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Synthesis and Properties of Novel Polyurethane−Urea/Multiwalled Carbon Nanotube Composites

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ABSTRACT: In this paper, a new method based on sol−gel process was developed to prepare polymer/carbon nanotube composites. By modifying the multiwalled carbon nanotube (MWNT) with coupling agent, MWNT was introduced into the polyurethane−urea (PU) system by chemical linkages, and a series of novel self-cross-linkable PU/MWNT composites were then prepared. The obtained PU/MWNT composites with various MWNT contents are homogeneous and transparent materials. Mechanical property measurements show that a small amount of MWNT in the samples may increase the Young's modulus and tensile strength significantly with no loss of elongation, indicating that MWNT is an excellent reinforcing agent for polyurethane. The PU/MWNT composites also show good optical limiting properties. The normalized extinction increases and the optical limiting threshold decreases with the increase of the contents of MWNT. Thus, it is possible to change the required transmittance and transmitted energies by changing the MWNT contents in composites.

1. Introduction

Carbon nanotubes (CNTs) are a family of new materials with unique structure and excellent mechanical, electrical, and optical properties.[1] Calvert[2] pointed out that CNTs can be ideal reinforcing agents for kinds of materials especially for polymers. Since then, many efforts have been made to explore the potential usage of CNTs as reinforcing agents. For example, Qian et al.[3] reported that introducing of 1 wt % MWNT to PS increased the tensile strength markedly. Kumar et al.[4] found that the addition of 10 wt % single-walled carbon nanotubes (SWNT) to PBO increased the tensile strength by about 50%. Zhu et al.[5] revealed that an epoxy composite containing 1 wt % of modified SWNT had led to a 30% increase in Young's modulus and an 18% increase in tensile strength. Geng et al.[6] added 4 wt % modified SWNT to PEO and found the storage modulus at room-temperature enhanced by 400%. Liu et al.[7] obtained a 28% increase in tensile Young's modulus in the rubbery epoxy resin using 1 wt % functionalized nanotubes, compared to the unreinforced epoxy, whereas such as a significant enhancement in tensile modulus was not observed in the glassy expoxy sample. Their results show that good nanotube dispersion and strong interfacial interaction are important for the improvement of the mechanical properties. Most of these works focus on the excellent strength of CNTS and the main aim is to increase the modulus and strength of the composites. Though attempt has been made to employ CNT to enhance the elasticity of polymers,[8,9] it seems that the characteristic of high aspect ratio and flexibility of CNTs has not received much attention. In this work, we have chosen deliberately a thermoplastic elastomer, polyurethane−urea, as the polymer matrix to study whether the MWNT can reinforce both the strength and toughness simultaneously.

With their excellent mechanical properties and industrial importance, polyurethane−urea polymers spurred enduring investigations into their structure−property correlations. In the past few decades, extensive investigations have been carried out in the field with countless papers, patents and books on synthesis, manufacturing, characterization and applications of polyurethane−urea published. The wide application of polyurethane−ureas in different field has brought about higher requirements of their properties. Developing high performance polyurethane−ureas, therefore, is always of great importance.

In this paper, we developed a new method to prepare polymer-MWNT composites, using a sol−gel process to combine of polyurethane−urea and MWNT. With this, a novel high performance material with both excellent mechanical properties and good optical limiting properties is produced.

2. Experimental Section

Materials. MWNT was purchased from Nanotech Port Co., Shengzhen, P. R. China, with diameter of 15−30 nm and length of 0.5−50 μm. Poly(tetramethylene oxide) (PTMO) ($M_n = 1000$), supplied by Aldrich, was dried and degassed at 80 °C/<10Pa for 2 h before use. 4,4′-diphenylmethane diisocyanate (MDI), aminoethyl aminopropyl trimethoxysilane (AEAPS) and aminopropyl triethoxysilane (APES) were purified by vacuum distillation. *N,N′*-Dimethylformamide (DMF) was dried over 4 Å molecular sieves for at least 24 h and vacuum distilled before use.

Preparation of Samples. The obtained MWNT was purified and shortened with a mixture of nitric and sulfuric acid (1:3 by volume) according to the literature.[10] In this step, the MWNT was shortened and carboxyl groups were imported onto the surface of MWNT. The aspect ratio of shortened MWNT is 15−100. Shortened MWNT (1.0 g) in 100 mL of $SOCl_2$ together with 1 mL of dimethylformamide (DMF) was stirred at 70 °C for 24 h. Then the unreacted $SOCl_2$ was distilled from the reaction system under reduced pressure. The obtained MWNT−COCl was dried at room temperature under vacuum for 24 h before use.

