Effect of Styrene-Methyl Methacrylate/Styrene-Butadiene Rubber on Properties of Poly(vinyl chloride)

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Abstract

Generally, poly(vinyl chloride) (PVC) without the addition of plasticizer or impact modifiers is rigid and brittle. The aim of this research was to improve the mechanical properties of PVC using styrene-methyl methacrylate/styrene-butadiene compound (SMMA/SBR rubber) as an impact modifier. The compound was obtained commercially. PVC containing SMMA/SBR rubber having SMMA/SBR contents of 2.5, 5, 7.5 and 10 phrs were prepared using two-roll mill set the conditions as follows: 170°C and 5 minutes. Then, compression molding was carried out to prepare testing samples. FTIR analysis of SMMA/SBR rubber containing PVC samples showed the absorption band at 1732 cm^{-1} (C=O stretching), 3025 cm^{-1} (=C-H stretching) and 636.8 cm^{-1} (C-Cl band). The PVC and SMMA/SBR rubber were compatible due to the specific interaction between carbonyl groups (C=O) of methyl methacrylate and hydrogen atom of PVC CH-Cl group that was confirmed by a slight shift of absorption band of methyl methacrylate carbonyl groups to lower wave number. The effects of SMMA/SBR rubber on mechanical properties, including impact strength and tensile properties were evaluated by standard tests. The impact strength of SMMA/SBR rubber containing PVC increased significantly with an increase in the SMMA/SBR content (ex. SMMA/SBR 5 phr and 10 phr produced impact strengths of 3.30 and 6.38 kJ/m^2 respectively), resulting from the action of SMMA/SBR rubber phase as impact modifier as revealed by SEM images. Furthermore, modulus, tensile strength and elongation at break and plasticizer migration ability were investigated.

Keywords : SMMA/SBR rubber compound, Impact modifier, PVC

Introduction

Poly(vinyl chloride) (PVC) is one of widely used polymers for a varieties of application products such as food packaging and medical applications due to its low cost and good chemical resistance.[1,2] Due to the brittleness characteristic, processing of PVC requires the addition of plasticizer or impact modifier to render PVC flexible. In practice, the additives addition is essential to alleviate the problem of PVC disadvantage, particularly, its low impact strength when compared to other thermoplastics.[3] Enhancement of the flexibility and the impact strength is achieved via adding the plasticizers[4,5] and the usage of the impact modifiers, respectively.[6] There are plenty of impact modifiers that are commercially used in PVC industry such as chlorinated polyethylene (CPE)[7], acrylonitrile-butadiene-styrene (ABS)[1,8] and methyl methacrylate-butadiene-styrene (MBS).[6,9] Fundamentally, the rubber particles dispersed in polymer play an important role in improving toughness property of PVC.[1] Importantly, the good compatibility between PVC and the impact modifier is a must for such property.[4]

In this research, styrene-methyl methacrylate/styrene-butadiene compound (SMMA/SBR rubber) as the impact modifier was employed to improve the toughness properties of PVC. It was believed that PVC and SMMA/SBR rubber were compatible, arising from the interaction between carbonyl groups (C=O) of methyl methacrylate moiety and hydrogen atom of PVC CH-Cl group.[10] Thus, the aim of this research was to investigate the effects of SMMA/SBR rubber content on chemical interaction, mechanical properties and morphology analysis of SMMA/SBR rubber containing PVC.

Materials and Experimantal Procedures

Poly(vinyl chloride) with K value of 58, was the commercial product (SG580 grade) obtained from Thai Plastic and Chemicals Public Company Limited, Thailand. Styrene-methyl methacrylate/styrene-

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butadiene compound (SMBC460 grade) purchased from Global Connections Public Company Limited was used as impact modifier. Additives including zinc stearate and epoxidized oil were provided by Chemmin Corporation Limited.

Preparation of SMMA/SBR rubber containing PVC

PVC resin was mixed with SMMA/SBR rubber at loadings of 2.5, 5, 7.5 and 10 phrs using two-roll mill (LRM-S-110/3E) at 170°C for 5 minutes. Then, the compounds were ground and mold into sheet by compression molding (LP-S-50) at 185°C under pressure of 50 bar. The compressed sheets were cut into required shape to prepare standard specimens for mechanical testing. The formulations of SMMA/SBR rubber containing PVC were presented in Table 1.

