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Preparation and Mechanical Properties of Layered Double Hydrotalcides/ /Polystyrene Nanocomposites Prepared by an in-situ Bubble Stretching Method

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Layered double hydrotalcides/polystyrene (LDHs/PS) nanocomposites were produced by an in-situ bubble stretching (ISBS) method and simple shear method; the effect of LHDs content on the dispersion and the mechanical properties of nanocomposites was studied. The field emission scanning electron microscopy (FE-SEM) images indicated that the ISBS method leads to a high degree of dispersion of LDHs nanoparticles in PS matrix. Furthermore, it did not form a significant re-aggregation after defoaming by means of twin-screw extruder. Compared with the simple shear method, the un-notched impact strength and tensile strength of nanocomposites prepared by ISBS method were higher at the same amount of LDHs. The un-notched impact strength of the nanocomposites prepared by ISBS method reached a maximum value at the LDHs mass fraction of 5 % , the strength increased is 57.29 % greater than that of pure PS. The enhanced mechanical properties attributed to the effective dispersion of nanoscale LDHs by ISBS method.

Keywords: in-situ bubble stretching (ISBS); polystyrene (PS); layered double hydrotalcides (LDHs); dispersion; mechanical properties.

1. INTRODUCTION

Compared to pure polymers, polymer matrix nanocomposites have excellent physical and chemical properties such as photooxidation properties [1], mechanical properties [2], fire resistance [3], thermal properties [4], barrier properties [5], biological properties [6]. Therefore, more and more nanocomposites have been prepared on today's materials researches. Nanoparticles possess rather small size and high surface energy, which is in the thermodynamic unsteady state. So nanoparticles are easy to agglomerate in the nanocomposites preparation. The dispersion degree of nanoparticles in polymer matrix affects the performance of the composite materials directly, in the preparation process to achieve nanometer level dispersion of nanoparticles in matrix is the key to realize the excellent properties of nanocomposites. The in-situ bubble stretching (ISBS) method proposed by Wu et al. [7] uses the bubbles produced by the rapid expansion of stretching rate to achieve the dispersion of nanoaggregate around the bubbles. The method has been applied to a variety of nanocomposites preparation successfully [8 – 13].

Layered double hydrotalcites have the functions of retardant, insulation, stability, anti-ultraviolet and have been widely utilized in the preparation of polymer nanocomposites [1, 14]. Polystyrene has the advantages of transparency, good formability, good rigidity and low moisture absorption. It is widely applied in the field of electronic and electrical appliances and daily necessities [14]. However, its brittleness and low impact strength limit its application. Therefore, nanoparticle filling in PS is widely used to improve its mechanical properties [15, 16].

There are few studies on the LDHs/PS [17, 18] nanocomposites currently and also very little research on the mechanical properties of LDHs on PS. In this paper we studied the microstructure and mechanical properties of LDHs/PS nanocomposites prepared by ISBS method and compared with those produced by co-rotating twin-screw extruder melt blending. This paper also studied the effect of the defoaming method of twin-screw extruder on LDHs dispersion and re-aggregation.The correlation of study on microscopic dispersion with macroscopic mechanical properties of LDHs/PS nanocomposites provided some insight into reinforced modified PS and preparing nanocomposites by ISBS method.

2. EXPERIMENTAL DETAILS

Materials. Polystyrene (PS PG-33) with MFR of 8 g (10 – 1) min was produced by Zhenjiang CHI MEI Chemical Co., LTD. Layered double hydrotalcides (LDHs) with granule size of (80 – 100) nm was obtained from Jiangyin RUIFA Chemical Co., LTD. Foaming was induced by azodicarbonamide (A.C. foaming agent) from Hengshui Jindu Rubber Chemical Co., LTD and the decomposition temperature of A.C. foaming agent was 200 ºC. The lubricant was paraffin oil from Beijing Yili Fine Chemical Co., LTD.

Preparation of LDHs/PS nanocomposites. The PS was first dried for 2 h at 80 ºC and then LDHs was dried for 2 h at 120 ºC. A fixed amount of PS, LDHs and paraffin oil were premixed for 3 min in a high speed stirrer. The compositions are listed in Table 1. These mixtures were directly compounded by a co-rotating parallel twin-screw extruder (TDS-20A/400-4-36, Nanjing Norda Extrusion Equipment Co., LTD) with temperature of 190, 195, 200, 205, 205, 200 ºC and screw speed of 200 rpm.

