle particles through the combination of the surface hydroxyls with the nearest free molecules until the sucrose molecules are exhausted. The final products of sucrose under hydrothermal conditions at 175°C were demonstrated by TEM. Figure 1(a,b) shows typical TEM images of CCS particles with a perfectly spherical morphology and a diameter of 230 nm.

The CCS structure was characterized with XRD and FTIR. The CCS XRD pattern in Figure 2 shows that the as-prepared CCSs were highly amorphous in nature, and no diffraction peaks can be observed, except for a wide peak at $2\theta \sim 20°$, which corresponds to the diffraction of (002) planes of graphite.[17] Shown in Figure 3 is the FTIR spectrum of CCSs. The absorption peaks at 3397 and 2922 cm^{-1} are the characteristic peaks of O—H and C—H bonds, respectively, and the peaks at 1705 and 1611 cm^{-1} are due to the stretching vibration of C=O and C=C bonds. The bands in the range of 1000–1300 cm^{-1}, which include the C—OH stretching and O—H bending vibrations, also imply the existence of large numbers of hydroxyl groups.[19] Moreover, the existence of hydroxyl groups on CCSs was also verified by the measurement of the hydroxyl value according to GB12008.3-89,[16] and the CCS hydroxyl value was 56 mg of KOH/g. From the
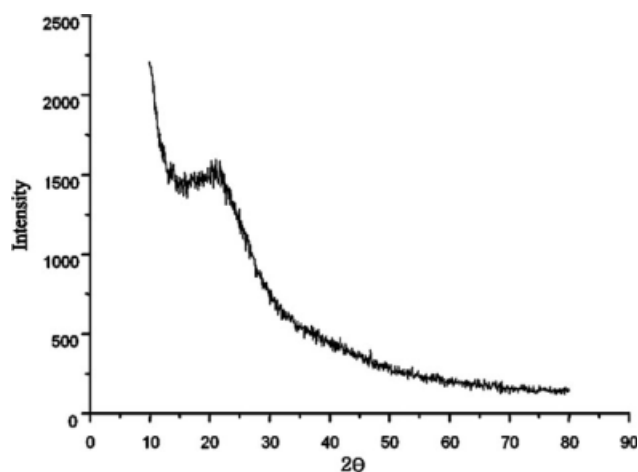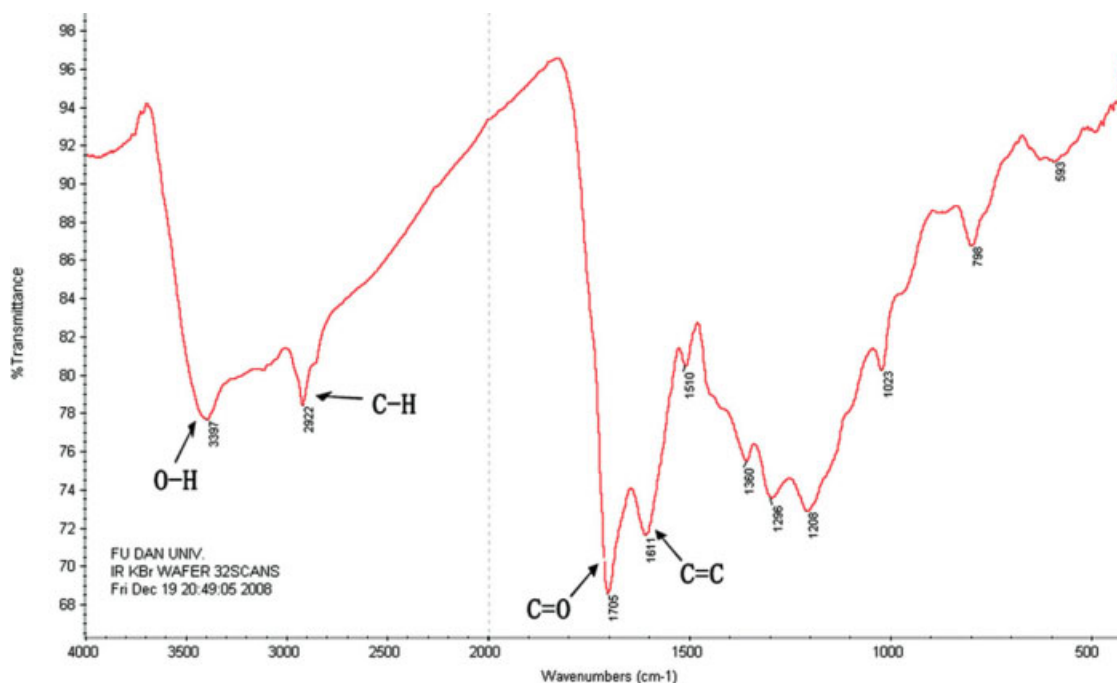

Figure 2 XRD pattern of CCSs.

