Effect of the Core-Shell Impact Modifier Shell Thickness on Toughening PVC

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The shell thickness of a core/shell impact modifier is found to be the single most important factor in the toughening of rigid polyvinyl chloride (PVC). When the shell thickness is greater than a critical value of 15.8 nm, these core-shell elastomeric particles are able to remain structurally intact and well dispersed within the PVC matrix after melt blending. However, too thick a shell thickness results in a hard core (high modulus) of these core/shell particles and loss of the rubbery nature required of an efficient impact modifier. Therefore, these over-thick particles can act only as rigid fillers, not as efficient rubbery modifiers. On the other hand, when the shell thickness is less than the critical value of 4.9 nm, too thin a shell layer is simply unable to fully protect and cover the inner rubbery core during vigorous processing conditions, and these core-shell particles tend to connect with one another through the partially exposed core to form a cellular-like structure, thus resulting in poor toughening efficiency. Regardless of the particle size, as long as the shell thickness of these core/shell elastomers is between these two critical values (15.8 nm and 4.9 nm), they all display high efficiency in toughening rigid PVC. Polym. Eng. Sci. 44:1885–1889, 2004. © 2004 Society of Plastics Engineers.

INTRODUCTION

Impact modifiers are generally compounded into rigid polyvinyl chloride (PVC) to improve toughness while retaining other critical performance properties necessary to achieve demanding application requirements (1–7). The modes and mechanisms of PVC toughened by various rubbery impact modifiers have been the subjects of intensive investigation in open literature (8–14). Impact modifiers are categorized into the following four types on the basis of manufacturing procedures: 1) core-shell microspheres, 2) block copolymers, 3) modified polyolefins, and 4) others (14). Since Feuer (15) developed the first emulsion-polymerized core-shell MBS in 1958, various core-shell impact modifiers have been leading candidates for toughening rigid PVC. This paper explores the effect of the shell thickness in the core-shell impact modifier on the toughening efficiency of the PVC.

EXPERIMENTAL SECTION

Materials

Various monomers such as methyl methacrylate (MMA), butyl acrylate (BA), butyl methacrylate (BMA), glycidyl methacrylate (GMA), allyl methacrylate (AMA), ethylene glycol dimethacrylate (EGDMA); sodium lauryl sulfate (SLS) as surfactant; and potassium persulfate (KPS) as initiator were obtained from Sigma-Aldrich Corporation and used without further purification. A PVC sample (trade name: H-66) was obtained from China General Plastics Corp. of Taiwan. Heat stabilizer (trade name: OTMR) was obtained from Coin Chemical Industrial Co., Ltd., of Taiwan. It is an organic tin compound; its function is to avoid PVC decomposition in the processing stage. Processing aids (trade name: Paraloid® K-125, K-175) were obtained from Rohm & Haas Company. Acrylic polymers accelerate the gelation of PVC during the processing stage. Processing lubricants—trade named R-1000ZE, R-1200ZG and obtained from Shin Nippon Nontox, Japan—are long chain fatty esters; they function to provide smooth processing.

Syntheses of Core-Shell Impact Modifiers

These core-shell impact modifiers were synthesized by sequential emulsion polymerization, described previously (16, 17). A four-necked one-liter flask equipped

Table 1. Compositions of Core-Shell Impact Modifiers (the Unit Is %).

