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Synthesis, properties of fullerene-containing polyurethane–urea and its optical limiting absorption

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Abstract

Based on the typical two step polyurethane–urea synthesis, self-crosslinkable polyurethane–urea compounded of poly(tetramethylene oxide), MDI (4,4′-diphenylmethane diisocyanate) and extended by AEAPS (aminoethylaminopropyltrimethoxysilane) were prepared. On the other hand, a C60-amine adducts by reacting C60 with excessive APES (aminopropyltrimethoxysilane) were synthesized and introduced into the polyurethane–urea to form the homogenous and transparent C60 containing polyurethane–urea films. FT-IR, UV, Electron Spectroscopy for Chemical Analysis, Wide-angle X-ray diffractions, dynamic mechanical thermal analysis and mechanical properties of samples were recorded. The optical limiting properties were also measured. The results show that the C60 containing polyurethane–urea is a kind of homogenous material with the ranging of C60 content. The solution state before processing makes it easy to be cast as variety configurations. With the difference in C60 content in polymers, the optical limiting properties are various and the required transmittance and transmitted energy can be altered with the C60 contents in polymers.

Keywords: Polyurethane–urea; Properties; Optical limiting absorption

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1. Introduction

As a kind of material with excellent mechanical properties, the strong industrial interest in polyurethane–urea polymers spurred durative investigations into their structure–property correlations. In the last few decades, many researches have been carried out on this fantastic polymer. Countless papers, patents and books on the synthesis, manufacturing, characterization and applications about polyurethane–urea are published. With wide uses in almost every department of industries, much higher requirements on polyurethane–urea are brought out. So, functional polyurethane–urea emerges as the times require, including in high performance, biocompatible materials fields and so on.

At the same time, the special structure and properties of fullerene attracts many attentions of scientists in the last few years. The Optical Limiting caused by reverse saturable absorption of fullerene is one of its most important characters. This character nicely satisfied the requirement of presenting human eyes or artificial optical sensor from the damage of high-energy laser, which are sticking out increasingly with the spread using laser equipment.

The basic character of fullerene, also the reason of optical limiting properties of fullerene, is the single and triplet electronic states, which can be shown using a five-level model [1]. But the disadvantage of insoluble and difficult in processing of fullerene makes its direct application difficulty. Thus, the modification of C60 becomes an important field on the fullerene studies, especially many attentions have been paid by chemists. Among the modification researches, the C60 combination with polymer is an important way.

Following our previous research [2], we report here the combination of polyurethane–urea and C60 using a sol–gel process to make a novel optical limiting material which has both the excellent mechanical properties of polyurethane–urea and the good optical limiting properties of C60.

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2. Experimental

2.1. Materials

Poly(tetramethylene oxide) (PTMO) ($M_n = 1000$), supplied by Aldrich, was dried and degassed at 80 °C/ < 10 Pa for 2 h before use. 4,4′-Diphenylmethane diisocyanate (MDI), aminoethylaminopropyltrimethoxysilane (AEAPS) and aminopropyltriethoxysilane (APES) were purified by vacuum distillation. C60 Fullerene (99.97%), purchased from Wuhan University, People's Republic of China, was used as received. *N*,*N*′-Dimethylformamide (DMF) were dried over 4 Å molecular sieve for at least 24 h and vacuum distillated before use.

2.2. Instruments and characterizations

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 300 spectrometer using chloroform-*d* as solvent with tetramethylsilane (TMS). Chemical shifts were reported in parts per million (ppm) on the δ scale referenced to TMS.

FT-IR spectra were obtained on a Nexus 870 spectrometer using the membrane samples.

The water contact angles were measured using a Rame-Hart NRL contact angle goniometer. The data were collected one minute after a drop of double-distilled water had been placed on the surface of the film. At least ten measurements were used and the average contact angles were calculated.