Figure 3 FTIR spectrum of CCSs. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

formation of CCSs, hydroxyl groups were located on the surface, and they reacted with polyisocyanate during foaming, forming an interface with PUF.

Viscosity of the polyol and CCS blends

Commonly, fillers raise the viscosity of a polyol significantly and then induce difficulties in the dispersion of CCSs in the polyol and foaming. The viscosities of polyols with different CCS contents were measured at 20, 25, and 30°C, respectively. According to Figure 4, CCSs indeed induced an increase in the viscosity but only slightly; for example, at 25°C,
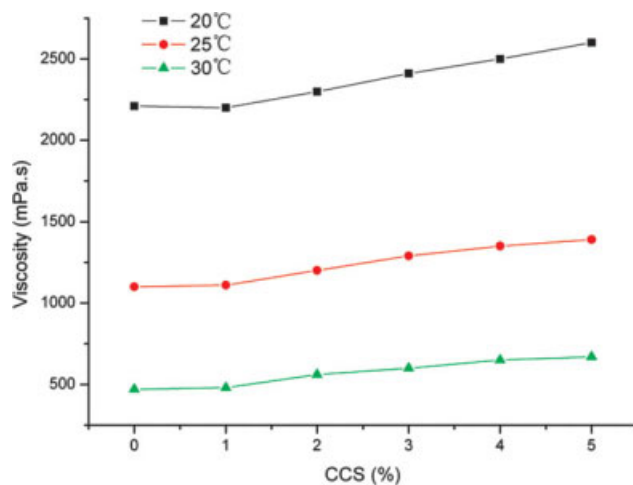

Figure 4 Viscosity of polyols with different CCS contents at 20, 25, and 30°C. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

the viscosity increased from 1100 mPa s for the polyol to 1390 mPa s for the polyol with a 5 wt % CCS concentration. This indicated that the effects of the increased viscosity on the dispersion of CCSs in the polyol were negligible. Additionally, the viscosities of the blends decreased obviously with the increase in the temperature.

Morphology of the foams

It is well known that the properties of composites are strongly dependent on the interaction of the filler and polymer. To evaluate this interaction, the CCS morphology in PU was observed with TEM, as
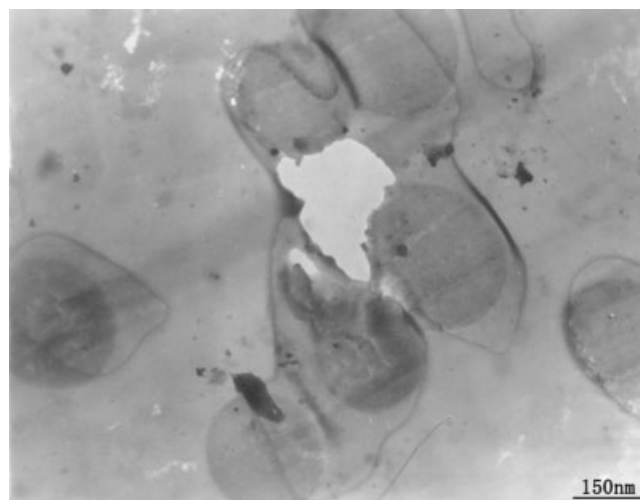

