

Investigation of Polyurethane (Urea)/Modified Nano-Calcium Carbonate Hybrid Aqueous Dispersions and Their Films

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Received 25 January 2011; accepted 10 May 2011

DOI 10.1002/app.34908

Published online 31 January 2012 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: This investigation was focused on properties of polyurethane (urea) (PUU) by incorporating silica sol-modified nano-calcium carbonate (CaCO_3). The FT-IR spectroscopy and ζ potential measurement indicated the presence of a hybrid effect due to the hydrogen bonding between the nano particles and the polymer matrix. For these hybrid aqueous dispersions, the particle size decreased as the modified nano- CaCO_3 content increased, and the polydispersity index was very narrow (<1.20). Films prepared with the hybrid PUU aqueous dispersions exhibited excellent waterproof performance: the amount of water absorption was as low as 9.0 wt %, and the

contact angle of water on the surface of this kind of film was as high as 93°C . TGA results indicated the high thermal stability of hybrid PUU polymers ($223\text{--}255^\circ\text{C}$). The properties like tensile strength, hardness, and elongation at break were influenced by the modified nano- CaCO_3 content in the polymers. The hybrid PUU with 15 wt % modified nano- CaCO_3 content showed the optimum properties. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2896–2901, 2012

Key words: polyurethane (urea); hybrid aqueous dispersion; nano-calcium carbonate; hydrogenbonding

INTRODUCTION

Research in organic-inorganic nano composites or hybrid materials is increasingly focusing on the development of polymer nanocomposites, which have attracted considerable attention and interest worldwide during the last decade.^{1–3} The development of organic-inorganic hybrid materials is an effective approach to get new type of materials, since they can not only combine the advantages of inorganic material and organic polymer, but also exhibit some other excellent performances.^{4,6} Polyurethanes (PU) are functional polymers whose properties can be tailor-made by simply adjusting the compositions to meet the highly diversified demands of modern technology such as coatings, adhesives, reaction injection molding, fibers, foams, rubbers, thermoplastic elastomers, and composites.⁷ Recently,

for better performance of aqueous polyurethane, they are modified either by varying polyurethane microstructures or by dispersing inorganic fillers, especially by incorporating nano-sized inorganic particles within the polyurethane continuous matrix. Among all the inorganic fillers, nano- CaCO_3 has attracted intensive research interest for the preparation of PU/filler nano-composites because of its high impact resistance, strength and hardness, low cost as well as other advantages.⁸ There are many papers in the literature about solvent-based PU/ CaCO_3 composites and these research papers have described the effect of the incorporation of CaCO_3 on the thermal stability, mechanical strength, morphology and elasticity properties of these composites.^{9–11} However, monodisperse nano- CaCO_3 particles with rather large particle size (≥ 100 nm) is very difficult to disperse homogeneously among the organic polymer structure, so as to be useless to make organic/inorganic hybrid aqueous dispersions for further preparing coatings and adhesives etc.¹²

To our best knowledge, papers dealing with the hybrid of silica sol-modified nano- CaCO_3 and waterborne PUU polymer are less common. The primary interest of this paper was to study the effect of well-dispersed modified nano- CaCO_3 on properties of PUU dispersions and their films and to determine the optimum PUU/modified nano- CaCO_3 ratio. The experimental results showed that, up to a modified nano- CaCO_3 content of 15%, excellent properties of

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Contract grant sponsor: Jiangsu Planned Projects for Postdoctoral Research Funds; contract grant number: 0602037B.

Contract grant sponsor: Fund of Jiangsu University; contract grant number: 06JDG076.

Contract grant sponsor: Natural Science of Jiangsu Education; contract grant number: 08KJB150004.

Contract grant sponsor: Natural Science of Jiangsu Province; contract grant number: BK2008247.

the hybrid aqueous dispersions and films made from them were obtained.

