

Article

Characterizations of Poly(vinyl chloride)/Acrylonitrile Styrene Acrylate Blends for Outdoor Applications

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Abstract. Significant enhancement on impact property of poly(vinyl chloride)/acrylonitrile styrene acrylate (PVC/ASA) blends was observed. The effect of ASA content on mechanical characteristics, including impact strength, thermomechanical properties, water absorption, and outdoor weathering durability were investigated. The results suggested that the impact strength of the PVC/ASA blends increased drastically at the ASA content of about 30-40 wt% and at the ASA content of 50 wt%, the significant high impact strength of up to 77.6 kJ/m² was obtained. The modulus and strength under tensile and flexural loads of PVC/ASA blends were found to increase with the PVC fraction while glass transition temperature of PVC and heat deflection temperature of the blends systematically increased with increasing ASA content. The blends are partially miscible in nature as evidenced from the shift of the two glass transition temperatures towards each other in the dynamic mechanical analysis. In addition, ASA fraction in the blends provides improved resistance to UV radiation for the PVC/ASA blend sample under natural weathering. The obtained PVC/ASA blends clearly showed a potential use as high impact plastic products for outdoor application.

Keywords: Polymer blends, impact strength, thermomechanical property.

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1. Introduction

Currently, poly(vinyl chloride) (PVC) belongs to the widely used commodity polymers, especially in house construction, medical, food packaging, housekeeping, sewer system, electrical wires and cables as well as automotive industries. PVC has been utilized extensively due to a relatively low price, widely developed processing, mechanical property modification and environmental resistance by incorporation of varied additives [1-3]. This is the reason for standing growing production and application of this polymer. Recently, PVC becomes highly attractive for products in building and construction market by an incorporation of natural fibers to form PVC wood composites [4-8]. However, compared to other commodity thermoplastics, PVC has a disadvantage of being inclined to occasional brittleness and is notch sensitive [9-11]

To gain more flexibility with enhanced impact strength of PVC, impact modifiers are used as additives for various applications. Operations such as chemical modification, compounding or blending with conventional polymers have been generally regarded as the means of adjusting or producing a desired property balance of PVC. If properly directed, these methods can be a convenient way of developing materials with novel or selectively enhanced properties which are possibly superior to those of the starting components [12, 13]. By blending an elastomeric component into PVC, it is possible not only to toughen the PVC but also enhance other properties of the polymer according to the type and quantity of modifier used. One notable example is blends of PVC with styrenic polymer such as acrylonitrile-butadiene styrene (ABS) terpolymer which is a compound with highly balanced properties of impact strength, stiffness, and processability or with methacrylate-butadiene-styrene (MBS) copolymers [14]. In case of the PVC blended with ABS [6,15], the result is a material having remarkable enhancement in impact strength and toughness with inherent flame resistance. The obtained impact property was also reported to be superior to those of the individual components [6, 12, 13, 16]. Furthermore, the inherent flame retardancy of PVC, due to the presence of chlorine in large quantities in the polymers, makes it suitable for applications where the more expensive flame retarded ABS could not be employed [17]. This blend has recently been reported to show substantial affinity with natural fiber and is a good candidate for a matrix of natural fiber composites with outstanding impact strength [6].