The synthesis routes of the polyurethane−urea samples are shown in Scheme 1. A typical preparation was carried out as follows: Into

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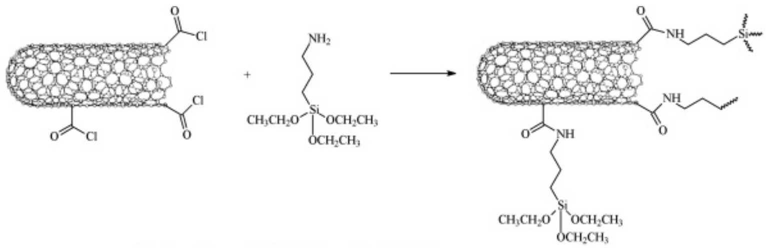
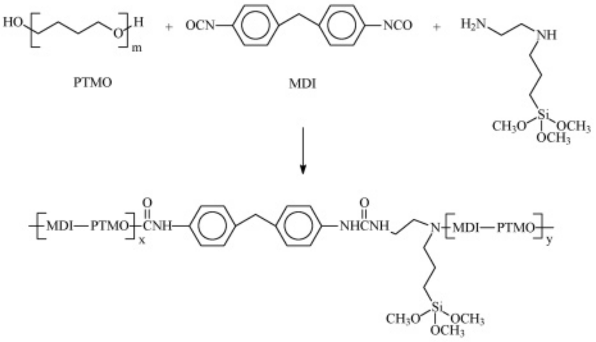
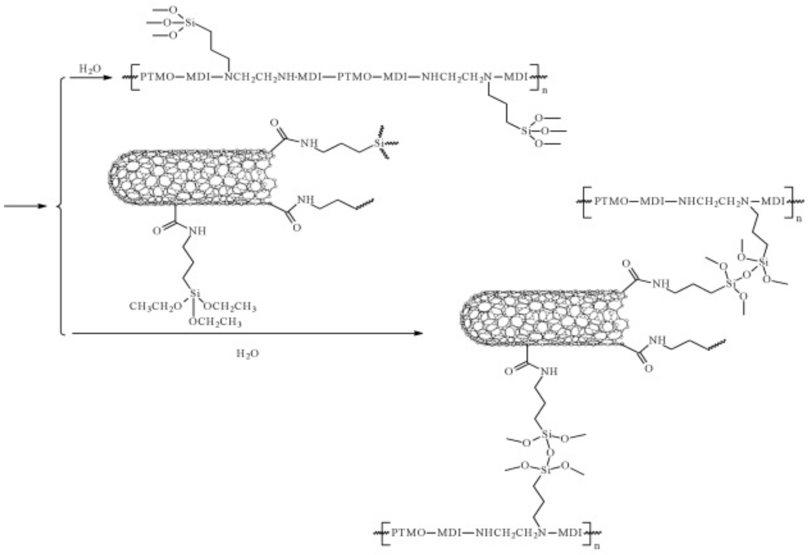
Scheme 1. Synthetic Procedures for Polyurethane−Urea/MWNT Composites



Amination of MWNT with APES



Synthesis of self-crosslinkable polyurethane-urea



Hydrolysis and co-hydrolysis of trimethyloxysilane

a 500 mL dried four-neck round-bottom flask equipped with thermometer, reflux condenser, dropping funnel and drying tube was charged 10 g of PTMO dissolved in 80 mL of DMF, followed by the addition of stoichiometric amounts of MDI in DMF, 7.8 g/80 mL, and one drop of stannous octoate as catalyst. The reaction system was stirred by magnetic stirring for about 3 h in an oil bath at 70 °C under dried N_2 atmosphere to obtain the −NCO terminated prepolymers. Then the extender, 4.44 g of AEAPS in 80 mL of DMF, was added dropwise. After the drop funnel was washed with 20 mL of DMF and the reaction mixture diluted, the reaction continued for another 8 h at 90 °C to ensure the completeness of reaction. The synthesized polymers were kept in solution in sealed bottle to avoid moisture.