Table 1. Formulations of SMMA/SBR rubber containing PVC (unit of phr)

Sample code	PVC	SMMA/SBR rubber	Zinc Stearate	EPO
PVC	100	-	2	10
C2.5	100	2.5	2	10
C5	100	5	2	10
C7.5	100	7.5	2	10
C10	100	10	2	10

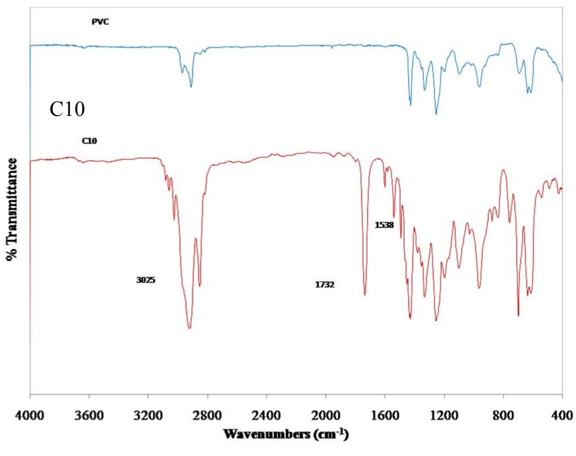

Figure 1. Representative FTIR spectra of PVC and C10

Characterization and properties evaluation of SMMA/SBR rubber containing PVC

FTIR spectra were recorded in the range of 400-4000 cm^{-1} by FTIR spectrometer (Nicolet 6700 FT-IR). The fracture surface after impact testing was observed using a scanning electron microscope (JSM-6400, JEOL). Prior to the testing, samples were exposed to vapor of 1% w/w OsO_4 solution overnight and then, coated with gold and sticked to SEM stub. For mechanical testing, the notched Izod impact tests were carried out according to ASTM D256 standard method with energy of hammer 5.5 J by impact testing machine (GT-70-MDH). The dimension of notched Izod impact specimens was 12.7×60×3.2 mm^3 with notched depth of 10 mm. The average values were computed from results from 10 tests on each sample. Tensile properties were determined in accordance with ASTM D638 standard method by using universal testing machine (LLOYD LR 100K). Crosshead speed of 50 mm/min with 10 kN load cell was used at ambient temperature of 25°C. The samples were cut to dumbbell shape with 3 mm thickness. The five samples were analyzed for determination of the modulus, tensile strength and elongation at break.

Plasticizer Migration testing

Thin sheets of plasticized PVC and polystyrene (approximately 3 mm × 3 mm (width × length) and thickness was 1 mm were prepared. Then, PS sheet was sandwiched between two plasticized PVC sheets. The sandwiched sample was kept for a week in an oven set the temperature of 50°C to allow the migration of plasticizer. Due to the migration ability of plasticizer, plasticized PS was anticipated. The plasticization of PS was evaluated by the determination of PS Tg using differential scanning calorimetry (DSC) method.

Results and Discussion

FTIR analysis

Figure 1 shows spectra of PVC and C10. PVC exhibits the strong peak at 614 cm^{-1}, corresponding to the C-Cl bonding. Considering the FTIR spectra of SMMA/SBR rubber containing PVC, the absorption bands observed at1538 cm^{-1}, 1732 cm^{-1} and 3025 cm^{-1} are assigned to C=C benzene ring stretching, C=O stretching and C=C-H stretching, respectively. The slightly shift of absorption peak of carbonyl group (C=O) of methyl methacrylate from 1735 to 1732 cm^{-1}[(11)], corresponding to hydrogen bonding between these carbonyl groups and PVC which is indicative of the compatibility between the additives and PVC matrix.[(12)]

Tensile properties

The tensile properties including modulus, tensile strength and percent elongation at break of PVC and SMMA/SBR rubber containing PVC specimens are presented in Table 2. As found, PVC has modulus of 3.61 GPa and tensile strength of 81.12 MPa, respectively which is considered to be rigid materials. The addition of SMMA/SBR rubber causes a noticeable decrease in modulus and tensile strength due to the presence of rubber phase. On the contrary, the elongation at break increased with an increase in the SMMA/SBR rubber content, as a result of the effect of rubber particle. In this case, rubber particles acted as centers of stress raisers where stress is concentrated.(1)

Table 2. Tensile properties of PVC and SMMA/SBR rubber containing PVC

Sample code	Young's Modulus (GPa)	Tensile Strength (MPa)	Elongation at Break (%)
PVC	3.61 ± 0.04	81.12 ± 0.85	6.31 ± 0.81
C2.5	3.52 ± 0.07	73.43 ± 1.38	7.74 ± 1.46
C5	3.37 ± 0.01	69.15 ± 0.59	8.03 ± 0.36
C7.5	3.34 ± 0.08	65.87 ± 1.23	9.26 ± 2.07
C10	3.02 ± 0.19	60.99 ± 1.54	10.95 ± 1.25