However, an addition ABS into PVC tends to cause lower weathering durability of the PVC [18, 19]. When the PVC-based polymer blend is used for long period in outdoor applications or under fluorescent light, photo-yellowing or deterioration of properties will occur. Discovering weathering resistant impact modifiers for PVC becomes a more significant research field. Ethylene propylene diene monomer (EPDM) and acrylic modifiers are weathering resistant impact modifiers for PVC, while MBS and ABS are not because the major drawback for these polymers is that the residual double bond in the butadiene is readily attacked by ultraviolet light, so these polymers cannot be used for outdoor applications [20]. Although acrylic modifiers are durable to weathering, they impart low thermal stability to PVC. Therefore, in this study, a more preferable impact modifier of PVC for an outdoor application is acrylonitrile styrene acrylate copolymer (ASA) which has a two-phase thermoplastic material, comprising a acrylonitrile-butadiene styrene (SAN) matrix with acrylate rubber particles dispersed with SAN inclusions. The presences of the rubber particles help enhance fracture toughness by fracturing after crazing and yielding [7, 21]. The rubber component of ASA is far more thermally stable than the polybutadiene in ABS. This is a significant characteristic particularly for the blend system that might experience high processing temperatures. Additional advantage of ASA copolymer compared to ABS terpolymer is its enhanced weatherability compared to ABS due to excellent discoloration resistance and anti-aging performance [22, 23].

As a consequent, the aim of this paper is to investigate the effect of ASA contents on PVC/ASA blend properties. It is expected that blends of PVC with ASA might provide similar enhancement on impact strength as ABS with minimized color change of the sample due to superior weathering durability of the ASA to ABS. Major properties include mechanical properties i.e. impact, tension, and flexure properties, dynamic mechanical properties, and water absorption of the PVC/ASA blends will also be characterized as the information on these properties of the blends is very scarce and receives little attention. The blend is expected to replace PVC/ABS matrix recently reported to impart outstanding impact strength to its composite with natural fiber.

2. Experimental

2.1. Materials

Poly(vinyl chloride), PVC, grade 258RB with K -value = 58, degree of polymerization about 680 and bulk density-compaction of 0.56 kg l^{-1} compounded with stabilizer, processing aid, and external lubricant in high speed mixer in order to allow ease of PVC handling and further processing. The PVC was obtained from Vinythai Public Co. Ltd. (Rayong, Thailand). Internal lubricant (Loxiol P1141) was supported by Siam Chemical Solutions Co., Ltd. (Bangkok, Thailand). Extrusion grade acrylonitrile styrene acrylate (ASA) resin as an impact modifier for PVC, KIBILAC PW-997S, was purchased from Global Connections Co., Ltd. (Samuthprakarn, Thailand). It was suitable for extrusion application with high impact performance including construction and automobiles.

2.2. Preparation of PVC/ASA Blends

PVC dry blend was blended with ASA pellet ranging from 0-50 wt% of ASA content by two-roll mills with 0.125 mm gap at various temperatures of 160, 170, and 180°C for 6 minutes to yield a homogeneous blends. The two-roll mills with 0.125 mm gap at a mixing temperature of 170°C for 6 min was used to provide a homogeneous blend mixture. The obtained PVC/ASA compound was then preheated for 3 min and pressed into sheet by a compression molding machine from Labtech Engineering Co., Ltd (Samuthprakarn, Thailand) at 170°C and pressure of 15 MPa for 4 min. The compression-molded sheet was then cut into desired shapes for further property evaluations.

2.3. Characterizations of PVC/ASA Blends

Density of PVC/ASA blends was measured by a water displacement method (ASTM D792) with equipments consisted of Mettler Toledo Balance and density kits from Mettler-Toledo (Thailand) Co., Ltd. (Bangkok, Thailand). The samples were **disk shape** with a 3 mm thickness. Notched Izod impact test was performed on an impact tester following ASTM D256 from Yasuda Seiki Seisakusho, Ltd. (Hyogo, Japan). Tensile and flexural properties of the **blends** were measured using a universal testing machine from Instron Engineering Co. (Massachusetts, United States), model 5567 according to ASTM D638 and ASTM D790. Five replicated samples of each composition were tested for tensile and flexural properties while the impact strength value of twelve replicated samples was determined. The resulting average data as well as their standard deviation were reported. A dynamic mechanical analyzer (DMA) model DMA242 from Netzsch, Inc. (Bavaria, Germany) was used to investigate viscoelastic properties of all specimens in the flexure geometry at 1 Hz with a strain amplitude of 30 μm and at a heating rate of 2°C/min from 30°C to 150°C using a sample size of 10 mm \times 50 mm \times 2 mm.