Exp. No.		1	2	3	4	5	6	7	8	9	10	11	12	13
Stage 1 (core nucleation)	H_2O	112.4	91.6	113.6	114	104.4	104.4	104.4	104.4	104.4	104.4	104.4	104.4	66
	SLS (5%)	2.12	2.5	2.9	3.1	0.8	1.6	4.0	8.0	16	64	64	0.4	102
	BA	17.3	20.4	23.5	25.1	24.6	24.6	24.6	24.6	24.6	24.6	24.6	11.76	39.2
	EGDMA	0.4	0.44	0.48	0.52	0.52	0.52	0.52	0.52	0.52	0.52	0.52	0.24	0.8
	KPS (1%)	5.3	6.3	7.2	7.7	12.6	12.6	12.6	12.6	12.6	12.6	12.6	6.1	20.1
Stage 2 (core glowth)	H_2O	41.44	49.1	56.6	60.4	60	60	60	60	60	60	45.8	63.8	59.7
	SLS (5%)	23.9	28.2	32.6	34.8	35.3	35.3	35.3	35.3	35.3	35.3	25.8	36.9	33.6
	BA	195.1	230.6	266.1	283.8	283.1	283.1	283.1	283.1	283.1	283.1	210.6	296	274
	EGDMA	4	4.7	5.4	5.8	5.8	5.8	5.8	5.8	5.8	5.8	4.3	6.0	5.6
	KPS (1%)	59.7	70.6	81.4	86.9	72.2	72.2	72.2	72.2	72.2	72.2	53.7	75.5	69.9
Stage 3 (shell 1)	H_2O	10.1	15.9	6.16	5.16	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0
	SLS (5%)	5.8	4.7	3.6	3.0	3.1	3.1	3.1	3.1	3.1	3.1	3.1	3.1	3.1
	BA	3.3	3.9	4.52	4.8	4.8	4.8	4.8	4.8	4.8	4.8	4.8	4.8	4.8
	MMA	31.3	24.4	17.4	13.9	13.0	13.0	13.0	13.0	13.0	13.0	13.0	13.0	13.0
	AMA	0.2	0.16	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12	0.12
	BMA	13.5	10.52	7.52	6.0	7.7	7.7	7.7	7.7	7.7	7.7	7.7	7.7	7.7
	KPS (1%)	14.5	11.68	8.84	7.44	12.8	12.8	12.8	12.8	12.8	12.8	12.8	12.8	12.8
Stage 4 (shell 2)	H_2O	28.2	35.4	15.6	12.5	18.4	18.4	18.4	18.4	18.4	18.4	41.36	18.4	16.7
	SLS (5%)	16.4	12.6	9.0	7.2	7.3	7.3	7.3	7.3	7.3	7.3	16.24	7.3	6.6
	MMA	133.6	104	74.2	59.6	59.8	59.8	59.8	59.8	59.8	59.8	133.86	59.8	53.86
	GMA	1.4	1.04	0.76	0.6	0.6	0.6	0.6	0.6	0.6	0.6	1.34	0.6	0.54
	KPS (1%)	40.5	31.5	22.5	18.0	30.2	30.2	30.2	30.2	30.2	30.2	67.2	30.2	27.2

with a mechanical stirrer, a reflux condenser, a nitrogen gas inlet, a temperature controller, and a recorder was used as the reactor. During the first stage polymerization (core nucleation), water and SLS were charged into the reactor and stirred to form a solution. Then, calculated quantities of BA and EGDMA were added. Under nitrogen atmosphere, the mixture was stirred thoroughly for an additional 30 minutes. Afterwards, the reaction temperature was raised to 80°C and a solution of KPS was added into the system. Then, the polymerization reaction proceeded for another 20 minutes. During the second stage polymerization (core growth), the emulsion solution (containing water, SLS, BA, and EGDMA, (EGDMA as crosslinking agent) and solution of KPS were added slowly drop by drop for 150 minutes into the product from the first stage polymerization. The first and second stage are core components, the same as rubber components. In the third stage polymerization (shell 1), the emulsion solution (containing water, SLS, BA, MMA, AMA and BMA; AMA has two different reactivity double bonds, so it can act as a grafting agent for the fourth stage) and a solution of KPS were added slowly drop by drop for 20 minutes into the product from the second stage polymerization. In the fourth stage polymerization (shell 2), the emulsion solution (containing water, SLS, MMA, GMA) and a solution of KPS were added slowly drop by drop for 40 minutes into the product from the third stage polymerization. The reaction was carried out for additional 90 minutes and a latex product was obtained. *Table 1* lists the compositions of all stages carried out in this study.

These resulting latex particles were isolated by using a frozen method, followed by filtration, washing, and drying to obtain the final impact modifier with a core-shell structure.

PVC Mixing/Compounding

Testing specimens were prepared by mixing the desired ingredients (listed in *Table 2*) in a high-speed Henschel Mixer at 80°C, followed by mixing in a two-roll mill at 160°C and then pressed at 160°C in a hot press to yield specimens of 3-mm thickness for Izod impact strength testing.

Characterizations

The latex particle size was characterized using a Nicomp Submicron Particle Sizer (Model 270). The shell thickness was determined as the difference between the particle size of the final stage product and the core

Table 2. Standard Formulation Used for Blending.

Materials	Weights of Addition (Parts)
PVC (K=66)	100
OTMR	2.5
R-1000ZE	1.0
R-1200ZG	0.7
K-125	1.5
K-175	1.0
Impact modifier	8.0

Table 3. Notch Izod Impact Strength of PVC Blend With All Experiments Core/Shell Impact Modifiers.