The swelling ratios of the samples were studied as follows: the dry films were weighted and then be immersed into both water and DMF at room temperature (~25 °C). After equilibration for 120 h, the samples were blotted with laboratory tissue and weighed again. The swelling ratio was expressed as the weight percentage of water or DMF in the swollen samples,

$$\text{Swelling Ratio} = \frac{W_s - W_d}{W_d} 100\%,$$

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

Electron Spectroscopy for Chemical Analysis (ESCA), also named as X-ray photoelectron spectroscopy, was obtained using a V.G. Scientific ESCA Lab MK-II spectrometer equipped with a monochromatic Mg Kα X-ray source. ESCA analysis was done at a nominal photoelectron take off angle of 45° and the depth of analysis for these samples was 100 Å. The relative atomic percent of each element at the surface was estimated from the peak areas using atomic sensitivity factors specified for the spectrometer. The binding energies used were C(1s): 289 eV; Si(2p): 107 eV; N(1s): 404 eV; O(1s): 537 eV.

Wide-angle X-ray diffractions (WAXD) of samples were recorded on a Switzerland ARL X'TRA X-ray diffractometer using a Cu Kα source from 5° to 50°.

The Dynamic Mechanical Thermal Analysis (DMTA) of the membrane samples were conducted on a Rheometric Scientific DMTA V with strain 0.1% at the temperature ranging from −100 to 200 °C. The results at frequency 10 Hz were recorded.

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 mentioned before using an ASTM 1708 standard die and were tested using the crosshead speed of 50 mm/min at room temperature (about 18 °C) under 50% humidity.

The ultraviolet/visible spectrum of C60 in cyclohexane was recorded on a Shimadzu UV3100 spectrometer using the C60-cyclohexane solution as sample. UV spectrum of C60 containing polyurethane–urea samples were recorded on a Perkin–Elmer Lambda 35 UV/Vis spectrometer with scanning rate 480 nm/min and 2 nm per scan step.

The photographs of samples were taken on an N-Tek Nuscan 700 scanner with 600 dpi resolution zoomed in twice.

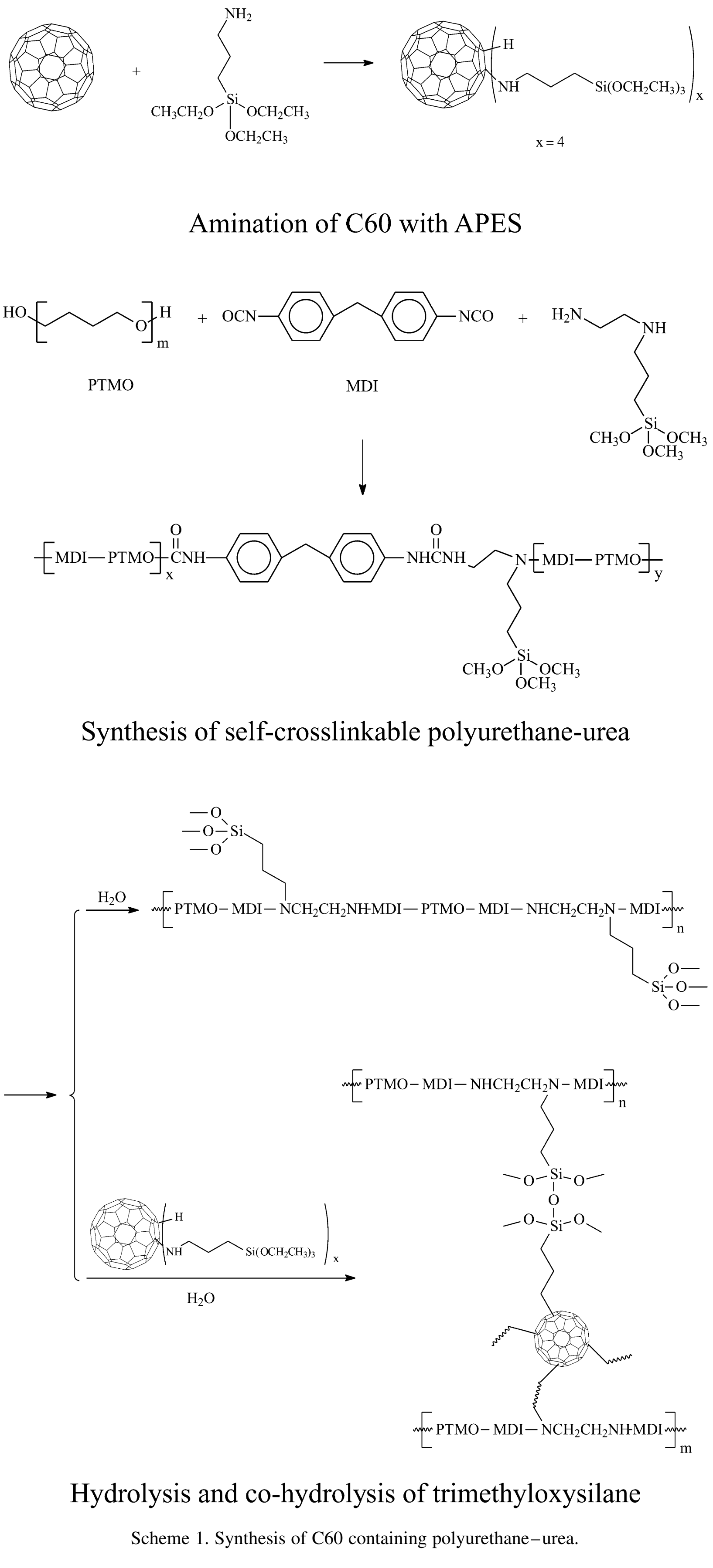
The optical limiting properties were recorded using a Cotinuum ND6000 frequency-doubled Nd:YAG laser and the experiments were performed at 532 nm with 15 μs pulse. The pulsed laser beam was focused into a facula with diameter 53.2 μm on the membrane samples. The incident and transmitted energies were measured by a Molectron EPM1000 detector, and every point of the optical limiting data was the automatic average value of 10 detected values done by the detector.

