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Effect of block copolymer coupling agents on properties of mica reinforced polymeric composites

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Abstract In the systems of mica reinforced polymers based on polystyrene and polypropylene, block copolymers polystyrene-b–polyisoprene-b–polyvinyltriethoxysilane (PS-b–PI-b–PVTOSI) and polystyrene–polyvinyltriethoxysilane (PS-b-PVTOSI) were used as macromolecular coupling agents to treat mica. Compared to common coupling agents, e.g. A-174, A-151 and A-1100, such block copolymer coupling agents can much more effectively improve the interfacial adhesion of mica reinforced polystyrene and significantly increase the mechanical properties of the composites. In a certain range, an appropriate increase in the block lengths of polystyrene and polyvinyltriethoxysilane is desirable for the mechanical properties. The introduction of the middle flexible polyisoprene block and the increase in its length are of advantage to the impact strength of the composites. The good compatibility of the matrix polymer and the block copolymer coupling agent is in favor of the improvement in the interfacial adhesion.

Introduction

Particulate filled polymer composites have been used in large quantities in numerous fields of applications for many years because of their extremely advantageous price/volume/performance relations [1]. Some properties of polymers such as rigidity, abrasion performance and heat resistance can be significantly improved with the addition of fillers [2].

Polypropylene and polystyrene are two kinds of widely used polymers. Compared with PP and PE, PS has better surface luster and rigidity. Although it is a brittle polymer, its toughness can be improved by means of the toughened modification such as compounding with elastomer, PP and PE.

Mica plays an important role and takes a considerable proportion of the filler market in plastics because of its unique platy shape. Mica filled polymer composites also extend their applications to fields traditionally occupied by other materials. As well as other inorganic fillers, both the aggregates of particles and the poor interfacial wetting between mica and polymer matrix result in inhomogeneous distribution of the particles, processing problems and insufficient reinforcement with accompanying poor mechanical properties [3].

Considerable efforts have been made to overcome these problems. One frequently used method is to treat mica surface with some types of coupling agents [4–8]. The commonly used coupling agents are silanes, titinates and stearic acid, in which one end can form strong interactions such as chemical bonding and hydrogen bonding with filler surface whereas the other end entangles with polymer molecular chains by physical interactions. For polymers that have functional groups present in their backbone, it is easy to select a coupling agent with a specific organofunctional group with which it will react. However, other polymers e.g. polystyrene and polypropylene have no functional groups present for such coupling agents to react with [3]. So the commonly used coupling agents can't effectively improve the compatibility and interfacial adhesion of mica filled polystyrene composite.

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Table 1 The mechanical properties of the used PP and PS

Matrix polymer	Tensile strength (S.D.) (MPa)	Tensile modulus (S.D.) (MPa)	Flexural strength (S.D.) (MPa)	Flexural modulus (S.D.) (MPa)	Notched Izod impact strength (S.D.) (kJ/m^2)
PS	23.34 (0.63)	1808 (56)	40.66 (0.92)	1945 (54)	6.05 (0.42)
PP	20.63 (1.12)	1179 (65)	31.38 (1.14)	1164 (91)	9.36 (0.49)

In this study, block copolymers polystyrene-b-polyvinyltriethoxysilane (PS-b-PVTOSI) and polystyrene-b–polyisoprene-b–polyvinyltriethoxysilane (PS-b–PI-b–PVTOSI) were used as macromolecular coupling agents to treat mica. The effect of such macromolecular coupling agents on the interfacial adhesion and mechanical properties of mica filled polystyrene and polypropylene composite were investigated.

Experimental

Materials

Polystyrene and PH-88 high-impact polystyrene were supplied by Zhengjiang Qimei Chemical Company Limited China. J746 polypropylene was the product of Plastics of Panjing Petrochemical Complex (China). The mechanical properties of the PP and PS were listed in Table 1. 100 mesh size mica came from Shanghai Humei Chemical Company Limited China.