To prepare aminated MWNT with trimethoxysilane group, a 25 mL dried round-bottom flask was charged with 150 mg of MWNT−COCl and 7.0 g of APES. Then the reaction mixture was stirred by magnetic stirrer for 48 h in an oil bath at 100 °C under dried N_2 atmosphere. The reaction products include MWNT-adducts (APES−MWNT) and excess APES. For a part of reaction mixture, the unreacted APES were distilled off from the reaction mixture under reduced press to obtain APES−MWNT sample for NMR analysis. The rest of the reaction mixture was used in the film formation without further treatment.

Table 1. Compositions of Samples

samples	composition (molar ratio) PTMO	MDI	AEAPS	APES-MWNT (wt %)	MWNT (wt %)
0% MWNT	1	2	1	0	0
0.1% MWNT	1	2	1	5	0.10
0.2% MWNT	1	2	1	10	0.20
0.3% MWNT	1	2	1	15	0.30
0.4% MWNT	1	2	1	20	0.40
0.5% MWNT	1	2	1	25	0.50

Polyurethane−urea/DMF solution was mixed with different amount of the reaction mixtures of APES−MWNT according to the ratios listed in Table 1, and the obtained mixtures were transferred into flat bottom dishes. The dishes were heated in an oven at 60 °C for at least 72 h to allow the formation of the membrane samples by utilizing H_2O in atmosphere to cohydrolyze the triethyloxysilane groups with the trimethyloxysilane groups on the polyurethane−urea. Transparent membranes were obtained and

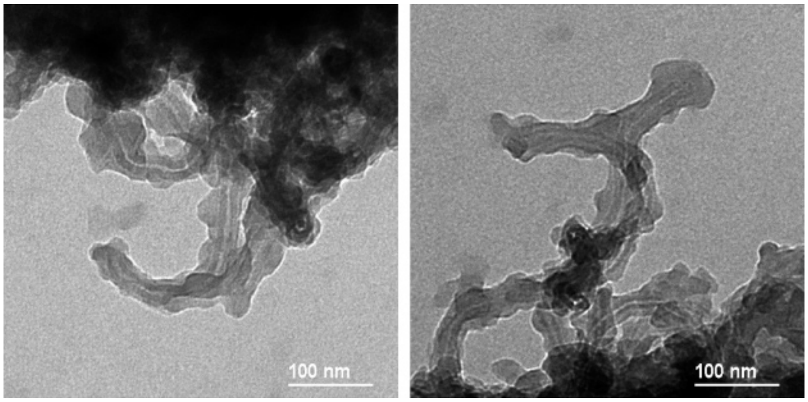


Figure 1. TEM images of MWNT/APES sample.

then vacuumed for about 1 week to ensure the complete volatilization of solvent and water.

Instruments and Characterizations. TEM samples were prepared by allowing a drop of APES−MWNT solution to dry onto holey carbon film and then imaged on a JEM-2010 transmission electron microscope at an accelerating voltage of 200 kV.

High-resolution ^{13}C NMR measurements were carried out at room temperature on a Bruker DRX-500 spectrometer operating at 125.03 MHz. DMSO-d_6 was used as solvent, to increase the solubility, a drop of DMF was added.

The morphology of the composites was studied by a scanning electron microscope (FEI Quanta 200F E-SEM) at an accelerating voltage of 3KV and in low vacuum mode. The images were taken at nitrogen pressure between 0.3 and 0.5 mBar.

The swelling ratios of the samples were studied as follows: the dry films were weighed and then immersed in either water or DMF at room temperature for 120 h. Then the samples were blotted with laboratory tissue and weighed again. The swelling ratio was expressed as the weight ratio of water or DMF in the swollen samples to the dry samples,

$$\text{swelling ratio} = (W_s - W_d)/W_d \times 100\%$$

where W_s is the weight of the swollen sample and W_d is the weight of the dry film.

The mechanic properties, such as Young's modulus, tensile strength and ultimate elongation were determined on a table model Instron Series IX Automated Materials Testing System with Interface type of 4200. The samples were stamped out of the films using an ASTM 1708 standard die and were tested using the crosshead speed of 50 mm/min at room temperature (about 18 °C) and 50% humidity. Five samples were tested for each specimen type.

The photographs of the samples were taken by Pentax Optio S4i digital camera.

The optical limiting properties were recorded using a Cotinuum NY81−10 frequency-doubled Nd:YAG laser and the experiments were performed at 532 nm with 7 ns pulse. The pulsed laser beam was focused into a facula with diameter 45.3μm on the membrane samples. The incident and transmitted energies were measured by a Molectron J3S-10 detector, and every point of the optical limiting data was the automatic average value of 10 detected values acquired by the detector.