2.3. Preparation of samples

The synthesis routes of the samples were shown in Scheme 1. A typical preparation was carried out as following:

In a 500 mL four-neck dried round bottom flask equipped with thermometer, reflux condenser, dropping funnel and drying tube, 10 g PTMO dissolved in 80 mL DMF was charged into, followed by stoichiometric amounts of MDI solution in DMF, 7.8 g/80 mL, and one drop of stannous octoate was added as catalyst. The reaction system was stirred with magnetic stirrer for about 3 h in an oil bath at 70 °C under dried N_2 atmosphere to obtain the NCO–terminated prepolymers. Then 4.44 g AEAPS in 80 mL DMF was added drop-wise as the extender. After the drop funnel was washed by 20 mL DMF and the reaction mixture was diluted, the reaction continued for about 7–8 h at 90 °C to ensure the complete reaction. The synthesized polymers were kept in solution in the carefully sealed bottle to strictly avoid the moisture.

On the other hand, a 25 mL dried round bottom flask was charged with 150 mg (0.21 mmol) C60 and 7.0 g (31.7 mmol) APES. The reaction mixture was stirred with magnetic stirrer for 24 h in an oil bath at 100 °C under dried



Scheme 1. Synthesis of C60 containing polyurethane–urea.

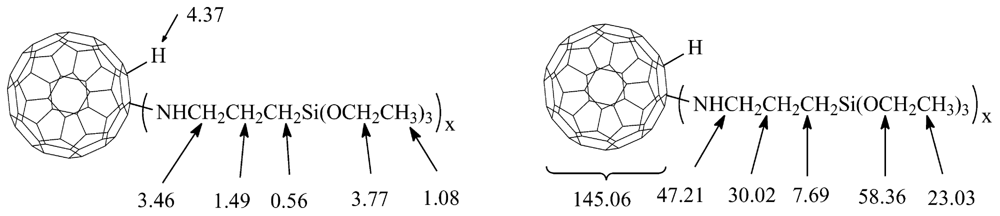


Chart 1. The ^{1}H NMR and ^{13}C NMR results of APES-C60.

N_2 atmosphere to prepare the aminated C60 with trimethoxysilane group [3]. For a part of the reaction mixture, the unreacted APES were distilled off from the reaction mixture under reduced pressure to obtain the APES-C60 samples used in NMR analysis. The other products without further treatments were used in the film formation.

