IOP Conf. Series: Materials Science and Engineering **439** (2018) 042023 doi:10.1088/1757-899X/439/4/042023

Study on Recycling ABS Plastic/Nano $CaCO_3$ /TiO_2 /POEModified Composites

Wu Ming-liang [1], He Shao-fen [1], Li Dao-hua [1,2,3*], Fan Jia-jun [1]

[1] College of Chemistry and Chemical Engineering; [2]Key Laboratory of Fruit Waste Treatment and Resource Recycling of the Sichuan Provincial College; [3]Academician Workstation of Agricultural Waste Recycling, Neijiang Normal University, Neijiang, Sichuan 641112, China

E-mail of Corresponding Author: daohl@163.com; lidh@njtc.edu.cn

Abstract. The nanocomposites were prepared by adding nano-$CaCO_3$, nano-TiO_2 and POE in different proportions to the recycled acrylonitrile butadiene styrene (ABS) plastic. Six different types of recycled ABS plastic modified nanocomposites were prepared. Three mechanical properties of the newly prepared materials were tested, including the tensile strength, impact strength, and flexural strength. The microstructures and physicochemical structures of the composites were further studied by means of scanning electron microscopy (SEM), infrared spectroscopy (FT-IR), X-ray diffraction (XRD), and thermogravimetric-differential thermal analysis (TG-DTA). Through the analysis to determine the best dosage range of toughening agent and filler, the performance of the modified recycled ABS plastic was improved. This also makes the recycled ABS plastic more widely used, which provides a certain value of reference for the recycling of recycled ABS. The results show that the nano-$CaCO_3$, nano-TiO_2 and POE are uniformly dispersed in the ABS matrix, the mechanical properties of the ABS plastic are improved, and the thermal decomposition temperature of the modified plastic is increased. It also reveals that the tensile, impact and bending properties of 6.6 % nano-$CaCO_3$, nano-TiO_2 composites are improved.

1. Introduction

ABS plastic is widely used in the automotive industry, electrical instrumentation industry and machinery industry. It is often made into gears, auto parts, fenders, handrails, refrigerator liners, blades, bearings, handles, pipes, fittings, instrument shells, dashboards, security caps and so on [1]. The application prospects for household appliances and home electronic devices are much broader, such as televisions, tape recorders, refrigerators, freezers, washing machines, air conditioners, vacuum cleaners, and various small appliances [2]. Daily necessities include shoes, bags, various travel boxes, office equipment, toys and various containers, etc. Low foaming ABS can replace wood, which is suitable for building materials, furniture and household products. Therefore, the amount of waste ABS produced by human beings is very large, and an efficient, environmentally friendly, sustainable development approach is needed to use recycled ABS [3].

This paper studies the preparation of modified nanocomposites with recycled ABS plastic, where its formula design and process flow are considered [4]. It uses the recycled ABS plastic as the main body of the resin, nano-$CaCO_3$ and nano-TiO_2 nanomaterial as the filler. The mixed material is formed with dibutyl phthalate (DPB), ordinary paraffin, antioxidant 1010, silane coupling agent (KH-550), dicumyl peroxide (DCP), composite anti-aging agent, and carbon black. The mechanical properties of

IOP Conf. Series: Materials Science and Engineering **439** (2018) 042023 doi:10.1088/1757-899X/439/4/042023

theproduct are tested and its structure is characterized by using SEM, FT-IR, XRD, and TG-DTA. Moreover, the different percentages of fillers, interface agents, coupling agents and lotion are studied in the experiment, which reveals the application performance and preparation mechanism [5, 6].

2. Experimental Method

A suitable amount of nano-$CaCO_3$ is dried at 100°C for two hours. After removing the water completely, it is added to a beaker together with an appropriate amount of absolute ethanol, mixed with an appropriate amount of carbonate, placed in an oven, and baked at 90°C for two hours. Then it should be grind into powder. The nano-TiO_2 is dried at 90°C for two hours, and then anhydrous ethanol is added. The beaker is placed in a magnetic stirrer and heated in a water bath at 80°C, while a 2% silane coupling agent is added to the suspension. The stirring is performed for one hour. Finally, it should be filtered, dried, and grinded.