Heat distortion temperature (HDT) determined according to ASTM D648 is the temperature at which the sample has a specified bending. The samples with the dimension of 13 mm \times 127 mm \times 3 mm are heated at a constant heating rate of 120°C/hr while a bending load is applied until they deflect to 0.25 mm. In this test the temperature at which a sample has a specified bending under influence of a constant load of 0.45 N/mm² is determined. The vicat softening temperature is the temperature at which a flat-ended needle penetrates the sample to the depth of 1 mm under a specific load. A test sample was placed in the testing apparatus so that the penetrating needle rested on its surface at least 1 mm from the edge. A load of 50 N was applied to the sample. The samples having dimension of 20 mm \times 20 mm \times 3 mm are heated up at a constant heating rate of 50°C/hr while a bending load is applied until the needle penetrated 1 mm following ASTM D1525.

Water absorption test was conducted in accordance with ASTM D 570. Before testing, the weight of each sample was measured. Three samples in a form of disk having a 50.8 mm diameter and a 3.2 mm thickness of each blend were submerged in distilled water at 25°C. Samples were removed at certain periods of time, blotted to remove the excess water on the surface and immediately weighed. Based on the initial mass and the dimension of each sample, the mass and the dimension of the samples after immersed in water was calculated.

Contact angle measurement was performed at room temperature using a contact angle meter model Cam-Plus Micro equipped with an optical microscope from Tanteq A/S (Lunderskov, Denmark). The

measured liquid was deionized water with a droplet radius of 10 μm . Contact angle of each sample was averaged from 10 measured values.

The specimens with a shape of 20*20*3 cm (width*length*thickness) are exposed in the natural outdoor weather in Rayong Province, Thailand for 30 days (during December 18th 2010 to January 18th 2011). The effect of ASA contents on weatherability of PVC/ASA blends was studied by the variation of color difference.

Color change measurement originally resulted from the consolidation of separately published methods for instrumental evaluation of color differences. The total difference, ΔE_{ab}^* , between two colors each given in terms of lightness (L^*) and chromaticity coordinate (a^* and b^*) is calculated following ASTM D 2244 by Ultrascan Pro spectrometer from Hunter Associates Laboratory, Inc (Virginia, United States), which measures both reflected and transmitted color and meets CIE (International Commission on Illumination) standard.

3. Results and Discussion

3.1. Impact Strength of PVC/ASA Blends

The effects of ASA content ranging from 0wt% to 50wt% on notched Izod impact strength at room temperature (28°C) of PVC/ASA blends are presented in Fig. 1. To obtain high quality samples, density measurement is highly crucial for screening qualified sample before further tests as several tests particularly mechanical tests are highly sensitive to void or defects present in the samples. The density of the PVC/ASA blends tended to decrease with an increase of the ASA fraction. The density of the PVC/ASA blend as increasing ASA content to 10, 20, 30, 40 and 50wt% was determined to be 1.33, 1.30, 1.26, 1.22, and 1.19 g/cm³, respectively. These results were also well predicted by a rule of mixture calculated based on the measured density of the PVC of 1.36 g/cm³ and the density of the ASA of 1.07 g/cm³. This good agreement between the measured and the theoretical density values suggested negligible amount of void in the blend samples implying suitable blending condition used in this investigation. Therefore, in the Fig. 1, we can see that the neat PVC exhibited a notched Izod impact strength value of 6.8 ± 0.5 kJ/m² whereas that of ASA was around 47.0 ± 3.1 kJ/m². Interestingly in PVC/ASA blend systems, the impact strength of the blends with a maximum value as high as 77.6 ± 4.0 kJ/m² was obtained at ASA content of 50wt%. The impact strength was observed to increase with an increase of ASA content up to 50wt%. The remarkable improvement of impact strength of the PVC/ASA blends was due to an ability of ASA to form optimal energy dissipation phase morphology i.e. co-continuous phase, with the PVC in the polymer blend [24]. When the polymer blend was subjected to an external stress, the elastomeric phase as acrylate rubber in ASA can be able to effectively initiate and terminate crazes. With this crazing, energy was transformed into deformation of the rubber particles in the ASA followed by the formation of voids in the rubber phase itself. However, further deformation can effectively be stopped by other rubber particles [21]. As also seen in Fig. 1, the impact strength increased slightly when ASA content was less than 30wt% and the sharp increase in impact strength was observed with ASA content greater than 30wt%. The point of drastic change in impact strength of the PVC/ASA blend systems is called a brittle-ductile transition.