Exp. No.	Core/Shell wt% Ratio	Final Particle Size (nm)	Shell Thickness (nm)	Notch Izod Impact Strength (Kgf · cm/cm)
1	55/45	296	26.7	15.1
2	65/35	302	20.2	17.9
3	75/25	299	13.7	118.7
4	80/20	314	11.3	119.2
5	78/22	397	15.8	120.3
6	78/22	337	13.4	117.6
7	78/22	238	9.5	120.8
8	78/22	201	8.0	119.2
9	78/22	160	6.4	115.4
10	78/22	91	3.7	9.9
11	60/40	63	4.9	111.6
12	78/22	473	18.8	17.1
13	80/20	65	2.4	4.9

particle size of second stage product. The notched Izod impact strength of the tested specimen was determined by a TMI Impact Tester at 23°C according to ASTM D 256. The morphologies of core-shell impact modifiers within the PVC matrix were characterized by transmission electron microscopy (TEM) on a JEOL JEM-200CX TEM from Japan. The specimen for TEM characterization was an ultra-thin specimen stained with ruthenium tetraoxide (RuO_4) to enhance contrast between phases (18).

RESULTS AND DISCUSSION

Table 3 summarizes the core/shell weight ratio, final particle size, shell thickness, and notched Izod impact strength of the various core-shell modifiers synthesized. Results from *Table 1* and *Table 3* indicate that at a constant emulsifier concentration (experiments 1 to 4), no significant difference is observed in the final particle size of these core/shell impact modifiers. However, the corresponding shell thickness of the core/shell impact modifier decreases as the core/shell weight ratio is increased. On the other hand, by maintaining the core/shell weight ratio constant (experiments 5 to 10), the final particle size and the shell thickness of the core/shell impact modifier decrease as the quantity of the emulsifier is increased during the core nucleation stage polymerization as shown in *Fig. 1*. Therefore, the final particle size and the shell thickness of the core/shell impact modifier can be controlled by adjusting the emulsifier concentration and the core/shell weight ratio during the core nucleation stage polymerization. With similar particle size, the shell thickness decreases with the increase of the core/shell weight ratio (experiments 11 and 13), as would be expected. It appears that the final particle size of the core/shell impact modifier is not dictated by the core/shell weight ratio. *Figure 2* plots the impact strength versus shell thickness of the core/shell impact modifier. The shell thickness of the core/shell impact modifier between 4.9 and 15.8 nm gives ductile impact failure with high impact strength (>115 kgf · cm/cm). If the shell layer of the

core/shell impact modifier is too thick (over 15.8 nm) or too thin (less than 4.9 nm), it loses its toughening efficiency. Within the range of compositions investigated, the particle size of the modifier is not an important factor in determining toughening efficiency, as shown in *Fig. 2. Figure 3* shows TEM morphologies of the core/shell impact modifiers containing different shell thickness within the PVC matrix. *Figure 3A* shows the morphology of the modifier with very thin shell thickness (< 3.7 nm); a cellular-like structure connecting all particles was formed. When the shell thickness is less
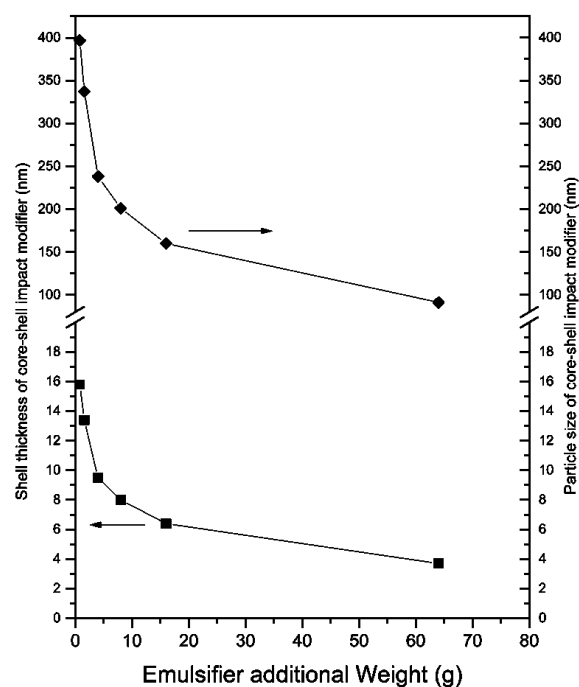