EXPERIMENTAL

Materials

Silica sol-modified nano-CaCO₃ aqueous dispersion with the particle size of 60–70 nm was synthesized using the sol-gel technique in the laboratory (their solid contents were 8%).¹³ Isophorone diisocyanate (IPDI, industry product) was supplied by Huls Co. Dimethylolpropionic acid (DMPA, industry product) was provided by Perstop Co. and was dried under vacuum at 60°C for 24 h. Difunctional polyether polyol (GE220, industry product, Hydroxyl number = 56 mgKOH/g) was produced by Qingdao Yutian Chemical Plant. Other chemicals were laboratory reagents and were purchased from different manufacturers.

Preparation of PUU/modified nano-CaCO₃ hybrid aqueous dispersion

A 250-mL round-bottomed, four-necked separation flask with a mechanical stirrer, nitrogen inlet, thermometer, and condenser was charged with GE220, DMPA, and IPDI dissolved in NMP. The reaction was performed in a silicone oil bath maintained at 80°C for 4 h under a nitrogen atmosphere until the theoretical NCO value was reached. The obtained NCO-terminated prepolymer was neutralized by the addition of tertiary amine at 50°C for 30 min and then dispersed into the silica sol-modified nano-CaCO₃ dispersions under vigorous stirring at 40°C. After chain extension by adding ethylenediamine dropwise, the PUU/modified nano-CaCO₃ hybrid aqueous dispersions (30 wt %) were prepared. For simplicity, they were coded as PUU-Ca-X, in which X represents the percentage of modified nano-CaCO₃ in the total solid component. Neat PUU has also been prepared by the same method without using modified nano-CaCO₃, just to compare with the hybrid polymers.

PUU hybrid films were prepared by casting the PUU hybrid aqueous dispersions into a poly (tetrafluoroethylene) mold at 25°C; then they were dried at 25°C for seven days and under vacuum at 60°C for 24 h to reach a constant weight.

Characterization

The particle size and distribution of the PUU/modified nano-CaCO₃ hybrid aqueous dispersions were measured by a Microtrac UPA 150 Particle Size Analyzer. The samples of dispersions were diluted with deionized water to adjust the solid content to around 1 wt % and directly placed in the cell. The

temperature of the cell was kept at around 25°C and the measuring time was 300 s.

The FT-IR spectra of PUU/modified nano-CaCO₃ hybrid aqueous dispersions were recorded by using a Nicolet Magna-IR 550 FTIR spectrometer at 25°C. Analyses were performed in the transmission mode in the range 400–4000 cm⁻¹ at room temperature with a resolution of 2 cm⁻¹ and accumulation of 32 scans. KBr disks were prepared after mixing (0.5%) each of the test samples with dry KBr.

The ζ potential of the hybrid PUU aqueous dispersion was measured by Delsa 440SX Zeta Potential Analyzer produced by Brookhown Company.

The contact angle of water on the hybrid film surface was measured by the sessile drop method at 25°C using a JC2000 Series instrument (Shanghai Zhongchen Powereach, China).

The water absorption of the PUU hybrid film (25 mm × 25 mm × 1 mm) was tested in water for 24 h at 25°C and was calculated as follows:

$$\text{Water absorption (\%)} = [(W_2 - W_1)/W_1] \times 100\% \quad (1)$$

where, W_1 and W_2 are the weights of the PUU hybrid film before and after soaking respectively.

Thermo-gravimetric analysis (TGA) was performed on Du Pont 1090 Analyzer. The programmed heating range was from room temperature to 700°C, at a heating rate of 20°C/min under a nitrogen atmosphere. The measurement was taken using 6–10 mg samples. TGA curves were recorded.

The mechanical properties for all specimens were conducted on an Instron 4465 testing machine under 50 mm/min crosshead rate, and the specimens were made in accordance with GB1040-79. The hardness of the hybrid PUU sample was measured according to GB/G1703-93.