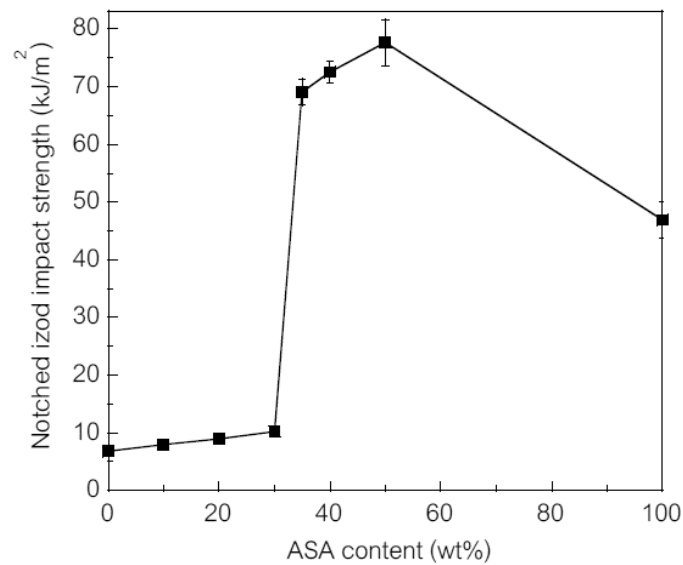


Fig. 1. Notched Izod impact strength of PVC/ASA blends at various ASA contents.

In our research, ASA content is a major factor that induces the brittle-ductile transition. At the ASA contents of 0-30wt%, the impact strength was low and brittle fracture was observed with little stress whitening zone as shown in Fig. 2. Beyond 30wt% of the ASA, ductile fracture with a pronounced stress whitening zone can be clearly seen. Stress whitening is the phenomenon possibly resulted from crazing in the matrix, internal cavitation of the rubber particles or debonding at the matrix-particle interface [25]. This transition behavior in impact strength of our PVC/ASA blend was also observed in other particle toughened polymers [25-28]. Sharma and coworkers [26] reported that the maximum impact strength can be achieved in this kind of polymer blend at the critical volume fraction of the elastomer phase. However, when this critical elastomer content is exceeded, impact strength drops. At the peak value of impact strength, optimum balance between sufficient elastomer content and the preferred combination of toughening mechanisms such as multiple crazing with interacting shear deformation might be attained.

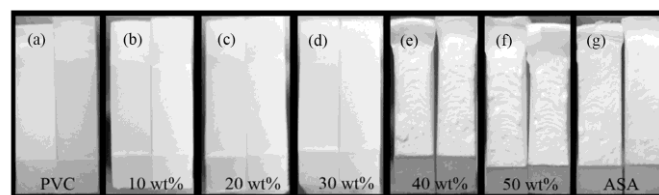


Fig. 2. Fracture surface of PVC/ASA samples after notched Izod impact tests with different ASA content.