The mixtures were extruded and foamed in a single screw extruder (SJ-20-20A, screw diameter of 20 mm, L/D of 20, Weifang Kaide Plastics Machinery Co., LTD). The

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weight ratio of PS to A.C. foaming agent was 100 : 0.6. Foaming experimental parameters were as follows: extrusion temperature of 190, 200, 205, 200 ºC, screw speed of 60 rpm.

Table 1. Compositions of precursor mixtures for preparation of LDHs/PS nanocomposites

Sample no.	PS, %	LDHs, %	Paraffin oil
1	97	3	pinch
2	95	5	pinch
3	92.5	7.5	pinch
4	90	10	pinch

The foamed material was then crushed by plastics granulator (DF180, Ningbo Dongfang Knitting Machine Works) and for subsequent defoaming using a co-rotating twin-screw extruder (TDS-20A/400-4-36, Nanjing Norda Extrusion Equipment Co., LTD) with temperature of 200, 205, 210, 215, 215, 210 ºC and screw speed of 180 rpm. In order to improve the effect of exhaust, water ring vacuum pump was employed when the twin-screw extruder was running.

Finally, the material before and after ISBS dispersion were dried and moulded to produce a standard tensile and impact specimen using an injection molding machine (HTF120, Ningbo Haitian Plastic Pachinery Co., LTD) with temperature of 180, 190, 200, 200, 190 ºC and injection pressure of 55 MPa .

Morphological analysis by field emission scanning electron microscopy (FE-SEM). The experimental samples were fractured in liquid nitrogen. The cross surface was coated with gold and then observed by FE-SEM (JSM-7800F, JEOL, Japan; S4700, Hitachi, Japan).

Mechanical properties. Un-notched impact strength tests were conducted on pendulum impact test equipment for plastics (ZBC31400-2, Shenzhen Sans Material Test Instrument Co., LTD) according to the GB/T 1043.1-2008 standard procedure. Tensile strength tests were conducted on an universal testing machine (XWW-20A, Chengde Jinjian testing instrument Co., LTD) with a loading speed of 5 mm/min at room temperature according to the GB/T 1040.2-2006 standard procedure.

3. RESULTS AND DISCUSSION

Effect of ISBS dispersion on LDHs. In order to illustrate the effectiveness of ISBS method on the dispersion of inorganic nanoparticles, LDHs/PS nanocomposites were prepared by ISBS method and simple shear method, and analysised the FE-SEM of the composite materials prepared by the two methods.

Fig. 1 shows the FE-SEM micrographs of the LDHs/PS composite materials produced by ISBS method and simple shear method with different LDHs contents. Fig. 1, a, shows the micrograph of directly extruded sample of simple shear method at LDHs mass fraction of 5 %. Fig. 1, b and c, show the micrographs of samples further dispersed by the ISBS method in which the mass fraction of LDHs is 5 % and 10 %, respectively.

From Fig. 1, a, it can be seen that, at 5 % LDHs content, simple shear method can induce a relative good dispersion although obvious aggregation is observable. From Fig. 1, b, it can be seen that when the mass fraction of LDHs is 5 %, LDHs around the bubble wall (3 μm) almost have not re-agglomerated, suggesting that the nanoparticles dispersion degree was improved effectively by the rapid expansion of the bubble in ISBS foaming process. Fig. 1, c, shows that LDHs around the bubble wall have certain aggregation phenomenon when the mass fraction of LDHs is 10 %. Compared with Fig. 1, a and b, it can be seen that with the same content of LDHs, ISBS have better dispersion effect than simple shear method. But, from the LDHs content of 10 %, the probability of collision in the ISBS dispersion process and the probability of re-aggregation increased, leading to the decreased dispersion degree of LDHs.