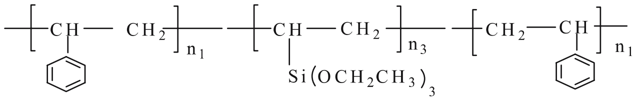
Coupling agent vinyltriethoxysilane (A-151) came from Qiangshengwei Chemical Ltd. China, γ-methacryloxypropyltrimethoxysilane (A-174) andγ-aminopropyltriethoxysilane (A-1100) were supplied by Shanghai Yaohua Glass Company. Styrene and cyclohexane were AR grade and purified before being used. Isoprene was supplied by Sigma-Aldrich Chemie GmbH. Butyllithium was prepared in our laboratory according to the procedure of Xue et al. [9].

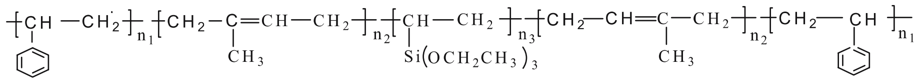
Synthesis of block copolymer

The block copolymers PS-b–PVTOSI and PS-b–PI-b–PVTOSI were synthesized by anionic polymerization, according to the progress described elsewhere [10]. A glass reactor was repeatedly evacuated and purged with pure nitrogen, then heated in 50 °C water bath. 50–100 mL cyclohexane and a known amount of styrene was transferred by an injector respectively. After 10 min the initiator butyllithium was added dropwise, the color of system changed gradually from orange to red. After 30 min the second monomer isoprene dissolved in cyclohexane was added and reacted for 90 min, which step would be omitted if copolymer PS-b–PVTOSI was synthesized. The third monomer A151 was subsequently added and reacted for another 90 min. A coupler *o*-dichlorobenzene dissolved in cyclohexane was fed by the injector and reacted for 30 min, followed by adding an excess water to terminate the reaction. The block copolymer was obtained after being precipitated and purified. The molecular chain length and each block length of the copolymers can be controlled by adjusting the feed molar level and ratio of monomers.

Surface treatment of mica

The mixture of 50 g block copolymer and cyclohexane (the weight fraction of block copolymer is 30%) was mixed with 200 mL water and high speed stirred for 20 min in a BME-100LX emulsifier (made in China), which caused the silane in PVTOSI block to hydrolyze. Then 1000 g mica was placed in a GH-100Y high-speed mixer, followed by adding slowly the above block copolymer solution (the weight fraction of block copolymer is 1.5% with respect to mica) accompanied by stirring. After being adequately mixed for 15 min, mica was removed and dried at 80 °C in an oven for 30 min. when most water and solvent were evaporated the temperature was raised to 110 °C, at which point mica reacted with the block copolymers for 90 min. Finally the treated mica was repeatedly stirred in the high-speed mixer to separate the aggregations formed in the treatment process.





Compounding of mica with polymers

Mixtures of mica, polymers and additives were extruded with a MAPRE GE2.8.30-41twin-screw extruder (Luxembourg) at a screw speed of 160 rev/min and cut into pellets. Each segment temperature of the extruder was maintained at 90, 140, 170, 190, 200, 200, 205, 210 and 205 °C from hopper to die, respectively.

Mechanical testing

The pellets produced in previous step were dried and injection molded with a TTI-80 plastic injection machine (China) to obtain the tensile, flexural and impact specimens, according to China Standard for Testing Methods GB/T 1040-92, GB 1039-79 and GB 1039-79, respectively. The tensile and flexural properties were tested with a CMT4204 universal testing machine (China), the notched Izod impact strength was carried out with a XJU-22 impact tester (China).

Observation of sections

The fractured cross-section of a flexural specimen was covered with gold and observed with a JSM-6360LV scanning electron microscopy (SEM), the product of JEOL Company in Japan.

Results and discussion

Effect of surface treatment of mica on properties of composites

Mica was surface treated by the block copolymer polystyrene-b–polyvinyltriethoxysilane whose feed level of styrene and vinyltriethoxysilane monomer was 0.2 mol and 0.08 mol, then compounded with polystyrene and polypropylene respectively. The mechanical properties of mica reinforced polystyrene and polypropylene composites were tested and showed in Tables 2 and 3.