In five flat bottom dishes, 25 mL polyurethane–urea/DMF solution were charged, each followed by different amount of the APES-C60 adducts were added, respectively, as listed in Table 1. After being mixed well, the dishes were put into an oven at 60 °C for at least 72 h to form the membrane samples utilizing the H_2O in atmosphere to co-hydrolyze the triethyloxysilane groups with the trimethyloxysilane groups on the polyurethane–urea, the transparent membranes were obtained then transfer to a vacuum oven for about one week to ensure the completely volatilization of solvents and water.

3. Results and discussion

3.1. Synthesis

The ^{1}H NMR and ^{13}C NMR results of APES-C60 are shown in Chart 1. The results are accordant very well to the results of Peng [3]. They also provided the MS data of the adduct [3]. According the MS results, the average degree of the multiple additions *x* was estimated to be 4.

The compositions of polyurethane–urea are listed in Table 1. Using AEAPS as extender, the self-crosslinkable polyurethane–urea were synthesized. The self-crosslinkage is formed from the hydrolysis of the trimethoxysilane group. On the other hand, it is well known that C60 could be aminated easily [4] to form soluable C60. APES-C60 is a good example. By adding APES-C60 adducts, the co-hydrolysis between AEAPS and APES-C60 adducts occurred to form the silsesquioxane formation and the C60 fullerene can be introduced into polymers on molecule level to form the homogeneous C60 containing materials. The reactions are shown in Scheme 1.

Table 1
The composition of samples

Samples	Composition (molar ratio)				C60 (wt%)
	PTMO	MDI	AEAPS	APES(-C60)	
0%C60	1	3	2	0	0
0.16%C60	1	3	2	1	0.16
0.30%C60	1	3	2	2	0.30
0.42%C60	1	3	2	3	0.42
0.52%C60	1	3	2	4	0.52

3.2. FT-IR analysis of polymers

Fig. 1 shows the differential FT-IR spectrum of samples with and without C60. From the spectrum, the peak at 1038 cm^{-1}, the characteristic peak of Si–O stretching moves up with the increasing of the APES-C60. It clearly indicated that the siloxane group had been successfully introduced into polyurethane–urea. While the characteristic peak of C60 (526, 574, 668 cm^{-1}) [5] cannot be assigned clearly for the complicated absorption of the system in this section.

3.3. WAXD analysis

Fig. 2 shows the WAXD spectrums of polyurethane–urea containing C60. From the WAXD, it is obvious that all polymers are amorphous. While C60 molecules have a strong tendency to aggregate in the solid state and also in the solution phase. In the solid state, C60 cages regularly pack in their crystal lattice, giving sharp and intense XRD reflection peaks at Bragg angles of 10.62, 17.64, 20.68 and 21.40°. The curve of sample without C60 reminds that our polyurethane–urea system is an amorphous polymer. When the C60 cages are attached to the polyurethane–urea chain,

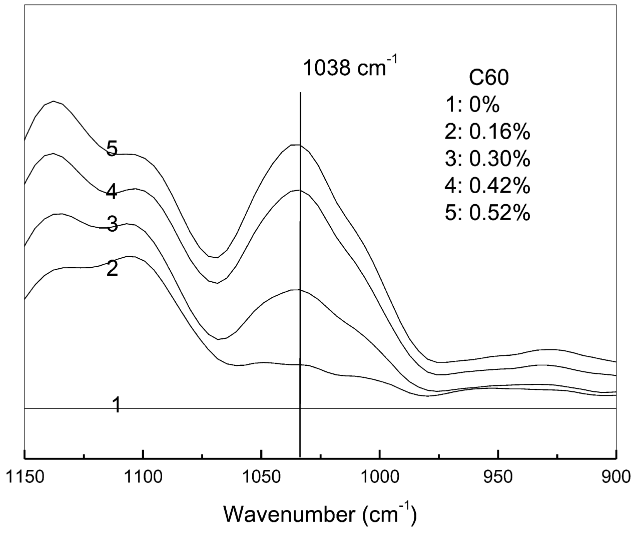


Fig. 1. Differential FT-IR spectrum of samples with and without C60.