3. Results and Discussion

Synthesis. The as obtained APES−MWNT system is a black solution. No deposition was found after it was centrifuged at 5000 rpm for 15 min. The dried APES−MWNT sample is a black solid and can be well dissolved in organic solvents such as DMF and chloroform. Figure 1 shows the typical images of APES−MWNT. From these images, carbon nanotubes can be observed clearly, though the nanotubes were thickly coated, due to the self-cross-linking of APES.

Many previous works including ours have shown that MWNT can be esterified or aminated,[11−13] and the resulting products can be dissolved in solvents. The same phenomenon was also observed in this work. To reveal if the MWNT is chemically bonded with APES, ^{13}C NMR experiments were carried out. The ^{13}C spectra of pure APES and APES−MWNT are shown in Figure 2. The assignments of resonance peaks are illustrated in the figure according to the standard spectra. Comparing these two spectra, we can find that three methylene peaks of $NH_2-CH_2-CH_2-CH_2$ of APES disappeared from the spectrum of APES−MWNT, demonstrating that the amino groups on APES have reacted with the carboxyl groups on the surface of MWNT. The disappearance of the signals of these three CH_2 groups is possibly due to the paramagnetic nature of the carbon nanotubes,[13] which leads to the broadening of the signals of the neighboring groups. A similar phenomenon was also observed on the ODA grafted MWNT[11] and discussed in detail in our previous work. Thus, we believe that the marked difference between the spectrum of APES and that of the APES−MWNT provides direct evidence that APES molecules are covalently combined with MWNT during the aforementioned reaction.

Table 1 lists the compositions of the polymers. Using AEAPS as extender, the self-cross-linkable polyurethane−ureas were synthesized.

The self-cross-linkage is formed from the hydrolysis of the trimethyloxysilane group. With the adding of APES−MWNT adducts, cohydrolysis can occur between AEAPS and APES−MWNT to form the silsesquioxane formation. MWNT can then be introduced into polymers by chemical bonds to form homogeneous MWNT-containing materials. The reactions are shown in Scheme 1.

The obtained PU/MWNT composite films are homogeneous in appearance, which is demonstrated in Figure 3, the photographs of the sample membranes with thickness of about 0.3 mm. With the increase of MWNT content, the color of the sample becomes deeper, from colorless to dark brown. Anyway, all the samples are homogeneous and transparent, indicated by the fact that the mark numbers under the membrane can be seen clearly. This demonstrates that MWNTs disperse homogeneously in the PU matrix.

Swelling Ratio of Polymers. The swelling ratio reveals the degree of cross-linking and the structure of polymer. Figure 4 shows the swelling ratio of PU-MWNT composites in water and DMF. It is interesting that with the increase of the amount of added APES−MWNT, the swelling ratio of the composites in water increases while that of the composites in DMF decreases. The almost linear increasing of swelling ratio in water is, we believe, caused by the increase of silsesquioxane