As be seen in Tables 2 and 3, all the mechanical properties of mica filled polystyrene and polypropylene composites increase to some extent when mica was modified by block copolymer. Especially in the case of polystyrene matrix, the tensile strength reaches to 30.93 MPa that is larger than that of the A-174 treated system by 60%.

The siloxane groups of PVTOSI block of copolymers can hydrolyze to Si-OH, which will form strong interactions e.g. chemical bonds and hydrogen bonds with the hydroxy groups of mica surface; On the other hand, the interactions between matrix polystyrene and block copolymer will be strengthened because their chain interdiffusions and entanglements arise from the same monomeric units of both matrix

Table 2 Effect of surface treatment of mica on mechanical properties of mica reinforced polystyrene composites

Surface treatment of mica	Tensile strength (S.D.) (MPa)	Tensile modulus (S.D.) (MPa)	Flexural strength (S.D.) (MPa)	Flexural modulus (S.D.) (MPa)	Notched Izod impact strength (S.D.) (kJ/m^2)
Untreated	18.22 (0.56)	3947 (180)	35.86 (1.13)	3682 (145)	1.98 (0.24)
A151	19.14 (1.06)	4218 (197)	38.92 (1.90)	3983 (168)	2.19 (0.16)
A1100	19.03 (1.66)	4295 (221)	38.85 (2.05)	3991 (168)	2.13 (0.17)
A174	19.21 (1.62)	4369 (239)	39.37 (2.09)	4007 (182)	2.17(0.24)
Copolymer A$_5$	30.93 (1.92)	4976 (140)	52.54 (2.30)	5371 (232)	2.45 (0.22)

The weight fraction of mica in composite is 20%, the weight fraction of coupling agent is 1.5% with respect to mica

Table 3 Effect of surface treatment of mica on mechanical properties of mica reinforced polypropylene composites

Surface treatment of mica	Tensile strength (S.D.) (MPa)	Tensile modulus (S.D.) (MPa)	Flexural strength (S.D.) (MPa)	Flexural modulus (S.D.) (MPa)	Notched Izod impact strength (S.D.) (kJ/m^2)
Untreated	18.77 (0.92)	1405 (74)	30.25 (1.41)	1231 (118)	7.25 (0.48)
A151	19.32 (0.88)	1469 (72)	33.57 (1.74)	1329 (102)	7.73 (0.61)
A1100	19.28 (1.20)	1477 (70)	33.92 (1.23)	1354 (100)	7.82 (0.52)
A174	19.35 (1.44)	1484 (84)	34.31 (1.29)	1386 (102)	7.85 (0.67)
Copolymer A$_5$	21.79 (1.68)	1560 (117)	37.92 (1.76)	1584 (132)	8.69 (0.75)

The weight fraction of mica in composite is 20%, the weight fraction of coupling agent is 1.5% with respect to mica, matrix resin is type J746 polypropylene polystyrene and PS block. So the copolymer coupling agents improve the compatibility of polymer matrices and mica and the interfacial adhesion between matrices and mica. At the same time, the dispersion of mica in matrix is modified because the mica surface is covered with the copolymer coupling agents. The comprehensive mechanical properties of composites are significantly improved.

When using small molecular silane coupling agents to treat mica surface, the surface energy of mica is decreased and the wettability of polymer matrices on mica is modified. Although the coupling agents can hydrolyze to Si-OH, which results in strong interactions between mica and coupling agents, they can't form strong interactions with matrix. When the interfacial adhesion between mica and matrix is poor, the external load can't be transferred effectively from matrix to mica because of the debonding of mica. The reinforcement of mica is not fully utilized and the improvement of composites is smaller.

In the case of polypropylene matrix, the improvement in properties is lower than that using polystyrene matrix because the compatibility between polypropylene matrix and PS block is worse than that between polystyrene matrix and PS block, the chain interdiffusion and entanglement between polypropylene matrix and PS block is also weaker.