Figure 5 TEM micrograph showing the CCS morphology in the PU resin at 60,000×.
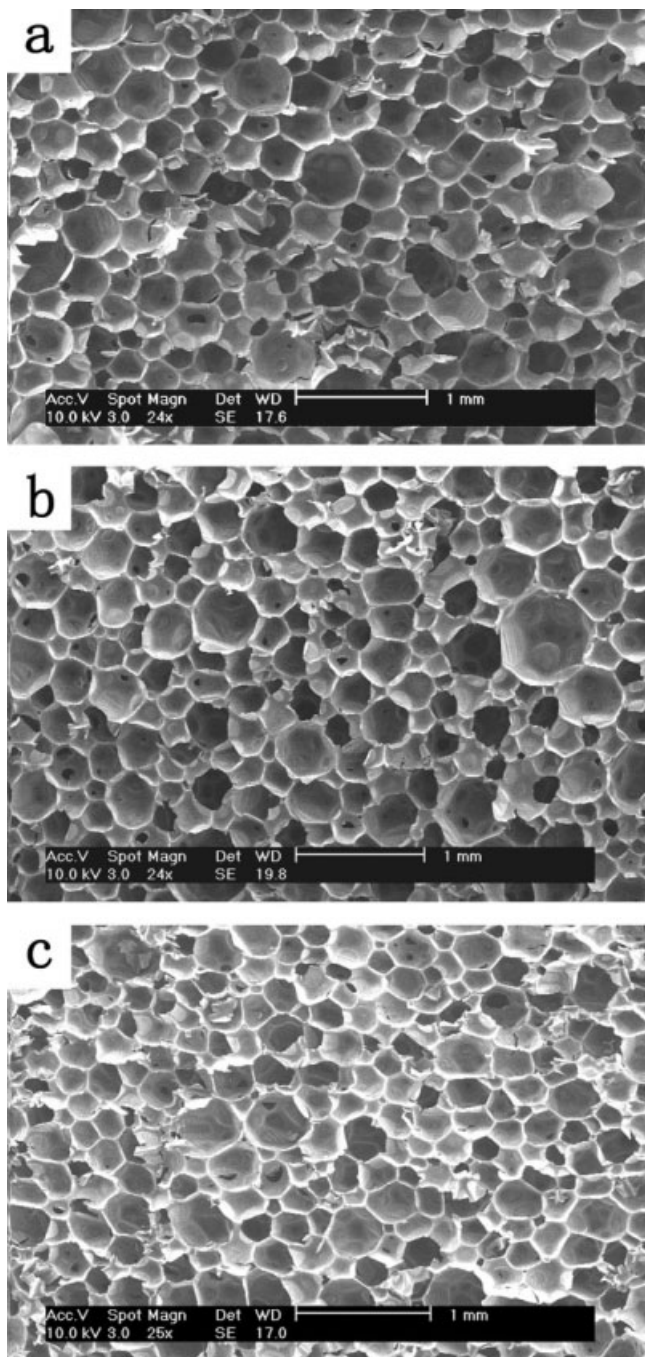
Figure 6 SEM micrograph showing the fracture surfaces of (a) neat PUF, (b) PUF with a 2.3 wt % CCS concentration, and (c) PUF with a 4.6 wt % CCS concentration.

To further investigate the microstructural effects of CCSs in PUF, SEM analyses were carried out on both neat and CCS-reinforced foams. Photomicrographs of neat PUF and PUF with 2.3 and 4.6 wt % concentrations of CCSs are shown in Figure 6(a–c). The cells of PUFs without and with CCSs were all polyhedral. However, PUF with CCSs exhibited finer cells in comparison with the neat foam. The average cell sizes were found to be approximately 476 µm
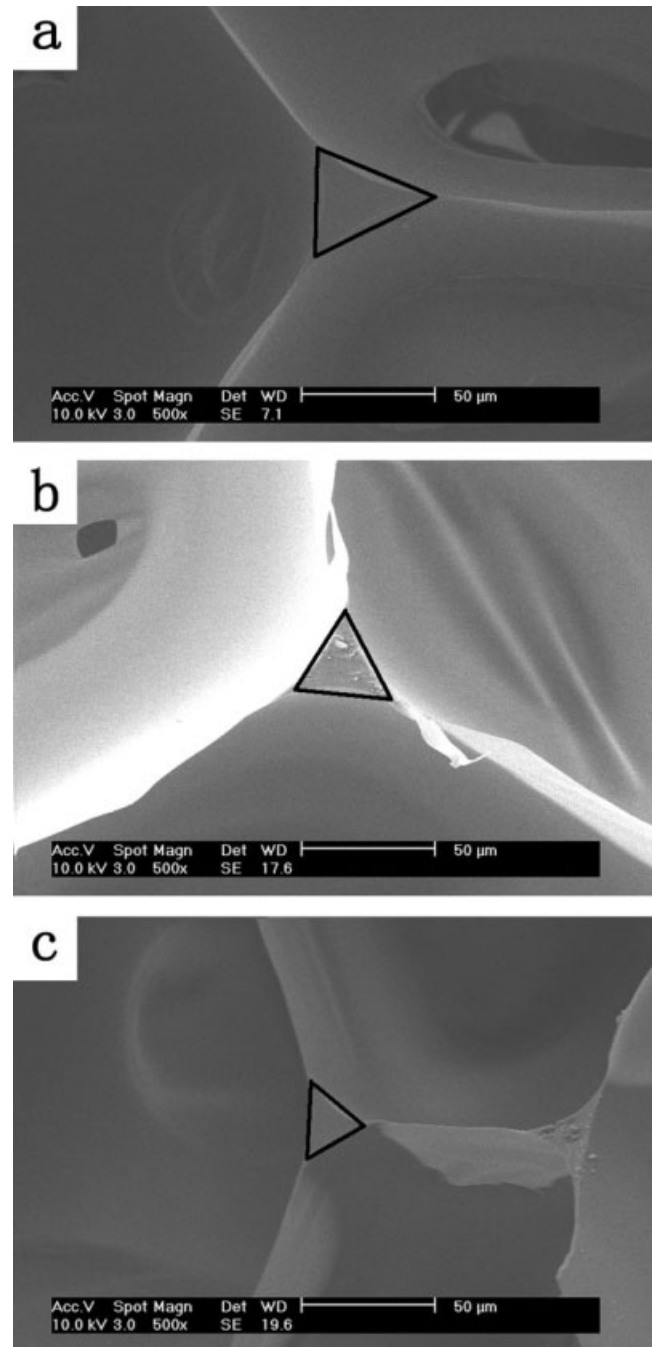