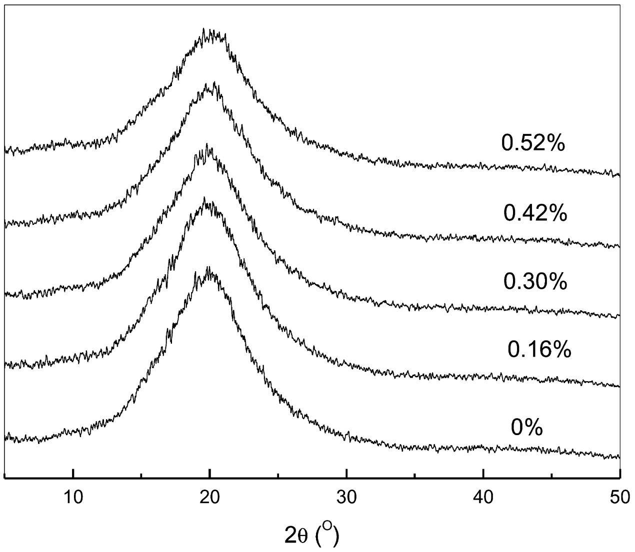


Fig. 2. WAXD of samples.

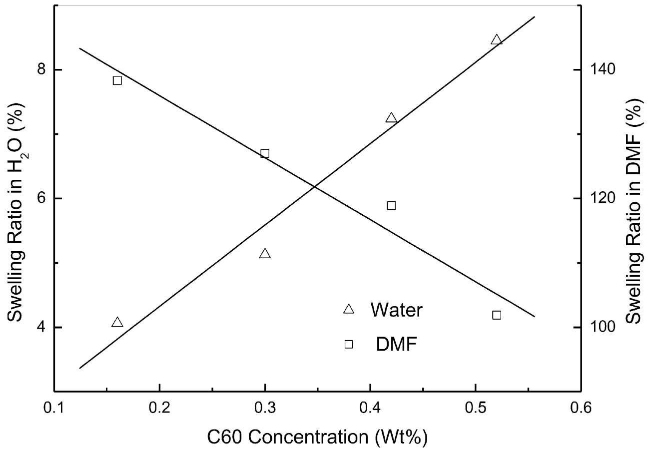


Fig. 3. Swelling ratio of the samples in water and DMF.

from the XRD spectrum of samples containing C60, hardly any sharp Bragg reflections can be observed. Clearly, the polymer chain wrapping around the C60 cages and the structure modifications to the C60 molecule have prevented the buckyballs from packing well and obstructed the growth of their crystals [6].

3.4. ESCA analysis and surface properties

From the results of ESCA listed in Table 2, Si obviously enriched on the surface of samples. The water contact angle of samples proved the same result: with the increasing of Si on the surface, the water contact angle is increased. In other word, the hydrophobic properties of samples increased with the introduction of more APES-C60. So, introducing APES into polyurethane not only provided the crosslink and silsesquioxane formation but also modified the surface properties of polymer obviously.

3.5. Swelling ratio of polymers

The swelling ratio indicates the crosslink degree and the structure of polymer. Fig. 3 shows the swelling ratio of C60 containing polyurethane–urea in water and DMF. It is interesting that with the increase of added APES-C60 amount, the swelling ratio of polymers in water is increased, but in DMF, it is decreased. The almost linear increasing of swelling ratio in water is caused by the increasing silsesquioxane formation: the APES-C60 introduced, the more silsesquioxane formation formed which could combine more water. On the other hand, with more APES-C60 introduced, more crosslinkage brought out, the sample becomes much more difficult to be swollen. That is why the swelling ratios of samples in DMF decreased with the increasing C60 concentrations.

3.6. Dynamic mechanic thermal analysis

Fig. 4 shows the results of the spectrum of DMTA, the separated peaks at about −10 and 130 °C on $tg\delta$ curve shows the obvious microphase separation. The two peaks are corresponded to the T_g of soft-segment and the T_g of hard-segment, respectively.