Microstructure of mica filled polystyrene composites

The SEM micrographs of the fractured cross-section of mica filled polystyrene composites were showed in Fig. 1. In the case of untreated mica, micas at the cross-section were not adhered with polymers and the debonding between mica and matrix was clearly observed. It indicates the interfacial adhesion between mica and matrix is poor. However, in the case of mica treated with block copolymer, the section is smooth and the mica surface is covered with polymers. Even the delaminated flake of mica was observed, which indicated the good interfacial adhesion between mica and matrix. So the block copolymers can be used as effective macromolecular coupling agents to improve the interfacial adhesion of composites.

Effect of molecular architecture of block copolymer coupling agent on mechanical properties of composites

For the anionic polymerization, as well be known, the molecular weight of polymers will be higher and the molecular chain is longer when increasing the feed level of monomers under the constant level of initiator. In a block copolymerization, the length of one block is determined with the feed level of its monomer.

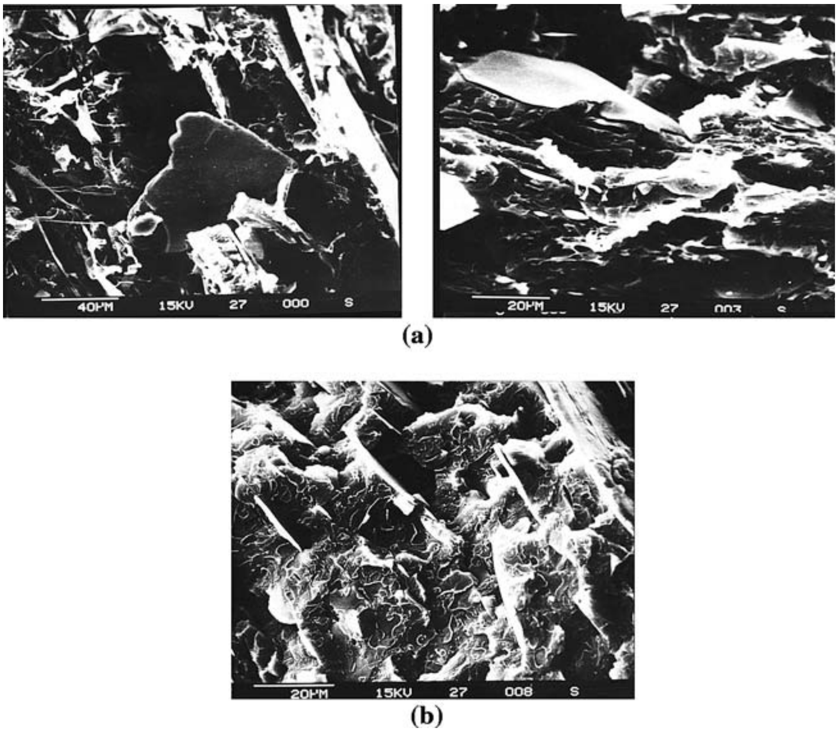


Fig. 1 SEM micrographs of fractured cross-section of mica filled polystyrene composites a. mica untreated b. mica treated with block copolymer A2

Table 4 Feed level of each monomer of block copolymer PS-b–PVTOSI during polymerization

Copolymer	St (mol)	VTOSI (mol)
A1	0.1	0.02
A2	0.1	0.04
A3	0.1	0.08
A4	0.15	0.08
A5	0.2	0.08

Table 5 Feed level of each monomer of block copolymer PS-b–PI-b–PVTOSI during polymerization

Copolymer	St (mol)	Isoprene (mol)	VOTSI (mol)
B1	0.1	0.1	0.02
B2	0.1	0.15	0.02
B3	0.1	0.2	0.02
B4	0.1	0.1	0.04
B5	0.1	0.1	0.08
B6	0.15	0.1	0.04
B7	0.2	0.1	0.04

To study the effect of each block length of copolymer coupling agents on the interfacial modification, a series of copolymer coupling agents were polymerized by changing the feed level of monomers (as be seen in Tables 4 and 5).