RESULTS AND DISCUSSION

PUU/modified nano-CaCO₃ hybrid aqueous dispersion

As most of the inherent properties of PUU like viscosity, glass transition temperature, mechanical properties, etc. are strongly influenced by the degree of hydrogen bonding present in the polymer, so any factor, which effects hydrogen bonding is very important to study in this case.¹⁴ As described elsewhere,¹³ the nano-CaCO₃ particles were modified by 3–5 nano silica sol particles with the hydroxyl groups enriched on their surface. So in general, two types of hydrogen bonding between the modified nano-CaCO₃ and PUU chains in the hybrid aqueous dispersion systems could be expected, as shown in Figure 1. These two types of hydrogen bonding were measured by FT-IR spectroscopy, as shown in

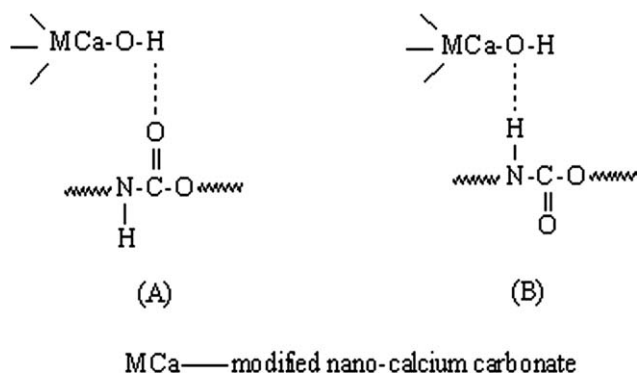


Figure 1 Two types of hydrogen bonds between the modified nano- CaCO_3 and PUU chains.

Figure 2. It was found that all absorption peaks of amine group and carbonyl group in hybrid PUU aqueous dispersions shifted from 3352 cm^{-1} and 1732 cm^{-1} to lower wavenumber of 3338 cm^{-1} (1729 cm^{-1}) [Fig. 2(B)] and 3322 cm^{-1} (1721 cm^{-1}) [Fig. 2(C)], respectively, attributing to the formation of the two types of hydrogen bonding between the hydroxyl group on the surface of modified nano- CaCO_3 and the carboxyl group [Fig. 1(A)] or amine group [Fig. 1(B)] in PUU chain, which indicated the hybrid interaction between the modified nano- CaCO_3 and PUU matrix in the hybrid aqueous dispersion. This phenomenon was consistent with the other observation of hydrogen bonding existed in the industrial silica sol/PSAE.¹⁵ Thus the hybrid aqueous dispersion could be formed and be stable, as both types of hydrogen bonding were observed.

The surface tension of different PUU hybrid aqueous dispersions was obtained by measuring the volume of liquid drop and calculating from eqs. (2) and (3)¹⁶:

$$\sigma = \frac{\rho v g}{2\pi r f} \quad (2)$$

$$f = 0.9045 - 0.7249 \left(\frac{r}{v^{1/3}} \right) + 0.4293 \left(\frac{r}{v^{1/3}} \right)^2 \quad (3)$$

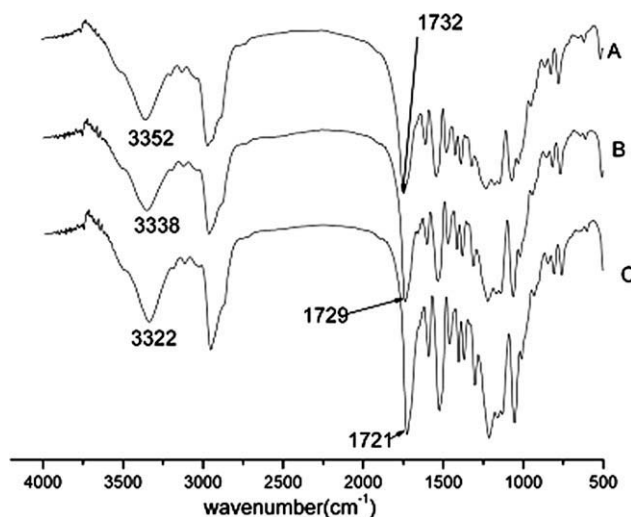


Figure 2 FTIR spectroscopy of different hybrid PUU aqueous dispersions. A: PUU; B: PUU-Ca-10; C: PUU-Ca-15.