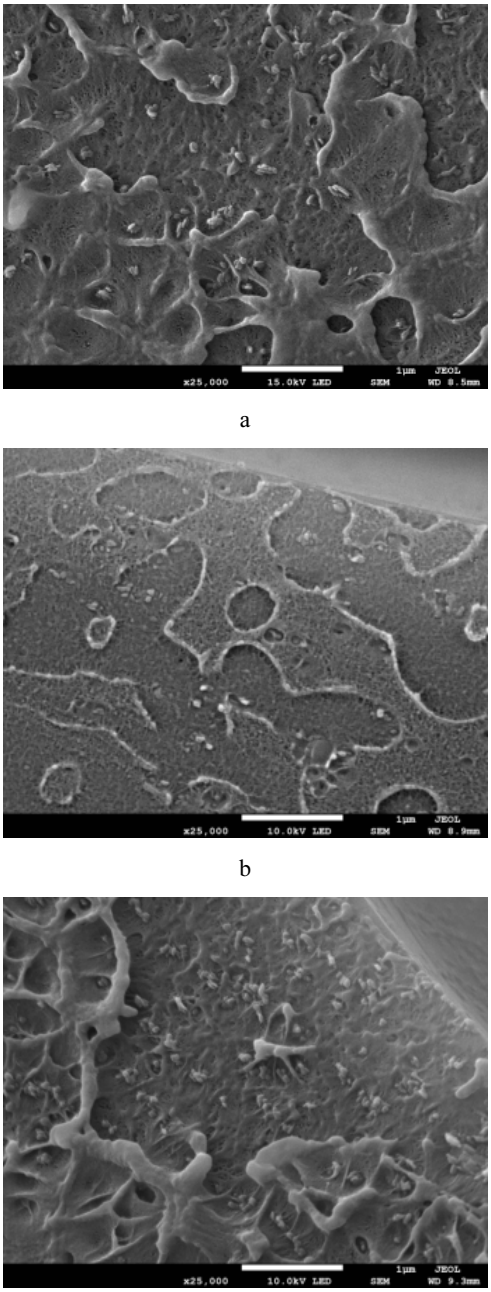
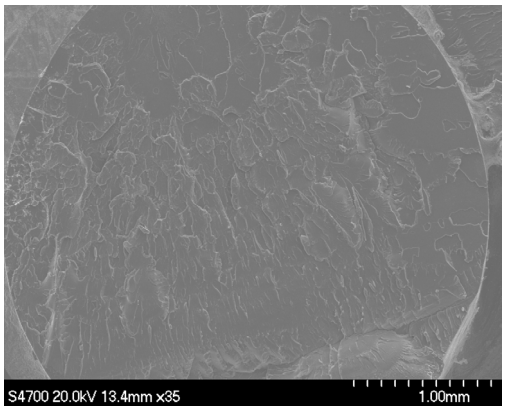
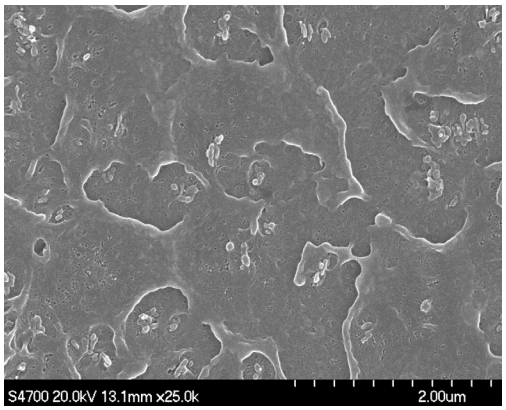


Fig. 1. The microstructure of LDHs/PS composite materials. 5 % (a, b) and 10 % (c) mass fraction of LDHs addition

Effect of defoaming process on LDHs dispersion. The presence of bubbles in composite materials will affect the performance of materials in ISBS method. In the previous study, the foamed material was ground into powder using a gas-lead grinder for subsequent defoaming under the protection of liquid nitrogen [10, 19]. This method has a complex process, high cost characteristics, and difficulty to scale-up for commercialization. Therefore, the twin-screw extruder equipped with water ring vacuum pump was used for exhaust defoaming on the foaming material.



a



b

Fig. 2. The SEM micrographs of LDHs/PS nanocomposites after defoaming. Magnification: a – ×35; b – ×2.500

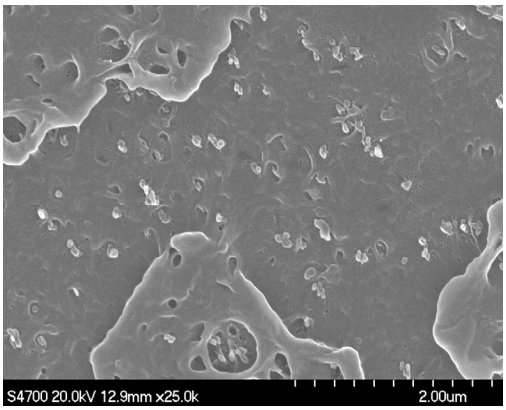


Fig. 3. The micrograph SEM of injection spline prepared by LDHs/PS nanocomposites after defoaming

