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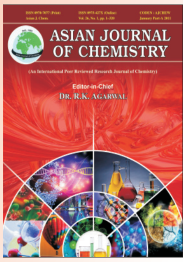

Preparation of Novel TiO_2-g-Polyacrylonitrile Nanocomposites and Their Applications as Ultraviolet Antiaging Agents†

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TiO_2-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 TiO_2) as an ultraviolet absorber. In this study, the synthetic ultraviolet antiaging agents made of TiO_2-g-PAN linked by covalent bonds were prepared *via* a solution polymerization method, with the optimal synthesis process explored through orthogonal experiments. The nano TiO_2-g-PAN particles were characterized by hydrophilic and lipophilic analyses, infrared spectra, energy dispersive spectroscopy, scanning electron microscopy and ultraviolet absorption tests. The nano TiO_2-g-PAN particles were blended with polypropylene particles (PP) and the dispersion and antiaging properties of PP/TiO_2 and PP/TiO_2-g-PAN blends were analyzed. The results showed that the nano TiO_2-g-PAN antiaging agent has excellent performances both in dispersion and UV antiaging.

Keywords: Nano TiO_2, Acrylonitrile, Graft polymerization, Polypropylene, UV antiaging.

INTRODUCTION

Nano TiO_2 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 TiO_2 has a promising application in the polyolefin antiaging field[1-4]. 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 TiO_2 and coated a PMMA layer on nanoTiO_2 nanosized fibers. Therefore, TiO_2-g-PMMA composites were prepared, with the thermal decomposition temperature and elasticity modulus improved[5]. 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 TiO_2 were prepared by a facile surface thiol-lactam initiated radical polymerization method (TLIRP). The dispersability of nano TiO_2 nanoparticles was improved significantly under the functionalization of PS chains[6]. Pan *et al.*[7] prepared the covalent bonds of (PMMA-AN)/TiO_2 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 TiO_2 has been widely used in many industries, such as pigments[8], sunscreens[9,10] and paints[11]. In 1972, Fujishima and Honda discovered the photocatalytic splitting phenomena of water on a TiO_2 electrode under ultraviolet lights[12-14]. Since then, enormous efforts had been devoted to the research of TiO_2 materials, which led to many promising applications in areas ranging from photovoltaics and photocatalysis to photo-electrochromicsand sensors[15-18]. However, based on literatures available, there is hardly any report concerning the an antiaging property of nano TiO_2-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 scavenger[19]. Nano TiO_2-g-PAN particles can not only ameliorate the serious reunion phenomenon of nano TiO_2, but also improve the mechanical strength and the resistance to the ultraviolet aging effect after PAN is grated on the surface. In this study, the nano TiO_2-g-PAN particles with novel resistances were synthesized and characterized. The UV aging and mechanical properties of PP/TiO_2-g-PAN blends were also analyzed.

EXPERIMENTAL

Rutile nanosized titanium dioxide was chosen as the nano TiO_2 (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 tri-*tert*-butyl peroxy silane coupling agents (AC-70, 70 % in toluene) were purified by vacuum distillation at 40 ºC. 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 Provence, China).

Methods: The grafting procedure of AC-70 on the surface of nano TiO_2 is as follows. After 2.5 g nano TiO_2 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 ºC. Then, the modified nano TiO_2 was isolated by centrifugation and washed repeatedly with acetone. Finally, nano TiO_2-g-AC-70 was obtained after being dried at 50 ºC in vacuum for 24 h.

A typical preparation process of nano TiO_2-g-PAN is as follows. 2 g AN, 0.01 g BPO and 1 g nanoTiO_2-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 ºC 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 TiO_2-g-PAN particles were obtained after being dried at 50 ºC in a vacuum atmosphere.

The nano TiO_2-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 ºC 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 TiO_2-g-PAN particles. The formula of the grafting ratio was calculated as follows:

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

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; V_1 is the volume of the hydrochloric acid solution before titration; V_2 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.

$$G = \frac{\frac{N}{14}\times 53}{100} \tag{2}$$

where, G is the grafting ratio.

The nano TiO_2-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 TiO_2-g-PAN: The orthogonal test was used to explore the synthesis condition of nano TiO_2-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 TiO_2-g-PAN COMPOSITE AGENTS

Level	Test factors			
	Temp. (ºC) 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 TiO_2-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	$A_3B_2C_2D_2$				

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 TiO_2-g-AC-70 to AN. There are no optimal combinations of $A_3B_2C_3D_3$ 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 TiO_2-g-AC-70 to AN is 14.