where, σ is the surface tension of dispersion (mN/m), ρ is the density of dispersion (g/mL), g is 9.8 N/Kg , r is the effective radius of burette (cm), f is the revised coefficient, v is volume of drop (mL). The results were listed in Table I. Table I showed that the surface tension of the PUU hybrid aqueous dispersion was closed to that of the neat PUU aqueous dispersion at low modified nano- CaCO_3 content ($\leq 15\%$), indicating that the PUU aqueous dispersion might play a key role on the surface tension of these hybrid systems. However, from Table I, it was of interest to note that the surface tension of the PUU hybrid aqueous dispersions increased appreciably at a higher modified nano- CaCO_3 content ($> 15\%$), it meant that more modified nano- CaCO_3 particles were covered or inlaid on the surface of PUU particles or in the PUU matrix and increased the amount of the polar hydroxyl groups as well as enlarged the surface tension of the hybrid system.

The particle size and its distribution for these PUU hybrid aqueous dispersions were also measured, as listed in Table I. It was clear that the particle size

TABLE I
Physical Properties of Different Hybrid PUU Aqueous Dispersions^a

Samples	Modified nano CaCO_3 content (wt %)	Particle size (nm)	Polydispersity index	Surface tension (mN/m)
PUU	0	99	1.07	46.7
PUU-Ca-5	5	103	1.07	46.3
PUU-Ca-10	10	105	1.08	46.5
PUU-Ca-15	15	107	1.08	46.8
PUU-Ca-20	20	115 ^b	1.13	48.6
PUU-Ca-25	25	120 ^b	1.18	49.3

^a All specimens are stable after storing 12 months at ambient temperature except PUU-Ca-20 and PUU-Ca-25.

^b Deposited out after storage for less than six months at the ambient temperature.

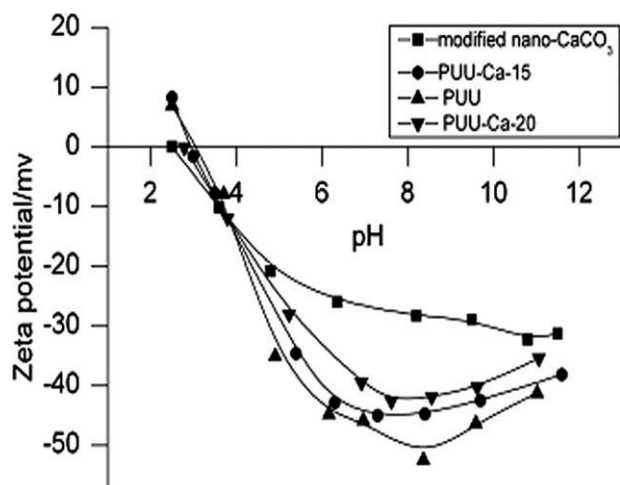


Figure 3 Zeta potential vs. pH value for different aqueous systems.

distribution for all the PUU aqueous dispersions was very narrow, but compared with the neat PUU aqueous dispersion, the particle size of the PUU hybrid aqueous dispersions increased with increasing modified nano- CaCO_3 content, as a result of the adsorption or insertion of small inorganic particles on the surface of the PUU particles or in the PUU matrix.