Fig. 2 presents the FE-SEM micrographs of the LDHs/PS sample after defoaming by twin-screw extruder. The magnification is 35 times in Fig. 2, a; the whole defoaming situation of foam extrusion spline can be observed. The magnification is 25000 times in Fig. 2, b; the dispersion of LDHs can be observed. Fig. 3 is the FE-SEM micrograph of injection spline prepared by LDHs/PS nanocomposites after defoaming.

Fig. 2, a, shows that there are almost no bubbles in the polymer matrix after defoaming by the twin-screw extruder, suggesting that the twin-screw extruder can eliminate the bubble of foam composites effectively; Fig. 2, b, shows that the particle size of LDHs remains at nanometer level. By comparison between Fig. 2, a and b, it can be seen that the particle size did not change significantly, suggesting that LDHs did not re-aggregate during defoaming. From Fig. 3, it can be seen that the particle size of LDHs remains at nanometer level in the injection spline prepared by LDHs/PS nanocomposites after defoaming. This further explained that there is no re-agglomeration during the defoaming process [20, 21], and suggest that the use of twin-screw extruder to eliminate the bubbles in ISBS nanocomposites is an efficient tool.

Mechanical properties of LDHs/PS nanocomposites. The experimental data of un-notched impact strength of the composites prepared by ISBS method and simple shear method are shown in Table 2. From Table 2, it can be seen that the un-notched impact strength of LDHs/PS composites manufactured by the two methods increases first and then decreases with increasing the mass fraction of LDHs. The un-notched impact strength of the composites prepared by simple shear method reached a maximum value which is 19.75 kJ m^{-2} when LDHs mass fraction is 3 %. The strength increased is 37.15 % than pure PS. For ISBS method, the un-notched impact strength reached a maximum value of 22.65 kJ m^{-2} when LDHs mass fraction is 5 %. The strength increased is 57.29 % greater than that of pure PS and the increased is 56.21 % compare to simple shear method. When the mass fraction of LDHs continued to increase, some aggregation of LDHs particles occurs, these reaggregates damaged first when the composites is subjected to external force, so the un-notched impact strength of the composite materials started to decrease. The maximum impact strength of ISBS method can achieve up to 14.68 % higher than the maximum impact strength of simple shear method. This indicates that LDHs/PS nanocomposites prepared by ISBS method can achieve higher impact strength and ISBS method can improve the impact property of PS resin more effectively.

The possible reason is that LDHs has a layered structure, when it reaches nanometer dispersion, and thus LDHs layers in the polymer play a role of "physical crosslinking point". These "physical crosslinking point" are damaged and absorb energy when the system is subjected to external force so that the impact properties of nanocomposites can be improved. So the impact strength of the nanocomposites can be imoproved dramatically when the amount of LDHs addition is small. When LDHs is not well dispersed, the "physical crosslinking point" in nanometer scale reduced due to the re-aggregated of LDHs, leading to the decreased impact strength and toughness of the nanocomposites [22, 23].

The experimental data of tensile strength of the composites prepared by the two methods are shown in Table 3. The tensile strength of the composites prepared by the two

Table 2. Influence of LDHs contents on impact strength for LDHs/PS composites

No. *i*	LDHs contents	Un-notched impact strength kJ m^{-2}		The increase percentage compared to pure PS material		The increase percentage of ISBS method compared to simple shear method (C_{1i}), %
		Simple shear method	ISBS method	Simple shear method (A_{1i})	ISBS method (B_{1i})	
0	0	14.40	14.40	0	0	0
1	3%	19.75	20.75	37.15 %	44.10 %	5.06 %
2	5%	14.50	22.65	0.69 %	57.29 %	56.21 %
3	7.5%	11.70	14.40	–18.75 %	0 %	23.08 %
4	10%	10.75	11.88	–25.35 %	–17.50 %	10.51 %

$$A_{1i} = \frac{a_{cU1i} - a_{cU0}}{a_{cU0}}; \quad B_{1i} = \frac{a_{cU2i} - a_{cU0}}{a_{cU0}}; \quad C_{1i} = \frac{a_{cU2i} - a_{cU1i}}{a_{cU1i}}.$$

