Preparation of Novel TiO₂-g-Polyacrylonitrile Nanocomposites and Their Applications as Ultraviolet Antiaging Agents†

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TiO₂-g-PAN (PAN = polyacrylonitrile) nanocomposites were synthesized through a surface initiated radical polymerization method, which integrates the advantages of both polyacrylonitrile as a radical scavenger and nanosized rutile-type titanium dioxide (nano TiO₂) as an ultraviolet absorber. In this study, the synthetic ultraviolet antiaging agents made of TiO₂-g-PAN linked by covalent bonds were prepared *via* a solution polymerization method, with the optimal synthesis process explored through orthogonal experiments. The nano TiO₂-g-PAN particles were characterized by hydrophilic and lipophilic analyses, infrared spectra, energy dispersive spectroscopy, scanning electron microscopy and ultraviolet absorption tests. The nano TiO₂-g-PAN particles were blended with polypropylene particles (PP) and the dispersion and antiaging properties of PP/TiO₂ and PP/TiO₂-g-PAN blends were analyzed. The results showed that the nano TiO₂-g-PAN antiaging agent has excellent performances both in dispersion and UV antiaging.

Keywords: Nano TiO₂, Acrylonitrile, Graft polymerization, Polypropylene, UV antiaging.

INTRODUCTION

Nano TiO₂ has many excellent properties. In addition to the surface effect and quantum orbital effect, it also has perfect photocatalytic performances, ultraviolet shielding capabilities and flip-flop effects. Nano TiO₂ has a promising application in the polyolefin antiaging field¹⁻⁴. However, this is greatly limited by its poor compatibility with polymer materials. In the recent years, many researchers have been devoted to solve this problem. Khaled *et al.*⁵ applied the methacrylic acid (MA) as a coupling agent to modify the surface of nano TiO₂ and coated a PMMA layer on nanoTiO₂ nanosized fibers. Therefore, TiO₂-g-PMMA composites were prepared, with the thermal decomposition temperature and elasticity modulus improved⁵. Bach *et al.*⁶ used 3-mercaptopropyl trimethoxysilane (MPTS) and butyrolactam as the coupling agent and the initiator, respectively. Hybrid nanocomposites of polystyrene (PS) and nano TiO₂ were prepared by a facile surface thiol-lactam initiated radical polymerization method (TLIRP). The dispersability of nano TiO₂ nanoparticles was improved significantly under the functionalization of PS chains⁶. Pan *et al.*⁷ prepared the covalent bonds of (PMMA-AN)/TiO₂ composite particles by an *in situ* emulsion polymerization method and improved the photocatalytic degradation of methyl orange.

Due to the commercial production in the early 1900s, nano TiO₂ has been widely used in many industries, such as pigments⁸, sunscreens^{9,10} and paints¹¹. In 1972, Fujishima and Honda discovered the photocatalytic splitting phenomena of water on a TiO₂ electrode under ultraviolet lights¹²⁻¹⁴. Since then, enormous efforts had been devoted to the research of TiO₂ materials, which led to many promising applications in areas ranging from photovoltaics and photocatalysis to photo-electrochromics and sensors¹⁵⁻¹⁸. However, based on literatures available, there is hardly any report concerning the antiaging property of nano TiO₂-g-PAN (PAN = polyacrylonitrile) particles, even though it has a great potential for UV aging resistance. Polyacrylonitrile (PAN) has an excellent antiaging performance as a radical scavenger¹⁹. Nano TiO₂-g-PAN particles can not only ameliorate the serious reunion phenomenon of nano TiO₂, but also improve the mechanical strength and the resistance to the ultraviolet aging effect after PAN is grafted on the surface. In this study, the nano TiO₂-g-PAN particles with novel resistances were synthesized and characterized. The UV aging and mechanical properties of PP/TiO₂-g-PAN blends were also analyzed.

EXPERIMENTAL

Rutile nanosized titanium dioxide was chosen as the nano TiO₂ (98 %, a rutile-type titanium dioxide) and the average

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particle diameter was 80 nm. Acrylonitrile (AN, 99.8 %) were distilled under reduced pressures before being used. Vinyl *tert*-butyl peroxy silane coupling agents (AC-70, 70 % in toluene) were purified by vacuum distillation at 40 °C. The toluene was purchased from Aldrich and used as received. Benzoyl peroxide (BPO, 99.9 %) was purified *via* recrystallization. N,N-dimethylformamide (DMF, 99.5 %) and polypropylene were provided by Daqing Huake Company Limited (Heilongjiang Province, China).