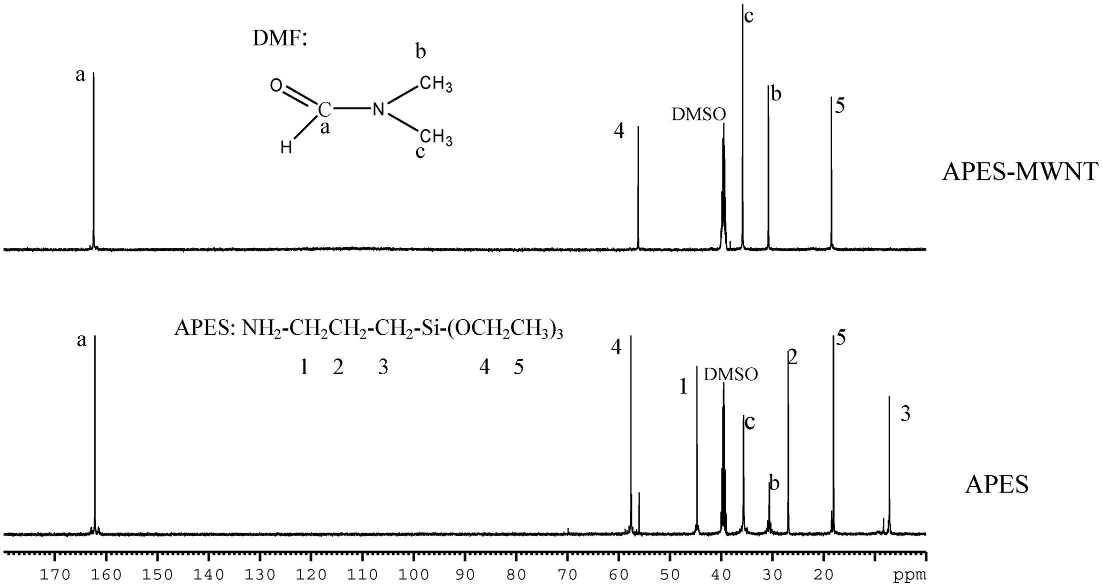


Figure 2. ^{13}C NMR spectra of APES and APES−MWNT samples.

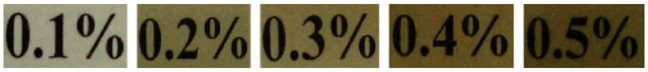


Figure 3. Photograph of PU/MWNT composite films, where the numbers indicate the content of MWNT in samples.

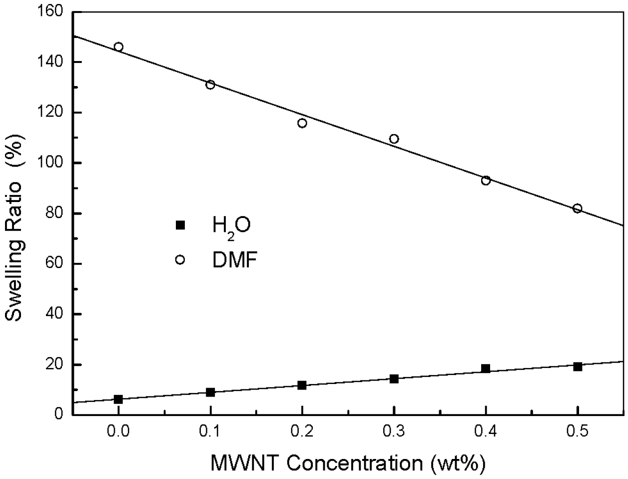


Figure 4. Swelling ratio of the samples in water and DMF.

Table 2. Tensile Properties of PU/MWNT Composites

sample	strain (%)	tensile (MPa)	modulus (MPa)
0% MWNT	249 ± 20	22.1 ± 2.5	9.7 ± 0.08
0.1% MWNT	296 ± 22	24.4 ± 3.1	10.2 ± 0.11
0.2% MWNT	281 ± 11	25.8 ± 1.2	13.9 ± 0.09
0.3% MWNT	252 ± 10	26.1 ± 1.6	20.2 ± 0.17
0.4% MWNT	207 ± 16	31.8 ± 1.6	36.2 ± 0.28
0.5% MWNT	222 ± 6	35.2 ± 2.2	36.4 ± 0.34

formation. Since the more APES−MWNT was introduced, the more silsesquioxane formation will be formed, which in turn could combine more water.[14] On the other hand, with more APES−MWNT introduced, more cross-linkage is produced; thus, the sample becomes more difficult to swell. That is why the swelling ratio of samples in DMF decreases with the increasing of MWNT concentrations.

Mechanical Properties. The mechanical properties, namely Yang's modulus, the tensile strength, and the tensile elongation of the composites, are listed in Table 2 and the stress−strain curves are shown in Figure 5.

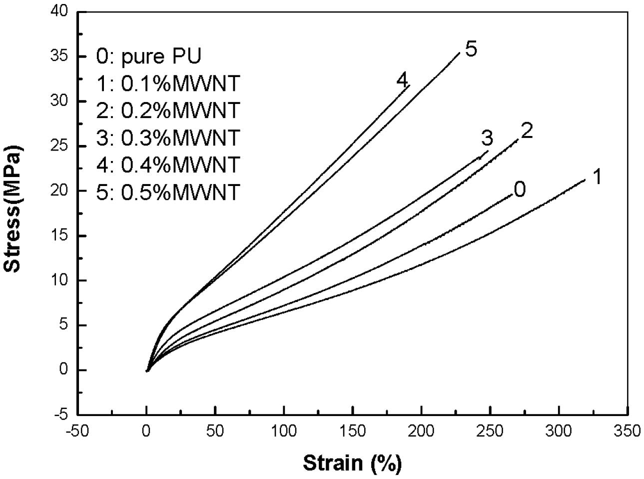


Figure 5. Stress−strain curves of samples.