The POE rubber, maleic anhydride grafted polyethylene (PE-g-MAH) and DCP cross-linker are weighed in the ratio of POE rubber: PE-g-MAH: DCP cross-linker = 200:4:1. The POE rubber and PE-g-MAH are mixed uniformly, and DCP cross-linker is added during grafting. The grafting process takes place in the extruder. After melt extrusion, the pelletizer is used to cut pellets, which are collected and dried at 70°C for two hours to prepare the modified POE rubber toughening agent.

Table 1 is the preparation formulation and composition of the modified nanocomposites. The recycled ABS plastic and other additives are weighed according to the formula and mixed uniformly. After reaching the set temperature, the temperature should be kept constant for 10~20 min. Then, we open the extruder motor and set the extrusion speed as 35 rpm/min.

Table 1 Process formulation of modified nanocomposite materials with recycled ABS plastics

No	Category	Ingredients	Sample number (quality and proportion)					
			A1/g	A2/g	A3/g	A4/g	A5/g	A6/g
1	Raw material	Recycled waste ABS plastic	150	150	150	150	150	150
2	Raw material	New ABS plastic	20	20	20	20	20	20
3	Coupling agent	3-Aminopropyltriethoxysilane (KH-550)	2	2	2	2	2	2
4	Toughening agent	Polyolefin elastomer (POE)	10	12	15	16	18	20
5	Filler	Modified nano-TiO_2	10	12	15	16	18	20
6	Filler	Modified nano-$CaCO_3$	10	12	15	16	18	20
7	Crosslinking agent	Dicumyl peroxide (DCP)	1	1	1	1	1	1
8	Stabilizer	Antioxidant (1010)	1	1	1	2	2	2
9	Plasticizer	Dibutyl phthalate (DPB)	2	2	2	2	2	2
10	Lubricant	Paraffin	1	1	1	1	1	1
11	Colorant	Carbon black colorant	2	2	2	2	2	2
12	Anti-aging agent	TiO_2 : Hindered amine stabilizers = 5 : 6	1	1	1	1	1	1

Extruder temperatures at different heating districts are set as: preheat 70~80℃, district one 180~220℃, district two 210~230℃, district three 215~235℃, outlet 220~240℃. Plastic injection molding machine temperatures at different heating districts are set as: preheat 70~80℃, front section 180~220℃, middle section 210~230℃, final part 215~235℃, mold 220~240℃.

The tensile property, impact property and bending property of modified nanocomposite materials are tested by XWW-20A universal test machine. The test results are obtained by averaging five experiments. The samples are scanned by using a VEA3SBH SEM. The samples are subjected to FT-IR test using a TJ270-30 infrared spectrophotometer. XRD tests are performed on a DX-2700 X-Ray. The XRD test is performed to adjust the control parameters, where the starting angle is 20°, the termination angle is 60°, the step angle is 0.03°, the sampling time is 0.5s, the tube voltage is 40 kV, and the tube current is 40 mA. The samples are cross-coated by ion sputtering, and the cross-sectional morphology is observed under the SEM. The samples are subjected to TG-DTA test using a comprehensive thermal analyzer (HCT-3 microcomputer differential thermal balance).

3. Results and Discussions

3.1 Mechanical properties of modified nanocomposites

Table 2 shows the mechanical properties of the modified ABS nanocomposite samples, which include the test results of modified nanocomposites' tensile strength, bending strength and impact strength. From Table 2, we can see that with the addition of a certain amount of nano-$CaCO_3$ and TiO_2, the tensile strength, bending strength and impact strength of the modified nanocomposites first increased and then decreased. When the addition amount of nano-$CaCO_3$ and TiO_2 is between 4.7 % and 6.6 %, the tensile strength, flexural strength, and impact strength of the modified nanocomposite increase with the increase of the addition of nano-$CaCO_3$ and TiO_2. When the addition amount of nano-$CaCO_3$ and TiO_2 exceeds 6.6%, the tensile strength, bending strength, and impact strength of the modified nanocomposites start to decline.