Fourier transformed infrared spectroscopy analysis: The chemical bonds of AC-70 on the surface of nano TiO_2 and the PAN grafting on the nano TiO_2 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

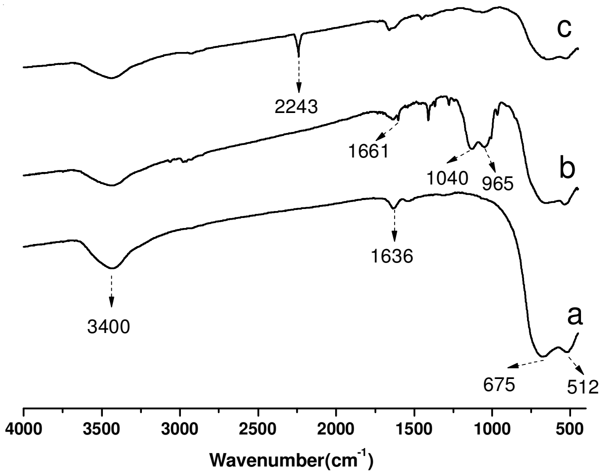


Fig. 1. FI-IR spectra of (a) TiO_2, (b) TiO_2-g-AC-70 and (c) TiO_2-g-PAN

hydroxyl groups existing on the surface of nano TiO_2. The absorption peaks at 675 cm^{-1} (-Ti-O-Ti-) and 512 cm^{-1} (-Ti-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 (CH_2=CH-) and (-Si-O-Ti-) exist at 1661 cm^{-1} and 1040 cm^{-1}. From the titanium oxide silicon bonds (-Si-O-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 (-C≡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) nanoTiO_2 part icles dispersed in the toluene and water mixed solution (d) nanoTiO_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. 4[20].

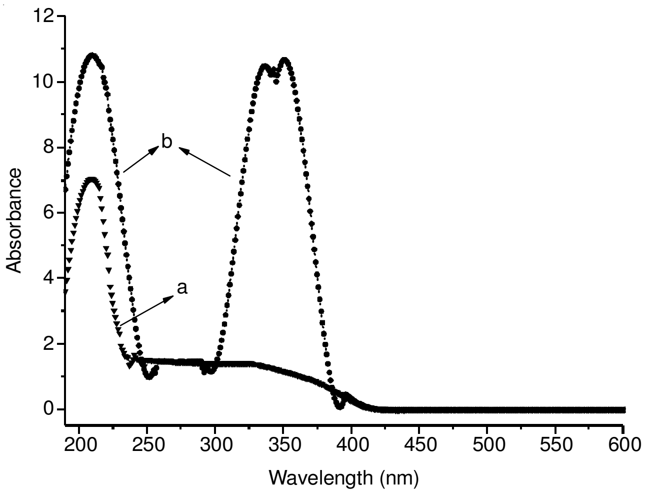
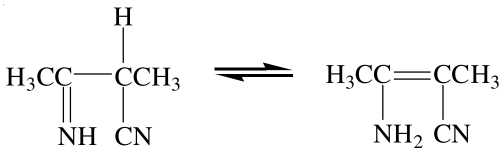


Fig. 3. UV-Visible spectra of (a) TiO_2 and (b) TiO_2-g-PAN



I **II**

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

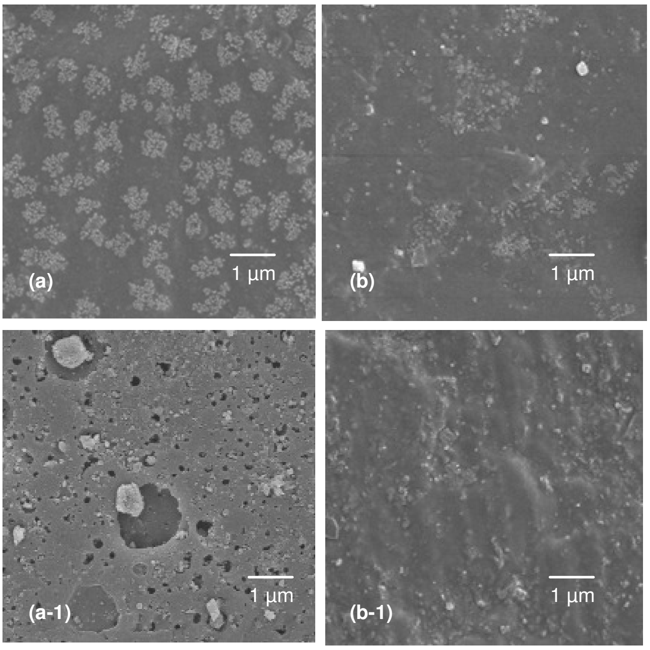


Fig. 5. SEM images of (a) PP/TiO_2 (5.0 %) and (b) PP/TiO_2-g-PAN (5.0 %); (a-1) PP/TiO_2 (5.0%) and (b-1) PP/TiO_2-g-PAN (5.0 %) after 42 days of aging