The results indicate that with the increase of MWNT content, Yang's modulus and the tensile strength increased greatly. To our surprise, the elongation experienced no loss at all, and it even increased at low cross-link density. Cross-linking is a normal way to improve the strength, modulus, and the solvent resistance of polyurethane, whereas samples often suffer from a significant decrease in elongation. Our results show that APES−MWNT can not only increase the strength and modulus of the material but also maintain its elasticity mostly. For samples with MWNT contents less than 0.4%, the maximum elongation ratio even increased to certain extent.

Some previous works[15,16] showed that in physically mixed composite systems, carbon nanotubes can be pulled out from the matrix and cause breakage, while in the copolymerized system, no such phenomenon was observed.[7,17] To further check the reinforcing mechanism of MWNT in our system, the fracture surfaces of the samples were studied by SEM. The bright dots shown in Figure 6 are the ends of broken MWNT, demonstrating that the nanotubes break apart rather than just be pulled out from the fracture surface. Such a result indicates the existence of strong interfacial bonding between the MWNT and the PU matrix in the composites. Figure 6 also reveals that MWNTs disperse homogeneously in the PU matrix. We believe, therefore, that the great enhancement of the strength and modulus of the samples are closely related to the strong interfacial binding

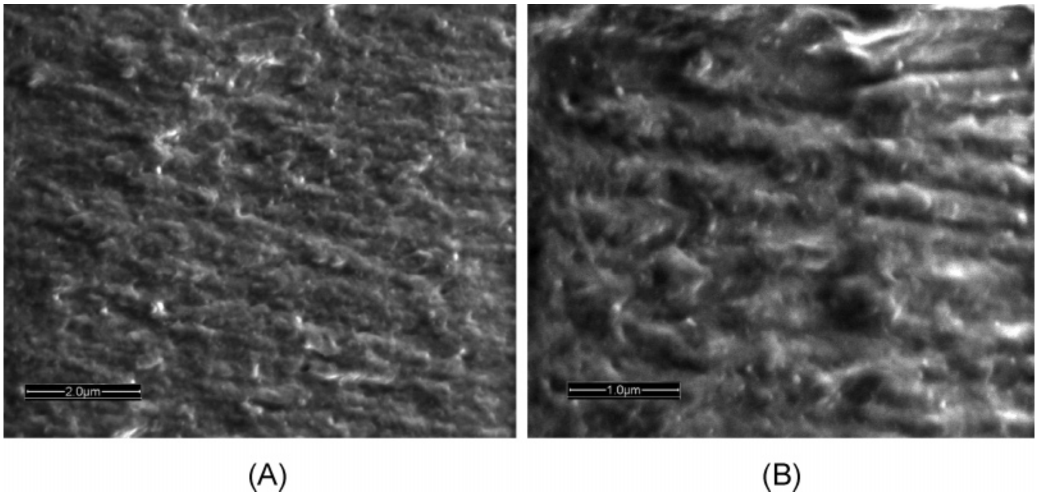


Figure 6. SEM images of the fracture of surface of PU/0.5% MWNT composite: (A) overall morphology; (B) detail of morphology from (A).

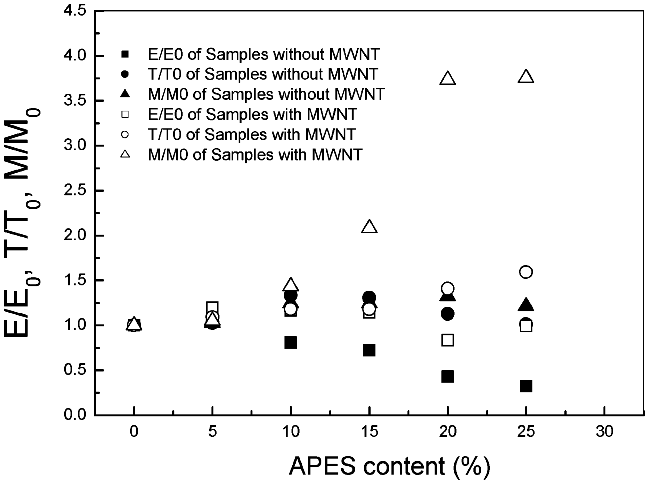


Figure 7. Comparison of mechanical properties with control samples.

interaction caused by inter-component chemical bonds and the homogeneous dispersion of MWNT in the matrix, while the retaining of and even increasing of the maximum elongation ratio is mainly due to the high aspect ratio and the flexibility of MWNT.