Because the electrophoresis of the colloid particles in water phase could be used to appraise their surface composition and morphology, thus the ζ potentials for modified nano- CaCO_3 , PUU-Ca-15, PUU-Ca-20, and PUU were measured, as shown in Figure 3. It showed that the ζ potential for modified nano- CaCO_3 was less negative than that of the neat PUU and hybrid PUU aqueous dispersions. The relatively high absolute value of ζ potential for such polymer dispersions must result from the $-\text{COOH}$ groups of DMPA units in the PUU macromolecular chains. From Figure 3 it could be seen that the values of ζ potential for PUU-Ca-15 and PUU-Ca-20 were just in the middle of those for neat PUU and modified nano- CaCO_3 when the pH value was more than 3.8. These experimental data also indicated that in all the hybrid PUU dispersions, most of the modified nano- CaCO_3 particles should adsorb on the surface of PUU particles or inlaid in PUU matrix, so

as to change the ζ potential of the hybrid system and increase the particle size of these systems. It should be pointed out that, however, these two kinds of particles had the same negative electric charge and they should repulse each other. In this case, the strong hydrogen bonding (See Fig. 2) could be expected, giving rise to the stable hybrid system. Figure 3 also indicated that when $\text{pH} < 4$, the value of ζ potential for PUU-Ca-15 increased rapidly and an isoelectric point (IEP) was found at $\text{pH} = 2.96$. This experimental behavior was interesting and should be studied further.

PUU/modified nano- CaCO_3 hybrid films

Table II showed the water absorption and some surface properties of the films prepared with different hybrid PUU aqueous dispersions. The surface energy of the PUU film was difficult to be measured directly, but it could be calculated indirectly through measuring the balance contact angles of some standard liquids (i.e., water and ethylene glycol) on its surface¹⁷:

$$(1 + \cos \vartheta_1)\gamma_1 = 4 \left(\frac{\gamma_1^d \gamma_s^d}{\gamma_1^d + \gamma_s^d} + \frac{\gamma_1^p \gamma_s^p}{\gamma_1^p + \gamma_s^p} \right) \quad (4)$$

$$(1 + \cos \vartheta_2)\gamma_2 = 4 \left(\frac{\gamma_2^d \gamma_s^d}{\gamma_2^d + \gamma_s^d} + \frac{\gamma_2^p \gamma_s^p}{\gamma_2^p + \gamma_s^p} \right) \quad (5)$$

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad (6)$$

where, θ_1 and θ_2 are the contact angle of water and ethylene glycol on the surface of PUU film, respectively; γ_s , γ_s^d , and γ_s^p are the surface energy, the dispersion part of the surface energy and the polar part of the surface energy for PUU film, respectively; γ_1 , γ_1^d , and γ_1^p are the surface tension, the dispersion part of the surface tension and the polar part of the surface tension for water ($\gamma_1^d = 51.0$ mN/m, $\gamma_1^p = 21.8$ mN/m), respectively; γ_2 , γ_2^d , and γ_2^p are the surface tension, the dispersion part of the surface tension and the polar part of the surface tension for ethylene glycol ($\gamma_2^d = 19.0$ mN/m, $\gamma_2^p = 29.3$ mN/m), respectively. The estimated results were listed in

TABLE II
Some Physical Properties of Different Hybrid PUU Films

Samples	Modified CaCO_3 content (%)	Water absorption (wt %)	Contact angle ($^\circ$)	γ_s (mN/m)	γ_s^d (mN/m)	γ_s^p (mN/m)
PUU	0	15.2	82	27.9	15.4	12.5
PUU-Ca-5	5	12.5	89	27.0	14.8	12.2
PUU-Ca-10	10	9.7	91	26.8	15.6	11.2
PUU-Ca-15	15	9.0	93	26.4	20.2	6.2
PUU-Ca-20	20	10.3	90	27.3	18.3	9.0
PUU-Ca-25	25	11.1	89	28.8	19.8	9.0