According the DMTA spectrum, the modulus of samples decreased 2 orders of magnitude, from thousands at −100 °C to decades at 200 °C. The platforms of E', storage modulus curves above 150 °C are due to the crosslink structure of polymers caused by the AEAPS and APES. With the increasing C60 content in samples, the modulus also increases. In our system, the C60 was introduced into the polymers as the amino-additive products of C60 with

Table 2
ESCA results and water contact angle of polymers

Samples	Real atomic percents (%)				Theoretical atomic percent (%)				Water contact angle (°)
	C	O	N	Si	C	O	N	Si	
0%C60	63.52	23.74	4.07	8.67	63.99	18.96	6.38	2.55	72 ± 2
0.16%C60	61.57	23.89	4.62	9.93	71.20	14.80	4.91	2.68	86 ± 2
0.30%C60	61.51	23.75	4.36	10.38	75.07	12.56	4.12	2.75	90 ± 3
0.42%C60	58.07	24.91	3.69	13.34	77.50	11.16	3.63	2.79	99 ± 1
0.52%C60	54.92	25.20	2.09	17.80	79.15	10.20	3.29	2.82	101 ± 3

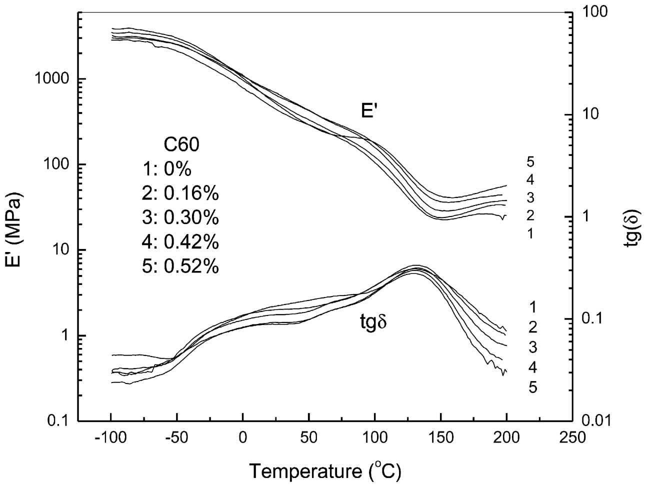


Fig. 4. DMTA Spectrum of samples.

APES. The increasing of C60 content means the increasing of the crosslinkage caused by the AEAPS and APES.

3.7. Mechanical properties

The mechanical properties, Young's modulus, tensile strength and tensile elongation are listed in Table 3 and Fig. 5 shows the stress–strain curves. The tensile results indicated that with the increasing C60 content, the Young's modulus is increased while the strength and the elongation are decreased. Obviously, it is caused by the increasing of crosslink density with the more C60 and APES adducts were introduced.

3.8. UV analysis

With the increasing C60 contents, the UV absorption of samples also increased, which can be seen obviously in Fig. 6. Especially in visible section, the absorption of samples containing C60 is much more distinctive. The appearance of samples indicted the same results which can be seen from Fig. 7, the photographs of samples membrane with thickness of about 0.3 mm. With the increasing C60 content, the sample is deep colored, from almost colorless to dark brown. Fortunately, all the samples are homogeneous and transparent; the mark numbers under the membrane can be seen clearly. According to the Peng's results [3], the C60 content is as low as ~0.01% in SiO_2, the C60/SiO_2 is inhomogeneous with many black particles embedded in the matrix in a non-uniform fashion. The homogeneous and transparent character of the C60 containing polyurethane–urea makes it suitable to be used in the preventing human eyes or artificial optical sensor from the damage of high-energy laser. Also the color ranging gives the possibility of readily tuning the color of materials in a large scale or in a wide spectral region by simply varying its C60 content.