Fig. 1. The effect of emulsifier concentration on particle size and shell thickness of the synthesized core-shell impact modifier. ♦: particle size of core-shell impact modifier and ■: shell thickness of core-shell impact modifier.
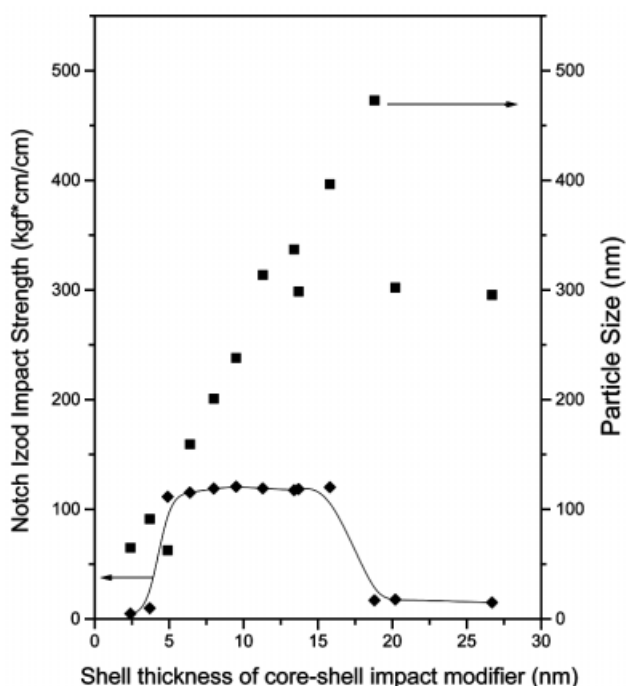
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Fig. 2. Shell thickness of core/shell impact modifier versus impact strength and corresponding particle size. ◆: notch Izod impact strength ■: particle size.

than the critical value of 4.9 nm, the shell layer is too thin to fully protect and cover the inner rubbery core during vigorous processing conditions, and these core-shell particles tend to connect with one another through the exposed core regions to form such a cellular-like structure, thus resulting in poor toughening efficiency. When the shell thickness of the core/shell impact modifier is greater than a critical value (4.9 nm), its core/shell structure remains intact and its distribution is well dispersed within the PVC matrix as shown in *Fig.*

3B. A good dispersion of impact modifier particles is necessary to produce high impact strength in the PVC. When the shell thickness is greater than a critical value of 15.8 nm as shown in *Fig. 3C*, these core-shell elastomeric particles are able to remain structurally intact and well dispersed within the PVC matrix after melt blending. However, if the shell is too thick, a hard core (high modulus) of these core/shell particles results, and the rubbery nature required for an efficient impact modifier is lost. Therefore, these over-thick particles can act only as rigid filler, not as an efficient rubbery modifier. *Figure 4* illustrates morphological diagrams from these three types of core-shell impact modifiers containing different shell thicknesses.

CONCLUSIONS

The shell thickness of a core/shell impact modifier is the single most important factor determining its effectiveness in toughening rigid PVC. When the shell thickness is greater than a critical value of 15.8 nm, these core-shell elastomeric particles are able to remain structurally intact and well dispersed within the PVC matrix after melt blending. However, if the shell is too thick, a hard core (high modulus) of these core/shell particles results, and the rubbery nature required for an efficient impact modifier is lost. Therefore, these over-thick particles can act only as rigid filler, not as an efficient rubbery modifier. On the other hand, when the shell thickness is less than the critical value of 4.9 nm, the shell layer is simply unable to fully protect and cover the inner rubbery core during vigorous processing conditions, and these core-shell particles tend to connect with one another through the exposed regions of the core to form a cellular-like structure, thus resulting in poor toughening efficiency. Regardless of the particle size, as long as the shell thickness of these core/shell elastomers is between these two critical values (15.8 nm and 4.9 nm), they all display high efficiency in toughening rigid PVC.