When the addition amount of nano-$CaCO_3$ and TiO_2 is 6.6% (i.e., sample A3), the mechanical properties of the modified nanocomposites are better. The tensile strength is 38.85 MPa, which is increased by 22.9%. Its bending strength is 50.73 MPa, which is increased by 16.3%. In addition, the impact strength is 46.12 kJ/m^2, which is increased by 41.4%.

Table 2 Mechanical properties of modified nano-samples from recycled ABS plastics

No.	Sample	Tensile Strength /MPa	Elongation at break /%	Impact strength kJ/m^2	Flexural strength /MPa	Flexural modulus
1	A0	31.61	4.41	32.61	43.62	3985.37
2	A00	41.57	5.93	56.82	52.82	7513.79
3	A1	35.26	5.12	36.52	46.84	6513.79
4	A2	35.55	5.24	41.21	48.85	6532.12
5	A3	38.85	5.68	46.12	50.73	6968.07
6	A4	34.47	5.62	44.53	46.80	6932.47
7	A5	33.58	5.33	43.84	45.39	5979.85
8	A6	32.36	4.79	43.17	43.26	5987.21

Description: A0 is the Recycled waste ABS plastic formula, A00 is the new ABS plastic formula, A1~A6 are the specific implementation formulas (see details in Table 1).

3.2 SEM Analysis of Modified Nanocomposites

Fig. 1 shows the SEM image of the modified ABS nanocomposite sample A3. From Fig. 1, it can be observed that dense pores are distributed in the sample, and there is no obvious undulation in the section, which appears to be more upright.

According to the role of various additives, it can be inferred that the small pores are caused by the addition of cross-linking agents, where the micro-particles form a network structure. This enhances the strength of the nanocomposites to a certain extent. The reason why the surface is relatively smooth and with no obvious undulations is due to the addition of lubricants, which makes the combination of microscopic particles more rounded. From the macro point of view, the surface is shiny, while microscopically, it is the observed section without undulations [7].

3.3 FT-IR Analysis of Modified Nanocomposites

Fig.2 shows the FT-IR image of the modified recycled ABS nanocomposite sample A3. From Fig.2, it can be seen that the absorption position of the modified nanocomposites and the recycled ABS plastics are basically the same, but the transmittance of the modified composites is lower than that of the recycled ABS plastics. This is due to the addition of nanometers and inorganic materials, which have been dispersed in the matrix of nanocomposites.