Impact strength

The notched Izod impact strength of PVC and SMMA/SBR rubber containing PVC are shown in Figure 2. The nature of PVC is that it has low impact strength (0.28 kJ/m^2). The addition of SMMA/SBR rubber improved the impact strength of PVC, confirmed by a significant increase in impact strength values with an increase in SMMA/SBR rubber content. In case of 10 phr SMMA/SBR content, the maximum value of impact strength of 6.38kJ/m^2 is achieved. As a result, the rigid PVC is able to be toughened by the addition of elastomeric rubber phase.(8) The effect of SMMA/SBR rubber phase as an impact modifier is understood to act as the energy absorber for PVC matrix.(1,13) In addition, the good compatibility between PVC matrix and rubbery phase, referring to SEM micrographs (Figure 3) contributes to the enhancement of the impact strength of PVC.

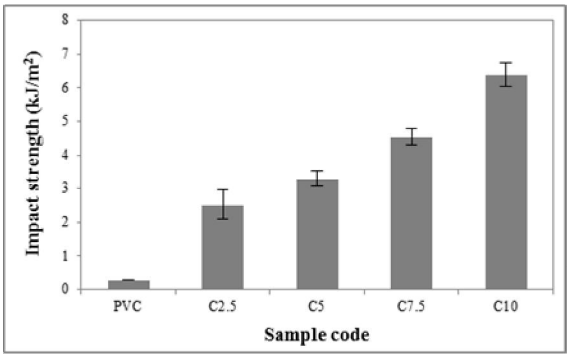

Figure 2. Impact strength of PVC and SMMA/SBR rubber containing PVC

Morphology analysis

Prior to the morphology observation, the samples were exposed to vapor of 1% w/w OsO_4 solution to eliminate rubber double bonds. The SEM images (Figure 3) show the fractured surface of PVC and SMMA/SBR rubber containing PVC. Fractured surface of PVC (Figure 3a) has a smooth surface, indicating typical rigidity and brittleness characteristic.(8,13,14) In contrast, the fracture surface of SMMA/SBR rubber containing PVC (Figure 3f) exhibits irregular surface with holes representing cavity after rubber phase removal.(14) In case of the compounds prepared with 2.5 and 5 phr of SMMA/SBR rubber contents (Figure 3b and 3c) the rough surface with small microvoids are observed. An increase in SMMA/SBR content from 7.5 to 10 phr (Figure 3d and 3e) resulted in the fractured surface that exhibited prominent roughness with the large and plenty of microvoids. The coarse surface morphology after being fractured exhibited ductile failure behavior. This behavior correlated well with the results obtained from the impact strength testing.(13)

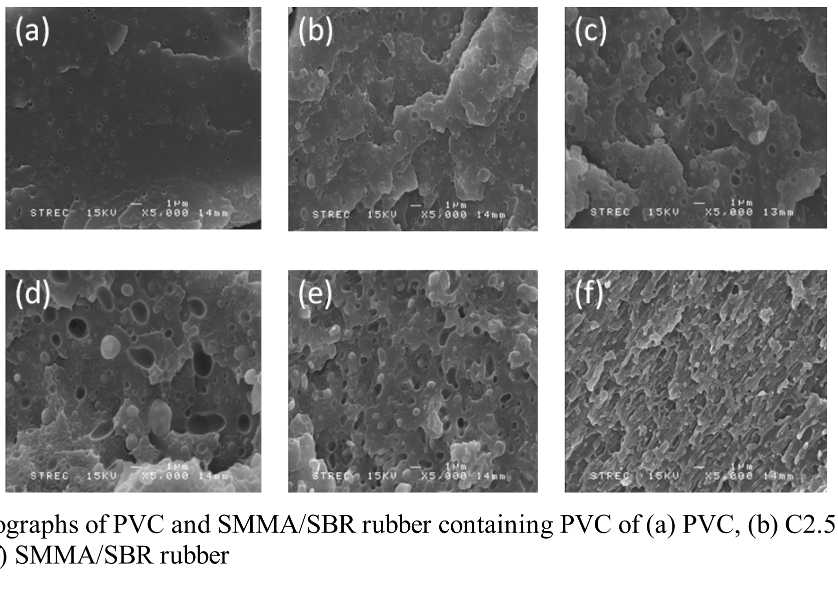

Figure 3. SEM micrographs of PVC and SMMA/SBR rubber containing PVC of (a) PVC, (b) C2.5, (c) C5, (d) C7.5 (e) C10 and (f) SMMA/SBR rubber

Migration ability of plasticizer

Migration of plasticizer (DINP) was detected using differential scanning calorimeter (DSC). During migration testing, plasticizer slowly migrated from PVC to PS, resulting in plasticized PS. As a result, T*g* of plasticized PS was shifted to lower temperature which was determined by DSC. In this study, the effect of DINP contents (R0P5, R5P5 and R5P10) on the T*g* was investigated.