3.2. Tensile and Flexural Properties of PVC/ASA Blends

In general, mechanical properties particularly strength of polymer blend were reported to be largely dependent on good interfacial adhesion between the component polymers of the blend. In this work, the tensile and flexural properties of PVC/ASA blends with various ASA contents are reported in Fig. 3. In the case of tensile properties, we can see that the tensile modulus of PVC was found to be 2.18 ± 0.05 GPa whereas that of ASA was 1.57 ± 0.02 GPa. As the PVC content increased, tensile modulus of PVC/ASA blends was found to systematically increase suggesting that PVC contributed to an improved stiffness of the blend. The behavior was found to follow a rule of mixture. Similar observation was also reported in PC/ABS blend [24, 27], PVC/ABS blend [29]. Furthermore, our PVC exhibits tensile strength of 53.0 ± 0.3 MPa

which is substantially higher than that of ASA (38.0 ± 0.9 MPa). The tensile strength of the PVC/ASA blends rendered the values between that of neat PVC and neat ASA as also being predicted by a rule of mixture. Similar behavior was also observed in the PVC/ABS blend [6], PC/ABS blend [27], PC/ASA/SAN blends [28] and HDPE/UHMWPE blends [30]. However, negative deviation in tensile strength was observed in PET/ASA system which was reported to be rather incompatible (poor interfacial interaction) in nature [31]. Lastly, the tensile elongation of the PVC/ASA blend was found to be enhanced with increasing the PVC fraction from $13 \pm 5\%$ at 50wt% PVC content to $84 \pm 24\%$ at 90wt% PVC while those of the neat PVC and the neat ASA were determined to be $113 \pm 29\%$ and $6 \pm 1\%$, respectively.

The flexural properties of the PVC/ASA blend systems at varied ASA content is also reported in Fig. 3. From the figure, the modulus and strength of the blend samples under flexural load of the PVC/ASA blends showed a similar trend to that of tensile modulus and strength. The flexural modulus of the blend systems was found to increase from 2.73 ± 0.05 GPa at 50 wt% PVC content to 3.00 ± 0.06 GPa at 90 wt% PVC content due to the higher rigidity of the PVC while those of the neat PVC and the neat ASA were determined to be 3.20 ± 0.08 GPa and 2.23 ± 0.04 GPa, respectively. In case of flexural strength, the PVC/ASA blends at various blending ratios exhibited the flexural strength at 79.0 ± 1.6 MPa for the blend containing 10 wt% ASA. With increasing ASA content, the flexural strength decreased to 69.0 ± 0.3 MPa for the blend containing 50 wt% of the ASA while the flexural strength of the PVC and the ASA was determined to be 87.0 ± 1.0 MPa and 63.0 ± 0.6 MPa, respectively. From the result, the effect of the ASA content on PVC/ASA blends tended to follow the additivity rule.

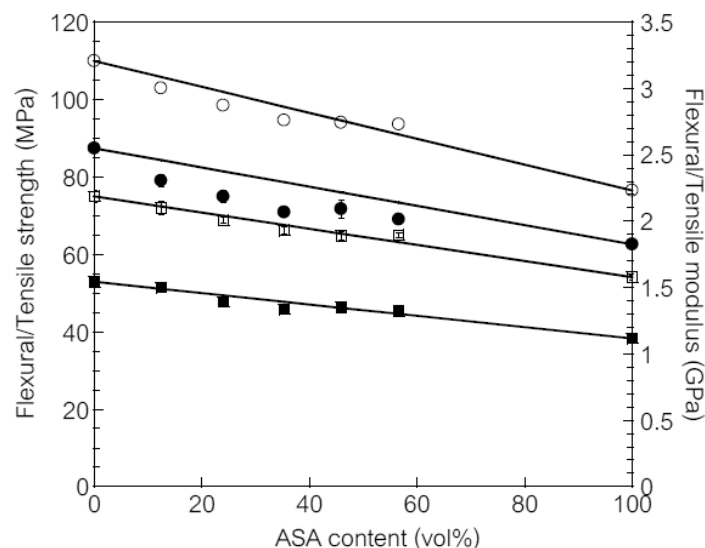


Fig. 3. Tensile (square marker) and flexural (triangle marker) properties of PVC/ASA blends at various volume contents of ASA; Opaque and transparent markers are the strength and modulus, respectively.