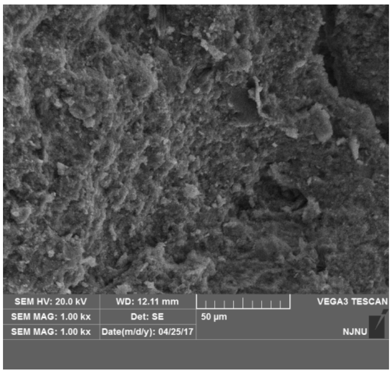

Fig.1 The SEM result of modified nanocomposites with sample A3

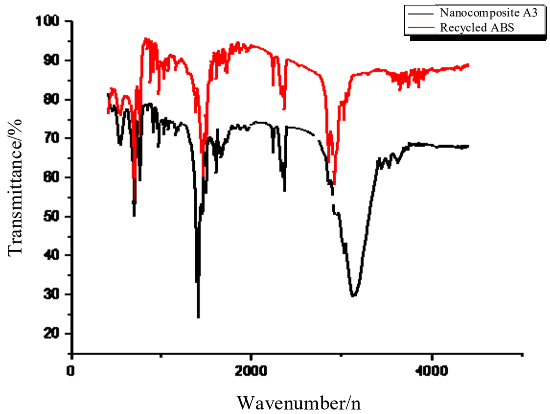

Fig.2 The FT-IR result of modified nanocomposites with sample A3

3.4 XRD Test and Analysis of Modified Nanocomposites

Fig. 3 shows the XRD pattern of the modified ABS nanocomposite sample A3. From Fig. 3, it can be seen that the characteristic peak of ABS appears at $2\theta = 21.453$ °, and there are no other distinct special diffraction peaks. After the modification, other obvious peaks appear. The peak value of the modified nanocomposites has been improved to some extent, indicating that the crystallinity of the modified nanocomposites is better than that of the unmodified ABS plastics. After $2\theta = 21.453$ °, there are several new characteristic peaks, which are the characteristic peaks of various additives such as nano-$CaCO_3$, nano-TiO_2, and POE elastomers, indicating that various nano-materials have been dispersed in the ABS matrix and combine with the ABS matrix well [8].

3.5 TG-DTA of Modified Nanocomposites

Fig. 4 shows the TG-DTA of the modified ABS nanocomposite sample A3. From Fig. 4, the differential thermal (DT) curve of the modified nanocomposites starts to decline before the temperature of 300°C, indicating that the nanocomposite composites begin to decompose before 300°C, and that the curve continues to decline rapidly in the temperature range of 300°C to 480°C.When the temperature is around 490°C, the curve is stable and there is no significant fluctuation, indicating that before the temperature, the easily decomposable substances in the sample have been completely decomposed. And after this temperature, other substances basically no longer decompose with the increase of temperature.

When the temperature reaches around 320°C, the DT curve of the recycled ABS plastic sample shows a downward trend, indicating that the plastic sample starts to decompose at this time. In the temperature range of 320°C ~ 420°C, the rapid and continuous decline of the curve indicates that the decomposition rate of the plastic sample in this temperature range increases, and then gradually decreases after 420°C. When the temperature reaches 550°C, the curve tends to be stable, indicating that the recycled ABS plastic will no longer decompose with increasing temperature.

Adding some auxiliaries to recycled ABS plastic will reduce its thermal decomposition temperature. And the decomposition rate of the modified ABS plastic will be much slower than the decomposition rate of recycled ABS plastic during the rapid decline range of the curve. This is due to the addition of minerals as fillers, resulting in a certain increase in the temperature at which the composites are fully decomposed, and slowing down the rate of decomposition.

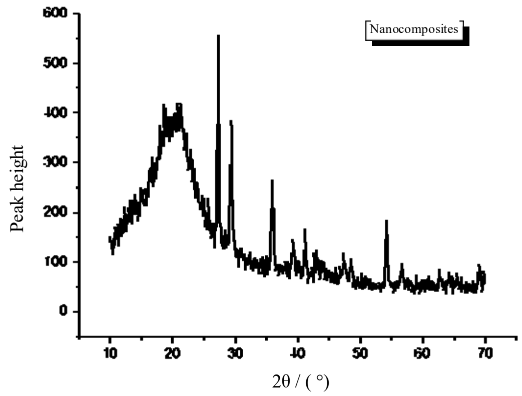

Fig. 3 The XRD pattern of modified ABS nanocomposite sample A3

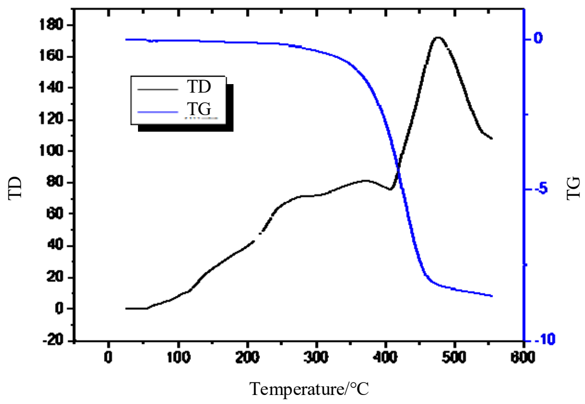

Fig. 4 The TG-DTA of modified ABS nanocomposite sample A3

4. Conclusions

After nano-$CaCO_3$, TiO_2 and POE were added to obtain the modified nanocomposite, the tensile strength, flexural strength and impact strength were all increased first and then decreased.