Table 3
The tensile properties of samples

Sample	Strain (%)	Tensile (MPa)	Modulus (MPa)
0%C60	123	40	294
0.16%C60	77	33	302
0.30%C60	41	26	321
0.42%C60	20	23	340
0.52%C60	18	22	394

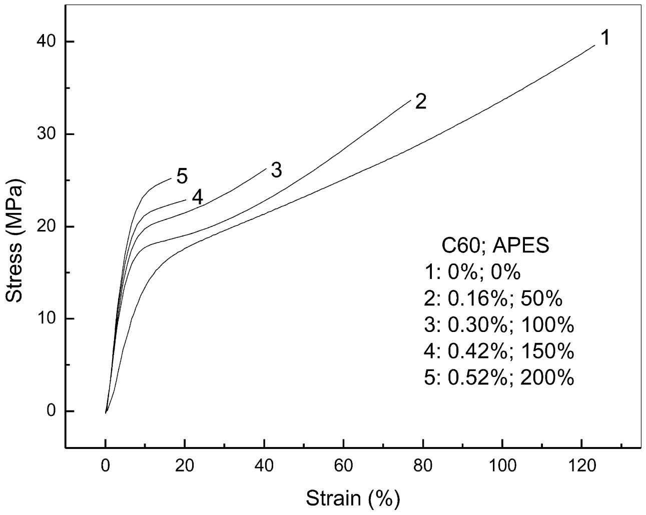


Fig. 5. Stress–strain curves of samples.

3.9. Optical limiting properties

Optical limiting materials transmit light of normal intensity but attenuate light of high power. This character makes it very suitable to be used in the preventing of sensors from damage especially in the space exploration. C60 is a good material to be used as optical limiting materials. But its poor solubility makes it difficult to be processed into parts. Combining C60 with polymers is one of the easiest ways to resolve the problem. In our polyurethane–urea system, C60 were combined with polymer well to form a

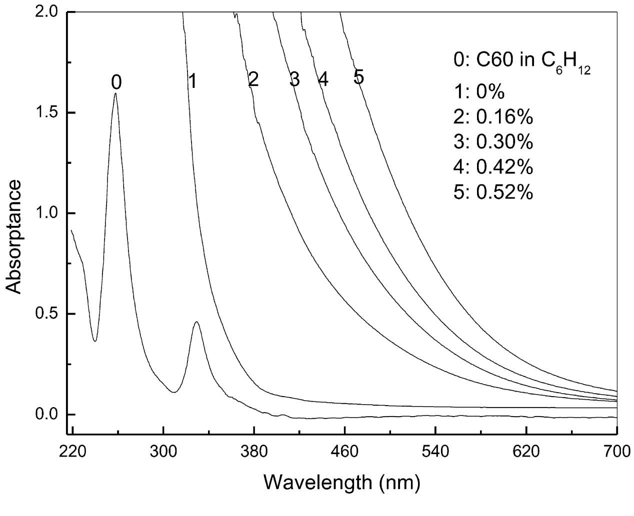


Fig. 6. Ultra-violet spectrum of C60 in cyclohexane and samples film.

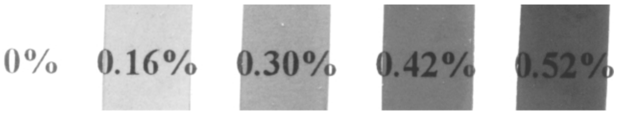


Fig. 7. Photograph of C60 containing polyurethane–urea film, the number indicated the content of C60 in samples.

homogeneous and transparent materials with good mechanical properties. The polymers with C60 were synthesized in solution. If the moisture is kept out, it could be stored for a long time before processing. This property makes it easy to be applied practically.

In the optical limiting measurement of C60 polyurethane–urea films (Fig. 8), all the samples showed the excellent limiting properties. With the increasing C60 content in samples, the transmittance is decreased and much more transmitted laser energy was limited. For the sample without C60, the transmittance is about 70%; while for the sample containing 0.52% C60, the transmittance is about 10% and the transmitted energy is limited under 25 mJ/cm^2.