A_{1i}: The un-notched impact strength increase percentage of composites at different LDHs contents prepared by simple shear method compared to pure PS material;

B_{1i}: The un-notched impact strength increase percentage of composites at different LDHs contents prepared by ISBS method compared to pure PS material;

C_{1i}: The un-notched impact strength increase percentage of composites at different LDHs contents prepared by the ISBS method compared to the simple shear method;

a_{cU0}: The un-notched impact strength of pure PS material;

a_{cU1i}: The un-notched impact strength of LDHs/PS composites at different LDHs contents prepared by simple shear method;

a_{cU2i}: The un-notched impact strength of LDHs/PS nanocomposites at different LDHs contents prepared by ISBS method;

Table 3. Influence of LDHs contents on tensile strength of LDHs/PS composites

No. *i*	LDHs contents	Tensile strength MPa		The decrease percentage compared to pure PS material		The increase percentage of ISBS method compared to simple shear method (C_{2i})
		Simple shear method	ISBS method	Simple shear method (A_{2i})	ISBS method (B_{2i})	
0	0	42.46	42.46	0	0	0
1	3%	40.42	42.25	4.53%	0.49%	5.06%
2	5%	38.77	40.74	5.08%	4.05%	56.21%
3	7.5%	37.85	39.89	5.39%	6.05%	23.08%
4	10%	36.33	39.42	8.51%	7.16%	10.51%

$$A_{2i} = \frac{\sigma_{M1i} - \sigma_{M0}}{\sigma_{M0}}; \quad B_{2i} = \frac{\sigma_{M2i} - \sigma_{M0}}{\sigma_{M0}}; \quad C_{2i} = \frac{\sigma_{M2i} - \sigma_{M1i}}{\sigma_{M1i}}.$$

A_{2i}: The tensile strength increase percentage of composites at different LDHs contents prepared by simple shear method compared to pure PS material;

B_{2i}: The tensile strength increase percentage of composites at different LDHs contents prepared by ISBS method compared to pure PS material;

C_{2i}: The tensile strength increase percentage of composites at different LDHs contents prepared by ISBS method compared to simple shear method;

σ_{M0}: The tensile strength of pure PS material;

σ_{M1i}: The tensile strength of LDHs/PS composites at different LDHs contents prepared by simple shear method;

σ_{M2i}: The tensile strength of LDHs/PS nanocomposites at different LDHs contents prepared by ISBS method;

methods decreased with increasing the mass fraction of LDHs, this decrease indicate an increase flexibility (plasticity) of the material. With the same LDHs content, the tensile strength of the nanocomposites prepared by ISBS method is higher than that prepared by simple shear method. However, the tensile strength values of nanocomposites produced by ISBS method are higher than those of the composites prepared by simple shear method for each loading of LDHs. This indicates that the weakening effect of the ISBS method on the tensile strength of nanocomposites is smaller than that of simple shear method. The main reason is that the ISBS method can make LDHs disperse better in PS matrix, leading to a reduced weakening effect of LDHs in PS matrix on the tensile strength. A better dispersion result in increase interface between the PS and the LDHs, which reduces the PS chain interactions and may easier PS chains sliding that justified the decrease of the tensile strength [24, 25].

4. CONCLUSIONS

Compared with simple shear method, the LDHs dispersion of LDHs/PS nanocomposites prepared by ISBS method is more homogeneous. The LDHs nanoparticles which the mass fraction is 5 % can be fully dispersed in PS matrix by the ISBS method.

The defoaming of foamed material by a co-rotating twin-screw extruder equiped with a water ring vacuum pump does not cause the dispersed nanoparticles to re-aggregate.

The un-notched impact strength of the nanocomposites prepared by the ISBS method reached a maximum value at LDHs mass fraction of 5 %. The strength increased is 57.29 % greater than that of pure PS and the strength increased using ISBS is 56.21 % greater than strength from simple shear method. The enhanced mechanical properties attributed to the effective dispersion of nanoscale LDHs by ISBS method.

The tensile strength of the nanocomposites prepared by the two methods decreased with increasing LDHs content. With the same LDHs content, the tensile strength of the nanocomposites prepared by ISBS method is higher than that prepared by simple shear method.

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