The analysis of SEM and XRD patterns showed that nano-$CaCO_3$ and nano-TiO_2 as fillers were modified and dispersed in the ABS matrix under the action of plasticizers and lubricants, so that the impact strength and elongation at break of the nanocomposites were improved.

When the addition amount of nano-$CaCO_3$ and TiO_2 was 6.6% (i.e., sample A3), the mechanical properties of the modified nanocomposites were better, the tensile strength was 38.85 MPa, the tensile strength of the recycled ABS plastic was increased by 22.9%, and the bending strength was improved. For 50.73 MPa, the bending strength of recycled ABS plastics increased by 16.3%, the impact strength was 46.12 kJ/m^2, and the impact strength of recycled ABS plastics increased by 41.4%.

When the addition amount of nano-$CaCO_3$ and TiO_2 is 6.6% (i.e., sample A3), the mechanical properties of the modified nanocomposites are better. The tensile strength is 38.85 MPa, which is increased by 22.9%. Its bending strength is 50.73 MPa, which is increased by 16.3%. In addition, the impact strength is 46.12 kJ/m^2, which is increased by 41.4%.

Acknowledgements

Corresponding Author:Li Dao-hua. This work was financially Supported by: A Project Supported by Scientific Reserch Fund of SiChuan Provincial Education Department(2018ZA0281); and Patent Project of Science & Technology Department in Neijiang Normal University (16ZL06) ; and "Basic Chemistry Teaching Team"- Undergraduate Teaching Project by Neijiang Normal University ([2015] 96); and National college students Innovation and Entrepreneurship Training Program in Neijiang Normal University (Higher Education Letter [2017] 40, X2017051).

References

[1] J. Liu, M. Xu, and B. Li. Hydrophobic modification of ammonium polyphosphate and its application in flame retardant polypropylene composites. *Chemical Journal of Chinese Universities*, 2015, 36(6), 1228-1235.
[2] M. S. Hamzah, I. N. Hidayah, and M. Mariatti. Dielectric and thermal properties of flame retardant

IOP Conf. Series: Materials Science and Engineering **439** (2018) 042023 doi:10.1088/1757-899X/439/4/042023

fillers in polypropylene/ethylene propylene diene monomer composites. *Journal of Reinforced Plastics & Composites*, 2014, 33(21), 1931-1940.
[3] M. D. Beg, S. Samahani and M. F. Mina. Simultaneous effects of coupling agent and flame retardant on empty fruit bunch fiber/polypropylene composites. *Journal of Reinforced Plastics & Composites*, 2013, 32(17), 1268-1284.
[4] A. Elshad, J. Anupam, and W.Wenbo. Enlargement of halloysite clay nanotube lumen by selective etching of aluminum oxide. *Acs Nano*, 2013, 6(8), 7216-7226.
[5] J. Z. Liang, B. Zhu and W. Y. Ma. Morphology and mechanical properties of PP/POE/Nano-$CaCO_3$ composites. *Polymer Composites*, 2016, 37(2), 539-546.
[6] D. L. Chen and H. M. Yang. Polypropylene/combinational inorganic filler micro/nanocomposites: synergistic effect of micro-/nanoscale combinational inorganic fillers on their mechanical properties. *Journal of Journal of Applied Polymer Science*, 2012, 115(1), 624-634.
[7] H. Ding and S. C. Lu. Surface modification of wollastonite by the mechano-activated method and its properties. *International Journal of Minerals*, *Metallurgy and Materials*, 2013, 18(1), 83-88.
[8] N. Sarier and O. Emel. Organic modification of montmorillonite with low molecular weight polyethylene glycols and its use in polyurethane nanocomposite foams. *Thermochimica Acta*, 2013, 510(1-2), 113-121.