The mechanical properties of mica reinforced polystyrene composites were showed in Table 6, in which mica were treated with different block copolymers PS-b–PVTOSI. The results show that the tensile strength and modulus increase almost 10% with the increases in the feed level of styrene monomer from 0.1 mol (A_3) to 0.15 mol (A_4) during the copolymerization of coupling agent. The length of PS block will prolong with increasing the feed level of styrene monomer, accordingly, the chain interdiffusions and entanglements between PS block and matrix polystyrene increase Thus, the interfacial adhesion is further improved and the mechanical properties of composites increase. However, the tensile and flexural strength and modulus change undetectable when the feed level of styrene monomer increases from 0.15 mol (A_4) to 0.2 mol (A_5). For the notched Izod impact strength, the change is unsignificant when the feed level of styrene increases from 0.1 mol (A_3) to 0.15 mol (A_4), even to 0.20 mol (A_5).

With the increase of VTOSI monomer from 0.02 mol (A_1) to 0.08 mol (A_3), all the tensile, flexural strength and impact properties have no significant changes.

Compared composites using A_5 and A_2, the tensile, flexural and impact properties of composite using A_5 are better. This is may be due to the factor that the molecular chain length of A_5 is double to that of A_2. Long molecular chains easily curl to form ‘clew’ structure, which is favor to increase the chain interdiffusion and entanglement between block copolymers and matrix polystyrene.

The mechanical properties of mica reinforced polystyrene composites were showed in Table 7, in which mica were treated with different block copolymers PS-b–PI-b–PVTOSI. The interfacial modification of block copolymer PS-b–PI-b–PVTOSI on mica/polypropylene system is superior to that of block copolymer PS-b–PVTOSI. The introduction of flexible PI block in the copolymer coupling agent can improve significantly the impact property of composites. Moreover, with the increase in the feeding level of isoprene monomer, the impact strength further increases but the tensile and flexural strength and modulus decrease to some extent. PI block in copolymers is a ductile segment; its introduction changes the structure of interlayer in composites. The prolongation of PI block increases the thickness of ductile interlayer between mica and matrix. The ductile interlayer can uniformly disperse the stress at interface and transfer to mica. It can also absorb impact energy to prevent craze propagation and further crack spread. So the toughness of composites and the impact strength increases slightly. However, the ductile interlayer is easy to deform under a stress, so the tensile and flexural properties of composites will be sacrificed with the length of PI block increasing.

For the composites using the block copolymer PS-b–PI-b–PVTOSI, when increasing the feed level of VTOSI monomer from 0.02 mol (B_1) to 0.04 mol (B_4), the tensile and flexural properties improve from

Table 6 Effect of block length of PS-b–PVTOSI on mechanical properties of mica filled polystyrene composites

Copolymer coupling agent	A_1	A_2	A_3	A_4	A_5
Tensile strength (S.D.) MPa	27.96 (1.24)	28.41 (1.15)	27.72 (1.56)	30.26 (1.72)	30.93 (1.92)
Tensile modulus (S.D.) MPa	4452 (330)	4474 (222)	4501 (167)	4954 (220)	4976 (140)
Flexural strength (S.D.) MPa	50.81 (1.87)	51.54(1.93)	49.53 (1.79)	51.98 (1.81)	52.54 (2.30)
Flexural modulus (S.D.) MPa	5186 (213)	5263 (229)	5129 (170)	5246 (205)	5371 (232)
Notched Izod impact strength (S.D.) kJ/m^2	2.38 (0.24)	2.31(0.20)	2.47 (0.26)	2.50 (0.20)	2.45 (0.22)

Conditions as in Table 1

Table 7 Effect of block length of PS-b–PI-b–PVTOSI on mechanical properties of mica filled polystyrene composites