A
Shell thickness=3.7 nm
Exp. No. 10

B
Shell thickness=6.4 nm
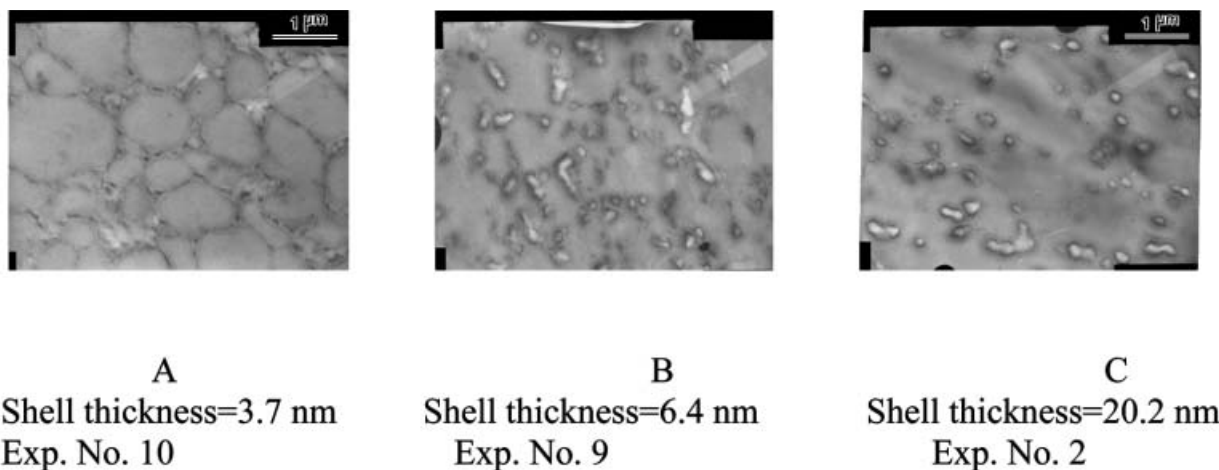Exp. No. 9

C
Shell thickness=20.2 nm
Exp. No. 2

Fig. 3. TEM micrograms of PVC/core-shell impact modifier blends. A: Shell thickness = 3.7 nm, Exp. 10; B: Shell thickness = 6.4 nm, Exp. 9; C: Shell thickness = 20.2 nm, Exp. 2.
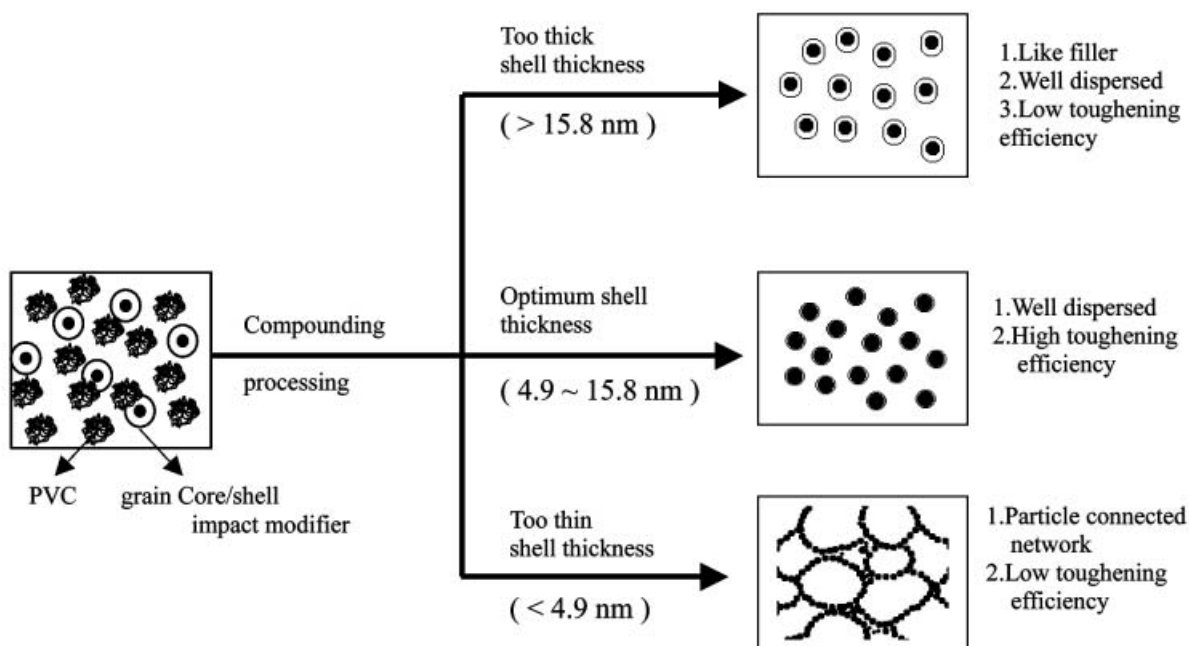
Fig. 4. Schematic morphological diagrams of core-shell impact modifiers containing different shell thicknesses within the PVC matrix.

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