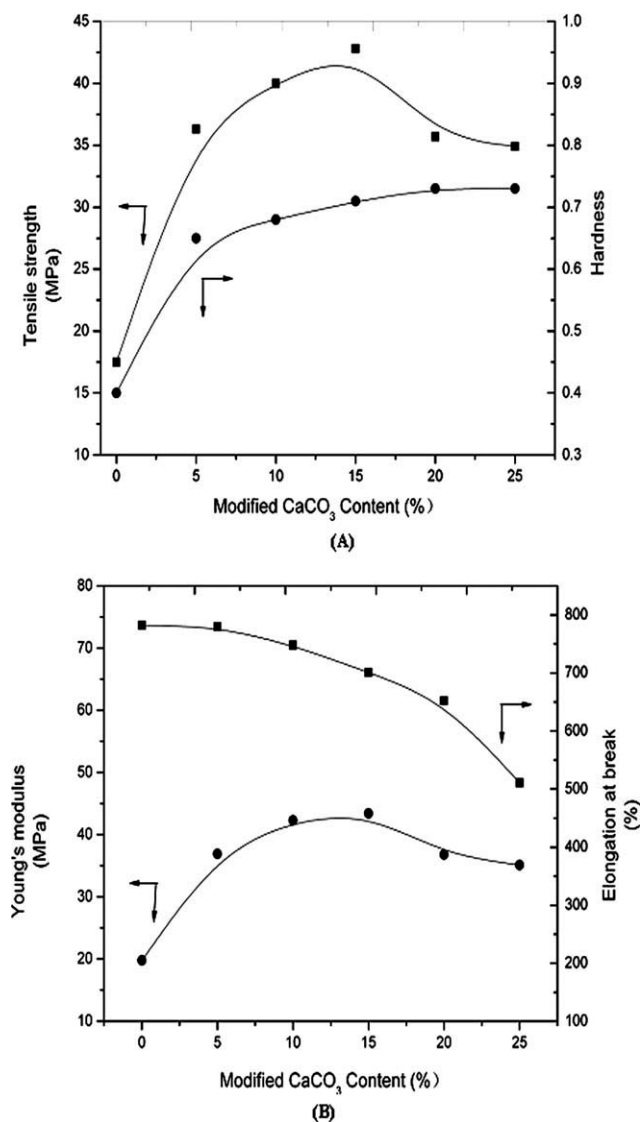


Figure 4 Mechanical properties of different hybrid PUU films.

Table II. It indicated that compared with the neat PUU film, the water absorption of the hybrid PUU films decreased from 15.2 wt % to 9.0 wt %, the values of contact angle of water on the surface of the hybrid films increased from 82°C to 93°C at the lower modified nano-CaCO₃ content ($\leq 15\%$). That is, the waterproof properties of the hybrid PUU films enhanced with the attribution of modified nano-CaCO₃, resulting from the hydrogen bonding between the hydroxyl group in modified nano-CaCO₃ and the carboxyl group or amine group in PUU. In these hybrid PUU films, physical cross-linking among the PUU macromolecular chains and modified nano-CaCO₃ particles was expected and the compact structures of the hybrid PUU films were formed, thus lower water absorption of the hybrid PUU films were obtained. But when the modified nano-CaCO₃ content ($>15\%$) was high,

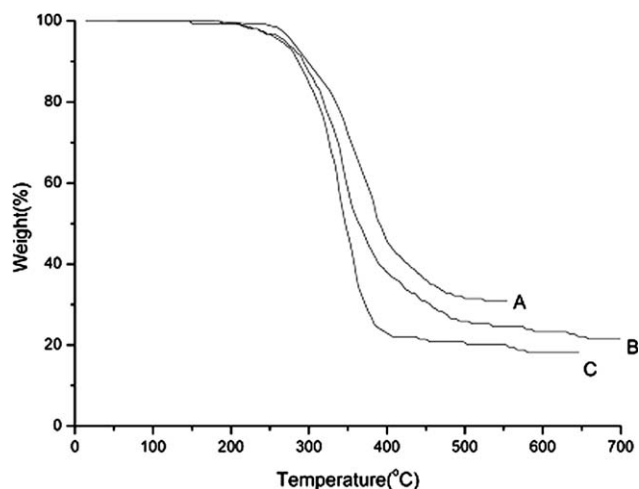


Figure 5 TGA curves of different hybrid PUU films. A: PUU-ca-15; B: PUU-Ca-10; C: PUU.