To determine that the improvement of mechanical properties is not solely caused by the increasing of the density of cross-linking, control experiments were performed. A series of polyurethane−urea samples were synthesized, using only APES as cross-link agent. The mechanical properties including Yang's modulus (*M*), tensile strength (*T*), and elongation (*E*) of these two series of samples with and without MWNT, are compared with those of the blank sample (PU without any cross-link agent) in Figure 7.

The solid dots are properties of the control samples and the blank sample (without any cross-link agent); the hollow dots are properties of PU coupled with APES−MWNT. From the figure we can see that for the group without MWNT, the modulus increases 50% and tensile increases 15% at the most, while the elongation decreases 70%. For the group with MWNT, the modulus increases more than 300%, tensile increases 50%, while the elongation remains unchanged, and even increased 15−20% at low cross-link density. This result further proves that the increasing of the strength and modulus, and especially the retaining of elongation, can be attributed mainly to the introducing of MWNT instead of cross-linking. By comparing with other polymer/CNT composite systems,[4,5] it seems that a smaller amount of MWNT is needed to acquire equivalent enhancement of Young's modulus and tensile strength for our system.

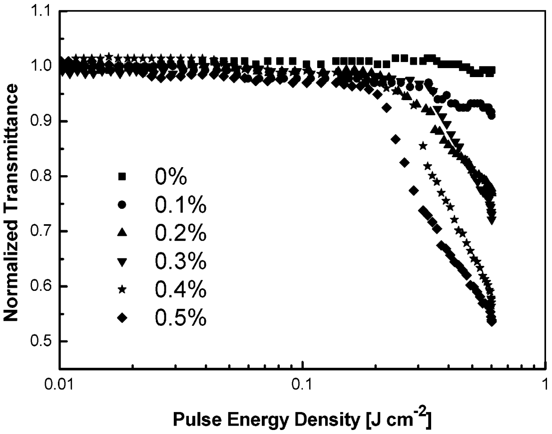


Figure 8. Optical limiting properties of PU/MWNT composites films, the numbers indicate the content of MWNT in samples.

Optical Limiting Properties. Optical limiting materials transmit light of normal intensity but attenuate light of high power. This kind of material is suitable to be used to protect optical sensors from damage, especially in space exploration. MWNT is proven to be a good candidate for optical limiting materials.[18,19] However, its poor solubility makes it difficult to shape it into parts. Combining MWNT with polymers provides a solution to the problem. In our polyurethane−urea system, MWNT was combined with polymer without problems to form a homogeneous and transparent material with good mechanical properties. The homogeneous and transparent character of the PU/MWNT composite films makes it suitable to be used as an optical limiting material. Moreover, the composites with MWNT were synthesized in solution. If moisture is kept out, it could be stored for a long time before processing. This makes it easy to be used for practical applications.

Figure 8 shows the optical limiting properties of all samples. For pure PU, no optical limiting behavior is observed, while all samples containing MWNT show positive nonlinear extinction, or optical limiting properties. As MWNT contents vary from 0.1% to 0.5%, the optical limiting threshold decreases from 0.4 to 0.2 J cm^{-2}. At 0.6 J cm^{-2}, the sample with 0.1% MWNT mass has a normalized nonlinear extinction of ~8%, while the sample with 0.5% MWNT mass has a normalized extinction of 46%. The fact that the normalized extinction almost increases linearly with the increase of the contents of MWNT indicates that with the MWNT mass increasing in samples, the transmittance decrease and much more transmitted laser energy was limited. For our samples, a smaller amount of MWNT offers better optical limiting properties, compared with the samples with physically blended MWNT.[19]

Conclusions

A new method was developed to prepare polyurethane−urea carbon nanotubes composites by sol−gel process with silsesquioxane like formation. The obtained samples are a kind of transparent material with promising mechanical and optical properties. Loading of 0.5 wt % MWNT to polyurethane−urea enhances the tensile strength and Young's modulus by nearly 150% and 400%, respectively, while the elongation was retained completely. The optical limiting properties are found to vary with the contents of MWNT in composites. The required transmittance and transmitted energy can therefore be tailored by changing the MWNT content in composites.

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