Methods: The grafting procedure of AC-70 on the surface of nano TiO₂ is as follows. After 2.5 g nano TiO₂ nanoparticles were dispersed in 100 mL toluene, an excess amount of AC-70 was added and the resulting solution was stirred for 8 h at 75 °C. Then, the modified nano TiO₂ was isolated by centrifugation and washed repeatedly with acetone. Finally, nano TiO₂-g-AC-70 was obtained after being dried at 50 °C in vacuum for 24 h.

A typical preparation process of nano TiO₂-g-PAN is as follows. 2 g AN, 0.01 g BPO and 1 g nanoTiO₂-g-AC-70 were added into a round-bottom four-necked flask equipped with a reflux condenser, a mechanical stirrer, a dropping funnel and a nitrogen inlet and outlet. The reaction system was dispersed by ultrasonic at room temperature for 0.5 h. Then, the polymerization was performed at 65 °C for 5 h in nitrogen atmosphere. The products were cleaned for several times with DMF, followed by a centrifugation process to remove possible monomers and homopolymers. After that, they were washed again with acetone for several times to remove the residual DMF. At the end, nano TiO₂-g-PAN particles were obtained after being dried at 50 °C in a vacuum atmosphere.

The nano TiO₂-g-PAN particles and PP were mixed in a high speed mixer for 10 min. The blends were extruded through a twin-screw extruder and dried in vacuum at 60 °C for 24 h. Then the blends were injected into molded splines at a ratio of 5 %.

The Kjeldahl method was used to measure the grafting ratio of nano TiO₂-g-PAN particles. The formula of the grafting ratio was calculated as follows:

$$N = \frac{C \times (V_2 - V_1) \times 0.014}{\frac{m}{100} \times 10} \times 100 \% \quad (1)$$

where, N is the nitrogen content; C is the concentration of standard solution of hydrochloric acid and it is 1.02×10^{-3} mol/L here; V₁ is the volume of the hydrochloric acid solution before titration; V₂ is the volume of the hydrochloric acid solution after titration; m is the quality of samples and it is 0.5 g in this study.

$$G = \frac{\frac{N}{14} \times 53}{100} \quad (2)$$

where, G is the grafting ratio.

The nano TiO₂-g-PAN particles were characterized by hydrophilic and lipophilic analyses, infrared spectra (FT-IR), energy dispersive spectroscopy (EDS), scanning electron microscopy (SEM) and ultraviolet absorption tests (UV-V).

RESULTS AND DISCUSSION

Investigation on the technological conditions of nano TiO₂-g-PAN: The orthogonal test was used to explore the synthesis condition of nano TiO₂-g-PAN particles in the experiment. The test factors and levels designed are shown in Table-1 and the corresponding test results are listed in Table-2.

TABLE-1
ORTHOGONAL TABLE OF THE SYNTHESIS EXPERIMENT
OF NANO TiO₂-g-PAN COMPOSITE AGENTS

Level	Test factors			
	Temp. (°C) A	TiO ₂ -g-AC-70/AN (wt %) B	BPO/AN (wt %) C	Time (h) D
1	65	2	0.02	3
2	70	4	0.05	4
3	75	6	1.00	5
4	80	8	2.50	6

TABLE-2
RESULTS OF THE SYNTHESIS EXPERIMENT
OF NANO TiO₂-g-PAN COMPOSITE AGENTS

Project	Test factors				Graft ratio (%)
	A	B	C	D	
1	65	2	0.02	3	1.89
2	65	4	0.05	4	5.02
3	65	6	1	5	22.03
4	65	8	2.5	6	16.23
5	70	2	0.05	5	12.56
6	70	4	0.02	6	7.24
7	70	6	2.5	3	17.59
8	70	8	1	4	80.17
9	75	2	1	6	63.76
10	75	4	2.5	5	110.21
11	75	6	0.02	4	23.12
12	75	8	0.05	3	4.23
13	80	2	2.5	4	32.43
14	80	4	1	3	32.78
15	80	6	0.05	6	22.25
16	80	8	0.02	5	14.45
k ₁	11.29	27.66	11.68	14.12	—
k ₂	29.39	38.81	11.02	35.19	—
k ₃	50.33	21.25	49.69	39.81	—
k ₄	25.48	28.77	44.12	27.37	—
R (range)	39.04	17.57	38.67	25.69	—
Primary and secondary sequence A > C > D > B					
Superior level	A ₃	B ₂	C ₃	D ₃	
Superior combination	A ₃ B ₂ C ₃ D ₃				