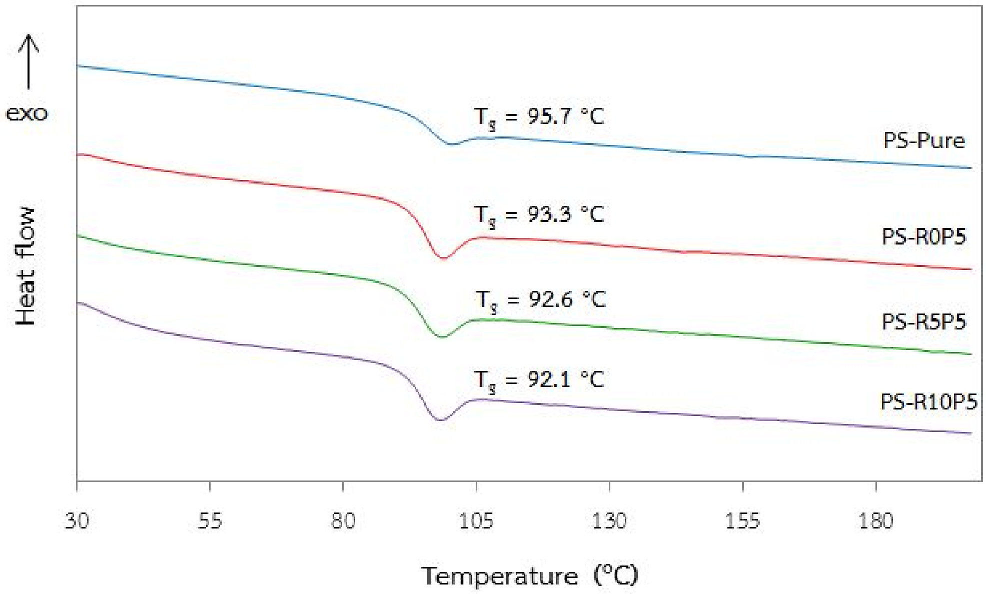

Figure 4. DSC thermogram of plasticized PS.

Figure 4 shows T_g of PS with various plasticizer contents. The T_g of neat PS is found at 95.7°C. For plasticized PS, T*g* values of PS-ROP5, PS-R5P5, and PS-R10P5 are 93.3°C, 92.6°C, and 92.1°C, respectively. A decrease in T*g* of PS with an increase in the amount of DINP in PVC indicates that the plasticizer migration ability is related to its content in PVC; the more the content of DINP the higher the migration rate. When compared to plasticized neat PVC, The migration ability of DINP in PVC containing SMMA/SBR rubber is relatively faster. This is due to the fact that DINP migration ability in the interphase was faster than those DINP in PVC matrix. Therefore, the usage amount of DINP addition into PVC/SMMA/SBR compound should be kept minimum as low as possible without the compromise of processing difficulty.

Conclusions

PVC/SMMA/SBR compounds were prepared via two-roll mill and formed by compression molding. The disadvantage of PVC which is low impact strength was overcome by the addition of SMMA/SBR compound as an impact modifier. Regarding the mechanical properties, the modulus and tensile strength decreased with the increase of SMMA/SBR rubber content, whereas the elongation at break automatically increased. The notched Izod impact strength of SMMA/SBR rubber containing PVC compound increased significantly with an increase in the SMMA/SBR content and the highest impact strength was 6.38 kJ/m^2 when 10 phr of SMMA/SBR rubber was loaded. The morphology observed by SEM correlated well with mechanical properties. The PVC and SMMA/SBR rubber were compatible due to the specific interaction between carbonyl groups (C=O) of methyl methacrylate and hydrogen atom of PVC CH-Cl group that was confirmed by a slight shift of absorption band of carbonyl groups of methyl methacrylate to lower wave number. The migration ability of DINP in PVC containing SMMA/SBR rubber was relatively faster than those in neat PVC due to the fact that DINP migration ability in the interphase was faster than those DINP in PVC matrix. It is, therefore recommended that the usage amount of DINP addition into PVC/SMMA/SBR compound should be kept minimum as low as possible without the compromise of processing difficulty.

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