Copolymer coupling agent	Tensile strength (S.D.) MPa	Tensile modulus (S.D.) MPa	Flexural strength (S.D.) MPa	Flexural modulus (S.D.) MPa	Notched Izod impact strength (S.D.) kJ/m^2
B1	30.23 (1.40)	4943 (206)	50.03 (2.11)	5674 (221)	2.55 (0.22)
B2	28.99 (2.05)	4646 (198)	48.86 (1.69)	5627 (163)	2.83 (0.17)
B3	28.41 (1.11)	4618 (154)	48.35 (1.18)	5580 (169)	3.37 (0.24)
B4	31.44 (2.17)	5600 (208)	54.62 (2.14)	5704 (182)	2.69 (0.22)
B5	31.39 (1.65)	5652 (210)	55.14 (1.93)	5729 (203)	2.60 (0.20)
B6	33.67 (1.55)	5791 (181)	58.34 (1.82)	5835 (185)	2.75 (0.27)
B7	33.49 (1.83)	5763 (183)	58.62 (1.99)	5809 (190)	2.71 (0.25)

Conditions as in Table 1

Table 8 Comparison of mechanical properties of mica and glass bead filled polystyrene composites

Filler	Mica	Glass bead
Tensile strength (S.D.) MPa	30.23 (1.40)	24.41 (1.37)
Tensile modulus (S.D.) MPa	4943 (206)	2694 (163)
Flexural strength (S.D.) MPa	50.03 (2.11)	44.38 (2.46)
Flexural modulus (S.D.) MPa	5674 (221)	3047 (149)
Notched Izod impact strength (S.D.) kJ/m^2	2.55 (0.22)	2.08 (0.23)

Block copolymer used to treat fillers is B_1. Conditions as in Table 1

30.23, 4943, 50.03 and 5674 MPa to 31.44, 5600, 54.62 and 5704 MPa, respectively, but the impact strength has no detectable changes. This is because that the interactions between coupling agent with mica become stronger with increasing the length of PVOTSI block. When further increasing the feed level of VTOSI monomer from 0.04 mol (B_4) to 0.08 mol (B_5), all the mechanical properties have no detectable changes. With the increases in the feed level of styrene monomer from 0.1 mol (B_4) to 0.15 mol (B_6), the PS block prolongs and the chain interdiffusions and entanglements with matrix polystyrene increase. The tensile and flexural properties increase to 33.67, 5791, 58.34 and 5835 MPa respectively but the change of the impact strength is slight. However, with increasing the feed level of styrene monomer from 0.15 mol (B_6) to 0.2 mol (B_7), all the mechanical properties of composites have no significant change because that the chain interdiffusions and entanglements between PS block and matrix polystyrene resulting from the prolongation of PS block tend to saturation.

Comparison of mica and other fillers

Two kinds of fillers mica and glass bead were treated with the same block copolymer and compounded with polystyrene, the mechanical properties of obtained composites were showed in Table 8. The results show that the mechanical properties of mica reinforced polystyrene are superior to that of glass bead reinforced polystyrene. The tensile, flexural and impact strength of the mica composite is higher than that of the glass bead composite almost by 20%, the tensile and flexural modulus of the former is higher than the latter above 70%. This is because that mica is a platy reinforcement with fairly high-aspect ratio.

Conclusions

Compared to common small molecular coupling agents, block copolymer coupling agents can much more effectively improve the interfacial adhesion of mica reinforced polystyrene and significantly increase the mechanical properties of composites.

The good compatibility between the matrix polymer and the block copolymer coupling agent is desirable for the improvement in the interfacial adhesion.

During the anionic polymerization of the block copolymers, an appropriate increase in the feed level of styrene and VTOSI monomers is desirable for the mechanical properties of polystyrene composites. The introduction of the flexible block PI and the increase in its length are advantage to the impact strength of composites.

For the polystyrene composites that fillers are treated with the same block copolymer coupling agents, the mechanical properties of mica reinforced polystyrene is superior to that of glass bead reinforced polystyrene.

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