the water absorption of the hybrid films increased, resulting from the enrichment of much more strong polar modified nano-CaCO₃ particles on the surface of the hybrid films. Table II also listed the values of γ_S^d , γ_S^p , and γ_S of different hybrid PUU films calculated from eqs. (4)–(6). The data were consistent with the results discussed above. That is, the hybrid PUU film exhibited optimum surface hydrophobic property at a modified nano-CaCO₃ content of 15%.

The mechanical properties of the hybrid PUU films were shown in Figure 4(A,B). It was found that the tensile strength, hardness and Young's modulus of all the hybrid PUU films were higher than that of the neat PUU films, while the values of elongation at break decreased. The modified nano-CaCO₃ could be regarded as a cross-linking agent of PUU matrix during film formation, consequently promoting the tensile strength and decreasing the elongation at break of the hybrid film. On the other hand, the improvement in the tensile strength of the hybrid films indicated that there was a strong interfacial interaction between the modified nano-CaCO₃ surface and the nearby PUU chains, as discussed above. From Figure 4, it was clear that when at a higher modified nano-CaCO₃ content more than 20%, the tensile strength of the specimen decreased,

TABLE III
Thermal Decomposition Temperature (°C) Data of Different Hybrid PUU Films

Samples	T_{on} (°C)	T_{end} (°C)	Temperature at different weight loss percentage (°C)			
			10%	20%	50%	60%
PUU	223	425	283	310	348	360
PUU-Ca-10	255	518	291	318	365	393
PUU-Ca-15	225	520	297	330	389	422

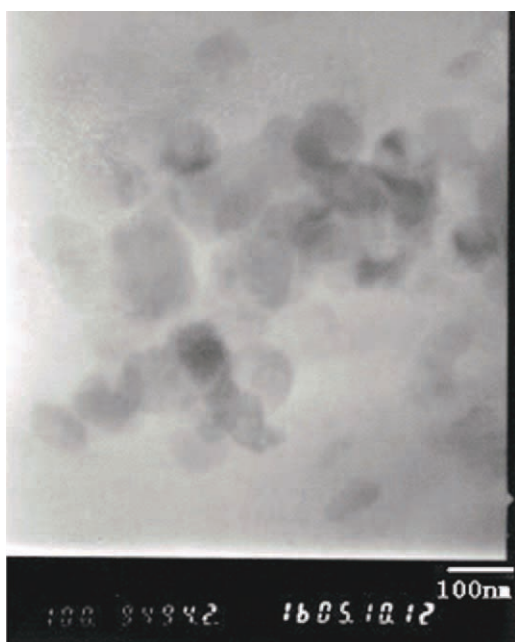


Figure 6 TEM photo of PUU-Ca-15 film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

resulting from the incompatibility between the modified nano-CaCO₃ and the PUU matrix.

Generally the thermo stability of PUU depends on number of the secondary interactions (such as hydrogen bonding) and urethane linkages in their matrix, as they can withstand a considerable amount of heat. And also the presence of inorganic nano particles increases the thermo-stability of the PUU.¹⁸ Figure 5 showed the TGA curves of neat PUU film, PUU-Ca-15 and PUU-Ca-10 films, the onset decomposition temperature (Ton), temperature corresponding to different weight loss and the endset decomposition temperature (Tend) for the hybrid and neat PUU were incorporated in Table III. It clearly showed that compared with the neat PUU film, the onset decomposition temperature of hybrid PUU films was found to be increased appreciably (from 223°C to 255°C). This was due to the increase of intermolecular attractions between modified nano-CaCO₃ and PUU matrix through hydrogen bonding, polar-polar interaction, etc.