polymer, resulting in the significant decline of polypropylene mechanical properties. While the surrounding nano TiO_2-g-PAN particle polymer barely degrades and no tiny micro pores appear in the PP/TiO_2-g-PAN blends, as shown in Fig. 6b-1. Thus, the polymer chains grafted to nano TiO_2 surface improve the dispersion and compatibility between nanoparticles and polypropylene.

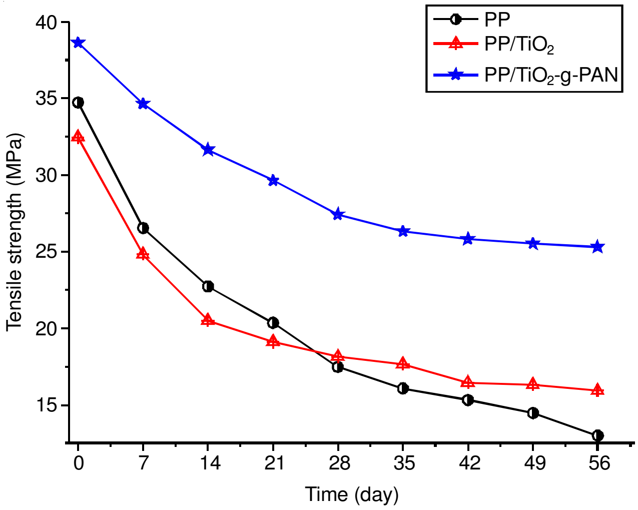


Fig. 6. Tensile strengths of PP, PP/TiO_2 and PP/TiO_2-g-PAN

EDS analysis: The aging degree of PP/TiO_2 and PP/TiO_2-g-PAN blends were studied though 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/TiO_2 increases to 44.17 % from 27.96 % after 42 days of aging, while the oxygen content of PP/TiO_2-g-PAN increases to 28.01 % from 26.47 %. It shows that PP/TiO_2 blends have a more serious UV aging phenomenon.

TABLE-3
WEIGHT PERCENTAGE OF OXYGEN IN POLYMER BLENDS AFTER 42 DAYS OF AGING

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/TiO_2. This is due to the poor compatibility between the polypropylene and nanoparticles and the nano TiO_2 particles also accelerate the degradation of the polymer matrix. After a long time of aging, the mechanical properties of PP/TiO_2 become better than those of PP. The reason is that the nano TiO_2 can absorb and reflect the ultraviolet light more effectively and reduce the damages of ultraviolet light on the internal polypropylene matrix.

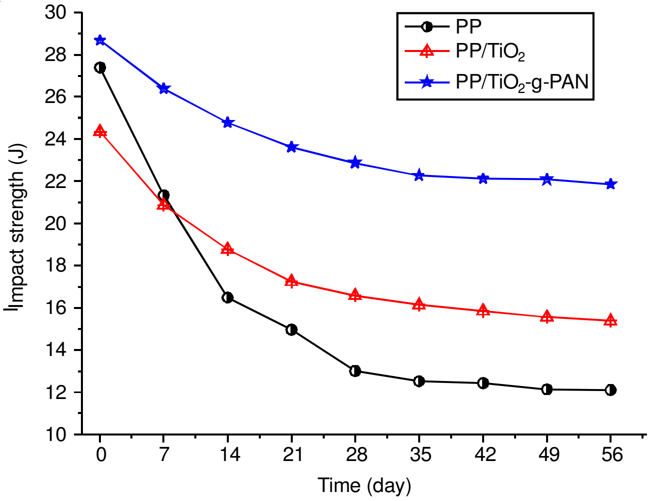


Fig. 7. Impact strengths of PP, PP/TiO_2 and PP/TiO_2-g-PAN

The PP/TiO_2-g-PAN has better mechanical properties (Figs. 6 and 7). In addition to the excellent UV shielding performance of nano TiO_2, 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 TiO_2-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 ºC; the mass ratio of benzoyl peroxide (BPO) to acetonitrile (AN) is 20; the reaction time is 4 h and the mass ratio of TiO_2-g-AC-70 to AN is 0.25. The nano TiO_2-g-PAN produced has a good UV absorption capacity. The results show that the mechanical properties and UV antiaging resistance are greatly improved by the nano TiO_2-g-PAN antiaging agents.

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