Figure 7 SEM images showing cross sections of the cell edges of (a) neat PUF, (b) PUF with a 2.3 wt % CCS concentration, and (c) PUF with a 4.6 wt % CCS concentration.

shown in Figure 5. Good compatibility of CCSs with PU was observed because of the reaction of hydroxyl groups on the surface of CCSs with isocyanate groups of PAPI. CCS particles were also well dispersed, and individual CCS particles could be observed clearly in PU. The good dispersion of CCSs in PU reduced the stress concentration and enhanced the uniformity of the stress distribution, improving the properties of the composites.
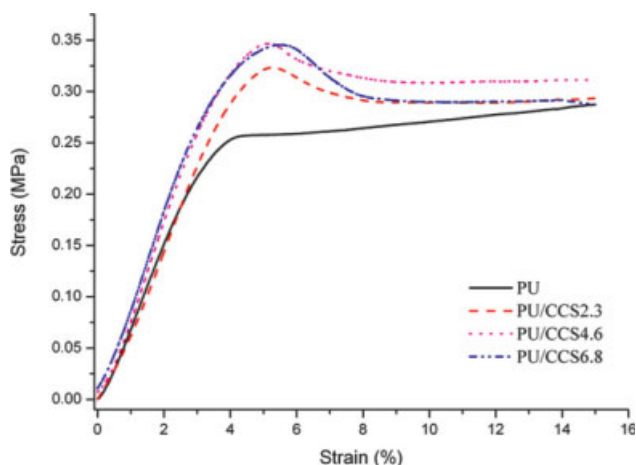
Figure 8 Compressive stress–strain curves of neat PUF, PUF with a 2.3 wt % CCS concentration, PUF with a 4.6 wt % CCS concentration, and PUF with a 6.8 wt % CCS concentration. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

for the neat foam and 411 and 351 μm for PUFs with 2.3 and 4.6 wt % concentrations of CCSs, respectively. It is usually believed that CCSs act as nucleating agents in the process of foaming and reduce the cell size.

As the foams had close foam densities and were fabricated in identical closed molds, the PUF/CCS composites with a smaller cell size had to have a thinner cell edge than the neat foam. This was confirmed by the SEM micrographs shown in Figure 7(a–c), which show that the cross-sectional areas of the cell edges were 914 μm^2 for the neat PUF and 593 and 402 μm^2 for the PUFs with 2.3 and 4.6 wt % concentrations of CCSs, respectively.[20]

Compressive properties

Typical compressive curves are shown in Figure 8 for PUF with a density of 55 kg/m^3. After an initial linear loading regime, the foam specimens showed relatively abrupt yielding, which was followed by a sustained plateau region.[21] The initial linear region, which is controlled by the stretching of the cell faces and edges, defines the modulus of the foam, whereas the yielding point, which indicates the beginning of cell collapse of the foam, is called the compressive strength. The compressive properties of

TABLE II
Compressive Properties of PU Filled with CCS

	PU	PU/2.3 wt % CCS	PU/4.6 wt % CCS	PU/6.8 wt % CCS
σ_m (MPa)	0.2558	0.3233	0.3467	0.3453
E (MPa)	7.76	8.13	8.94	8.89

σ_m = compressive strength; E = compressive modulus.