The main factors influencing the performance of antiaging agents are the temperature, the mass ratio of BPO to AN, the reaction time and the ratio of nano TiO₂-g-AC-70 to AN. There are no optimal combinations of A₃B₂C₃D₃ in the test, so we have to verify the test under these experimental conditions. The graft rate of PAN is 134.26 % under this condition. The optimal reaction condition is as follows. The ratio of BPO to AN is 20. The reaction time is 4h. And the ratio of TiO₂-g-AC-70 to AN is 14.

Fourier transformed infrared spectroscopy analysis: The chemical bonds of AC-70 on the surface of nano TiO₂ and the PAN grafting on the nano TiO₂ surface were confirmed by FT-IR spectroscopy (Fig. 1). We can see from the curve that the absorption peak at 3400 cm⁻¹ is corresponding to the

Fig. 1. FT-IR spectra of (a) TiO_2 , (b) TiO_2 -g-AC-70 and (c) TiO_2 -g-PAN

hydroxyl groups existing on the surface of nano TiO_2 . The absorption peaks at 675 cm^{-1} ($-\text{Ti}-\text{O}-\text{Ti}-$) and 512 cm^{-1} ($-\text{Ti}-\text{O}$) indicate the characteristic absorption of the nano TiO_2 . According to curve b in Fig. 1, in addition to the IR absorption of nano TiO_2 itself, the absorption peaks of unsaturated double bonds ($\text{CH}_2=\text{CH}-$) and ($-\text{Si}-\text{O}-\text{Ti}-$) exist at 1661 cm^{-1} and 1040 cm^{-1} . From the titanium oxide silicon bonds ($-\text{Si}-\text{O}-\text{Ti}-$), it is concluded that the nano TiO_2 is combined with coupling agents in the form of chemical bonds. The absorption peak at 2243 cm^{-1} is related to the cyano group ($-\text{C}\equiv\text{N}$) in curve c. And the presence of these vibration bands strongly suggests that PAN is successfully attached onto the surface of nano TiO_2 .

Analysis of hydrophilic and lipophilic: The hydrophilic were studied oleophilic test for both nano TiO_2 particles and nano TiO_2 -g-AC-70 particles. The images of nano TiO_2 and nano TiO_2 -g-AC-70 particles in the mixture of toluene and water are investigated for comparison as shown in Fig. 2. It is observed that the nano TiO_2 particles dispersed in water are milky white and turbid, while the nano TiO_2 -g-AC-70 particles are dispersed in acrylonitrile and toluene. The reason that nano TiO_2 particles can be well dispersed in water is that a large number of hydroxyl groups present on the surface of nano TiO_2 . The surface of nano TiO_2 becomes hydrophilic lipophilic after it is grafted by AC-70. Therefore, the nano TiO_2 obtains a good dispersion in acrylonitrile and toluene, making a good condition for the polymerization.

Fig. 2. Modified and unmodified TiO_2 after the hydrophilic oleophilic test, (a) nano TiO_2 particles dispersed in the acrylonitrile and water mixed solution; (b) nano TiO_2 -g-PAN particles dispersed in the acrylonitrile and water mixed solution (c) nano TiO_2 particles dispersed in the toluene and water mixed solution (d) nano TiO_2 -g-PAN particles dispersed in toluene and water mixed solution

UV-visible spectra: It is known to all that the ultraviolet occupied only seven percentages of the sunlight energy, but it is enough to make most of polymer chain bonds fractured. Polypropylene is most sensitive to the 300 nm ultraviolet part, which is the main factor causing the polymer photodegradation. From the UV-visible spectra of nano TiO_2 and nano TiO_2 -g-PAN (Fig. 3), we can see that there are two peaks at 190-240 and 300-390 nm in the curve of nano TiO_2 -g-PAN particles. However, there is only one absorption peak between 190-240 nm for nano TiO_2 particles. This indicates that the nano TiO_2 -g-PAN particles have a stronger UV absorption ability than nano TiO_2 particles as ultraviolet absorbers. The reason for this is the predominant content of enamines which possess a strong UV absorption ability. The corresponding structure I and II when the PAN is initiated by products resulting from the UV and oxygen attack are shown in Fig. 4²⁰.