The disperse capacity of modified nano-CaCO₃ in the hybrid PUU film of PUU-Ca-15 had been also investigated by TEM, as described in Figure 6. The photo showed that the modified nano-CaCO₃ particles dispersed uniformly in bulk of the hybrid PUU film with the particle size of 60–70 nm without aggregation. These results implied that the

homogeneous distribution of modified nano-CaCO₃ in the PUU matrix was well established by surface modification of the nano-CaCO₃, which was benefit to stabilize the hybrid PUU aqueous dispersions and increase the mechanical properties of hybrid PUU films.

CONCLUSION

In this study, silica sol-modified nano-CaCO₃ was dispersed homogeneously in PUU matrix by in-situ dispersing method. Incorporation of modified nano-CaCO₃ to PUU matrix had significant effect on its performance in terms of physical, mechanical and thermal properties. The increase of modified nano-CaCO₃ content increased the hydrogen bonding and polarity of the structure of the polymers. The addition of modified nano-CaCO₃ into PUU brought a simultaneous improvement in surface properties, mechanical properties and thermal resistance of hybrid PUU films as a result of the enrichment of inorganic nano filler particles covered or partially inlaid on the surface of PUU particles or in the PUU matrix. So this work confirmed the suitability of using these PUUs-modified inorganic nano materials as high performance coating and adhesive materials.

References

- Chen, T. K.; Tien, Y. I.; Wei, K. H. *Polymer* 2000, 41, 1345.
- Wang, T. L.; Yang, C. H. *Eur Polym J* 2009, 45, 387.
- Chen, Y. C.; Zhou, S. X.; Gu, G. X. *Polymer* 2006, 47, 1640.
- Huang, H. H.; Bruce, O.; Garth, L. W. *Polym Bull* 1985, 14, 557.
- Philip, G.; Schmidt, H. *J Non-Cryst Solids* 1984, 63, 283.
- Mascia, L.; Heath, R. J.; Vincent, S. Y. *J Appl Polym Sci* 2004, 94, 1279.
- Zhou, S.; Wu, L.; Shen, W.; Gu, G. *J Mater Sci* 2004, 39, 1593.
- Li, X. H.; Yuan, Q. L.; Wang, D. N.; Ying, S. K. *J Funct Polym* 2000, 13, 211.
- Gatos, K. G.; Martínez, J. G.; Psarras, G. C.; Thomann, R. *Compos Sci Technol* 2007, 67, 157.
- Cubas, S. A.; Foresti, E.; Rodrigues, J. A. D.; Ratusznei, S. M.; Zaiat, M. *Bioresource Technol* 2007, 98, 1411.
- Sánchez, A. M. S. *Int J Adhesion Adhesives* 2000, 20, 291.
- Milan, A. B. M.; Ma, Á. P. L.; César, A. O. B. *Macromol Symp* 2005, 221, 33.
- Yang, D. Y.; Qiu, F. X. *Rare Metal Mater Eng* 2007, 36, 169.
- Gunera, F. S.; Yagcib, Y.; Erciyas, T. *Prog Polym Sci* 2006, 31, 633.
- Huang, F. M.; Zhang, G. W.; Hu, C. P.; Ying, S. K. *Chinese J Chem Eng* 2005, 13, 816.
- Yang, D. Y.; Hu, C. P.; Ying, S. K. *J Polym Sci: Part A: Polym Chem* 2005, 43, 2606.
- Wu, S. H. *Polymer Interface and Adhesion*; Marcel Dekker: New York, 1982, p178.
- Jeon, H. T.; Moon Jang, K.; Kim, B. K.; Kim, K. H. *Colloids Surfaces A: Physicochem Eng Aspects* 2007, 302, 559.