the foams are summarized in Table II. The addition of CCSs improved the compressive properties of the foams; the compressive strength of 0.3467 MPa and modulus of 8.94 MPa for PUF with a 4.6 wt % CCS concentration were improved by 35.5 and 15.2%, respectively, in comparison with the strength of 0.2558 MPa and modulus of 7.76 MPa for neat PUF. Two factors can be invoked to explain the improvement: (1) the increased internal strength of the PU matrix due to the reaction of hydroxyl groups and isocyanate and (2) the finer cell structure of the PUF/CCS composites. With a finer cell structure, the PUF/CCS composites could withstand more strain in applications.[22]

Thermal stability

TGA measurements were carried out to obtain information on the thermal stability of PUFs with and without CCSs. Figure 9(a,b) depicts the TGA output for neat PUF and PUF with a 4.6 wt % CCS concentration. As shown in Figure 9(a), the neat foam was stable up to 350°C, and PUF with a 4.6 wt % CCS
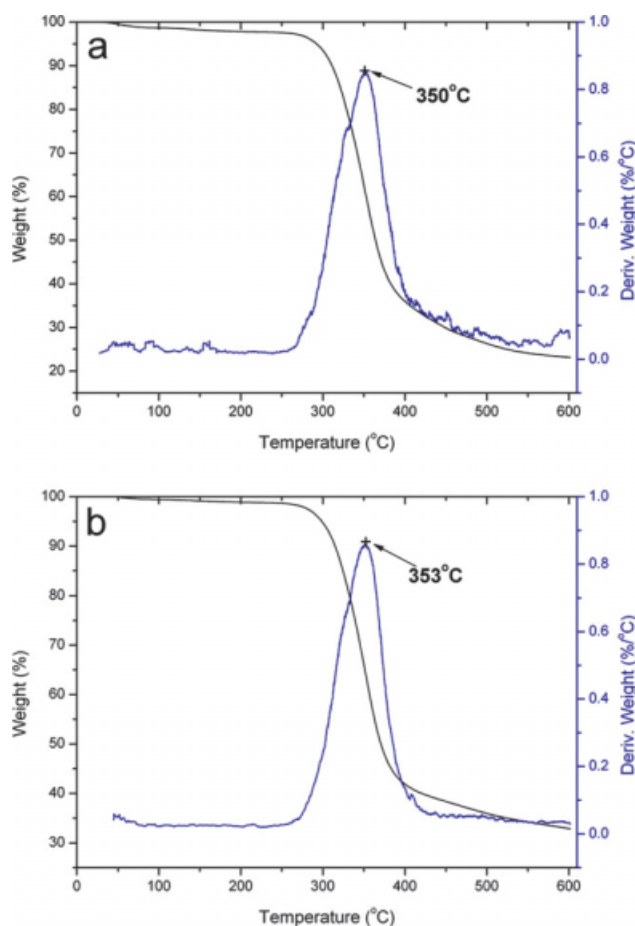

Figure 9 TGA of (a) neat PUF and (b) PUF with a 4.6 wt % CCS concentration. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

concentration was stable up to 353°C [Fig. 9(b)]; this indicated that the addition of CCSs slightly affected the degradation of PUF. The residue at 600°C was higher for PUF with CCSs in comparison with neat PUF. This was consistent with PUF with EG. The presence of EG led to a slight decrease in the thermal stability of PUF because of the uneven distribution of EG in the foam,[14] whereas CCS particles were well dispersed in PUF.

CONCLUSIONS

Under hydrothermal conditions, sucrose dehydrated and polymerized into a kind of amphiphilic compound, which formed spherical micelles as the concentration reached the critical micelle concentration, and the spherical micelles grew, generating CCSs. TEM showed that the CCSs were perfectly spherical, and FTIR and XRD indicated that the main component of CCSs was disordered carbon with massive hydroxyl groups on the surface.

A rotary viscosimeter was employed to determine the viscosity of the polyol and CCS blends. The results suggested that the addition of CCSs did not lead to an apparent increase in the viscosity, whereas the viscosity of blends with the same content of CCSs decreased obviously with an increase in the temperature. As a result, CCSs were well dispersed in PU, as confirmed by TEM; moreover, TEM showed good compatibility between PU and CCSs, which could be ascribed to the reaction of hydroxyl groups on CCSs and isocyanate groups of PAPI.

SEM measurements showed that the PUF/CCS composites exhibited a finer cell structure in comparison with neat PUFs because of the addition of CCSs, which acted as nucleating agents during foaming. The results of compressive testing showed that the addition of CCSs improved the mechanical properties of the PUF/CCS composites significantly; that is, the compressive strength and modulus were increased by 35.5 and 15.2%, respectively, at the CCS loading of 4.6 wt %, whereas the effects of

CCSs on the thermal stability of the composites were slight.

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