Fig. 3. UV-Visible spectra of (a) TiO_2 and (b) TiO_2 -g-PAN

Fig. 4. Corresponding structure I and II when the PAN is initiated by products resulting from the UV and oxygen attack

SEM: The morphology of the PP/ TiO_2 and PP/ TiO_2 -g-PAN blends were studied using SEM (Fig. 5). The seriously dioxide agglomeration exists in nano TiO_2 particles in PP/ TiO_2 , which is contrary to that nano TiO_2 -g-PAN particles are homogeneously dispersed in PP/ TiO_2 -g-PAN. The reason is that a large number of hydroxyl groups occur on the surface of nano TiO_2 particles, leading to poor hydrophilic, compatible and serious agglomerations between the nano TiO_2 particles and the polypropylene matrix. The polypropylene and nano TiO_2 -g-PAN particles are compatible with the long chain polyacrylonitrile. And the nano TiO_2 -g-PAN particles are uniformly distributed in the polypropylene matrix.

From the blends of PP/ TiO_2 after 42 days of aging shown Fig. 6a-1, it is revealed that it begins to degrade and forms numerous of micro-pores in the surrounding nano TiO_2 particle

Fig. 5. SEM images of (a) PP/TiO₂ (5.0 %) and (b) PP/TiO₂-g-PAN (5.0 %); (a-1) PP/TiO₂ (5.0%) and (b-1) PP/TiO₂-g-PAN (5.0 %) after 42 days of aging

polymer, resulting in the significant decline of polypropylene mechanical properties. While the surrounding nano TiO₂-g-PAN particle polymer barely degrades and no tiny micro pores appear in the PP/TiO₂-g-PAN blends, as shown in Fig. 6b-1. Thus, the polymer chains grafted to nano TiO₂ surface improve the dispersion and compatibility between nanoparticles and polypropylene.

Fig. 6. Tensile strengths of PP, PP/TiO₂ and PP/TiO₂-g-PAN

EDS analysis: The aging degree of PP/TiO₂ and PP/TiO₂-g-PAN blends were studied through EDS. Table-3 is the weight percentage of oxygen in polymer blends after 42 days of aging. From this table we can know that the oxygen content of PP/TiO₂ increases to 44.17 % from 27.96 % after 42 days of aging, while the oxygen content of PP/TiO₂-g-PAN increases to 28.01 % from 26.47 %. It shows that PP/TiO₂ blends have a more serious UV aging phenomenon.

Weight percentage of oxygen (%)	PP/TiO ₂	PP/TiO ₂ -g-PAN
0 day	27.96	26.47
42 day	44.17	28.01

Mechanical properties after UV aging: Figs. 6 and 7 are the tensile and impact strengths of blends, in which the mixture ratio of PP to nano particles is 5.0 %. At the initial beginning, the mechanical properties of PP blends are better than those of PP/TiO₂. This is due to the poor compatibility between the polypropylene and nanoparticles and the nano TiO₂ particles also accelerate the degradation of the polymer matrix. After a long time of aging, the mechanical properties of PP/TiO₂ become better than those of PP. The reason is that the nano TiO₂ can absorb and reflect the ultraviolet light more effectively and reduce the damages of ultraviolet light on the internal polypropylene matrix.

Fig. 7. Impact strengths of PP, PP/TiO₂ and PP/TiO₂-g-PAN

The PP/TiO₂-g-PAN has better mechanical properties (Figs. 6 and 7). In addition to the excellent UV shielding performance of nano TiO₂, the stabilization of polyacrylonitrile which can generate six-membered unsaturated cyclic structures is improved when its cyano is under the combined effects of light and oxygen, making the PP at a more stable state^{21,22}. Since the six-membered unsaturated cyclic structures acting as ultraviolet absorbers can capture the radicals more effectively and generate relatively more stable structures, the hydrogen atoms of PP can be protected. From the above analysis we can draw a conclusion that the nano TiO₂-g-PAN is an effective antiaging agent.

Conclusion

From this study, an optimal reaction condition for the synthetic process of composite antiaging agents is obtained as follow: the temperature is 75 °C; the mass ratio of benzoyl peroxide (BPO) to acetonitrile (AN) is 20; the reaction time is 4 h and the mass ratio of TiO₂-g-AC-70 to AN is 0.25. The nano TiO₂-g-PAN produced has a good UV absorption capacity. The results show that the mechanical properties and UV anti-

aging resistance are greatly improved by the nano TiO₂-g-PAN antiaging agents.

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