The optical limiting properties of C60 can be explained with a five-level model shown in Fig. 9 [7,8]. The five states included in the model as the ground state S_0, the first excited singlet state S_1, the next higher excited singlet state S_2, the lowest triplet state T_0, and the next higher triplet state T_1. Absorption of photons excites the electrons from the ground state S_0 to one of the many vibrational levels of the first excited singlet state S_1, which relaxes very fast (~1 ps) to the lowest vibrational level of the electronic states. From S_1, they can be further promoted to the next excited singlet state, S_2, by absorption of another photon. Alternatively, the molecule can return to its ground state by internal conversion, or through a process called inter-system crossing (ISC) they can be transferred to a lower triplet state T_0, from where transitions to a higher triplet state T_1 can occur. At 532 nm, the C60 molecule has the first triplet excited state absorption cross-section, $\sigma_{34} = 9.5 \times 10^{-18}\text{cm}^2$, larger than the ground state absorption cross-section, $\sigma_{01} = 3.1 \times 10^{-18}\text{cm}^2$, as reported by McLean et al. [8]. The value for the first singlet excited state absorption cross-section is $\sigma_{12} = 1.57 \times 10^{-17}\text{cm}^2$. The excited state absorption cross section T_0, has a maximum near 750 nm [9]. The ISC $S_1 \rightarrow T_0$ is fast (650 ps–1.2 ns), with quantum efficiency close to unity. Also, the decay from the higher excited states (S_2 and T_1) is very rapid ($k \sim 10^{15}$ and $k \sim 10^{11}\ s^{-1}$, respectively) [8], therefore, the states S_1 and T_0 are effectively not depopulated by absorption of light over the duration of the laser pulse. Another important property of the C60 molecule that makes it a good optical limiter is the long-lived triplet state T_0 (approximately 100 μs) compared with the temporal width of the pulse. Thus, over the course of the 15 μs pulse, T_0 is rapidly populated upon direct excitation of S_1 and is not depleted during the optical pulse.

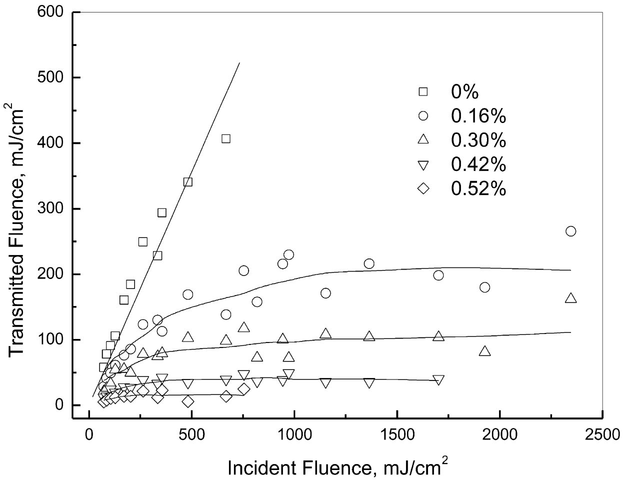


Fig. 8. Optical limiting properties of C60 containing polyurethane–urea.

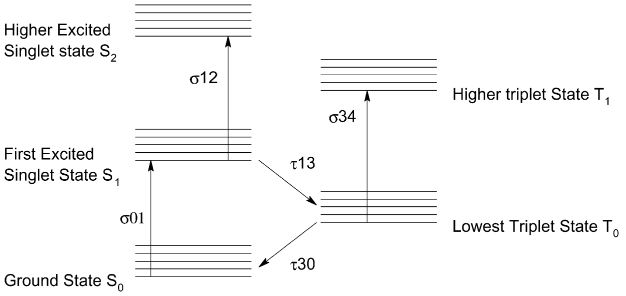


Fig. 9. Five-level model for C60.

4. Conclusions

By reacting C60 with excess APES, the aminated C60-ethoxysilane were synthesized successfully and the adducted products were introduced into polyurethane–urea by co-hydrolysis of triethoxysilane group with H_2O to construct the silsesquioxane like formation. The C60 containing polyurethane–urea is a kind of transparent homogenous material with the ranging of C60 content. The solution state before film formation makes it easy to be cast into different configurations. With the different C60 content in such polymers, the transmittance decreased from 70 to 10% and the transmitted energy is limited under 25 mJ/cm^2. The required transmittance and transmitted energy can be altered with changing the C60 contents in polymers.

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