3.3. Thermomechanical Properties of PVC/ASA Blends

Figure 4 exhibits storage modulus (E') as a function of temperature of the PVC/ASA blends. From this figure, storage modulus at room temperature (30°C) of PVC was determined to be 2.90 GPa while that of ASA was about 1.87 GPa as shown in inset to Fig. 4. The higher storage modulus at room temperature of the neat PVC with more rigidity segment compared to that of the ASA is consistent with those of tensile and flexural test discussed in the previous section. Furthermore increasing the amount of ASA in PVC from 0 wt% to 50 wt% tended to insignificantly decrease in storage modulus of the blends from 2.90 GPa to 2.50 GPa. However, as heating continued in the DMA test, an incorporation of the ASA into the PVC was observed to lose their rigidity at elevated temperature less readily than the PVC. The greater change in slope in the glassy state of the modulus curve vs. temperature of ASA compared to PVC is one parameter indicating better thermal stability of the PVC blended with ASA. The enhancement in thermal stability of the blends was thus obtained due to the superior thermal stability of the ASA to the PVC.

The temperature dependence of the loss tangent ($\tan \delta$) peak of PVC/ASA blends at different ASA content is illustrated in Fig. 5. Glass transition temperature ($T_{g,DMA}$), which indicates the interaction between the ASA and the PVC, were determined from the peak position of the $\tan \delta$ thermograms. The $T_{g,DMA}$ of the neat PVC and the neat ASA were found to be 96°C and 121°C , respectively. For the PVC/ASA blends, heavily overlapped with only one dominant peak was observed when ASA content in the blends is less than 30 wt%. However, when the ASA content was greater than 30 wt%, two clearly separated peaks of the PVC-rich phase ($T_{g,1}$) and of the ASA-rich phase ($T_{g,2}$) existed. This might also explain the sharp increase in impact strength of the blends at about 30 wt% of the ASA. Furthermore, the positions of both peaks tended to shift towards each other in the obtained polymer blends. Normally, the shifting of T_g s of two individual components towards each other means the improved compatibility while the final single broad relaxation denotes the complete compatibilization. The ratio of the T_g shift is related to the degree of component mixing. The similar shifting in T_g has also been reported in PVC/ABS [6] and PC/ABS systems [24, 27].

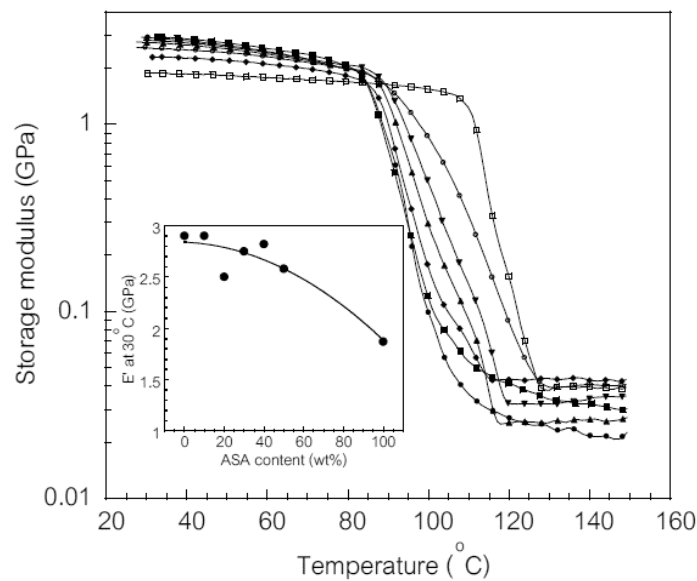


Fig. 4. Storage modulus of PVC/ASA blends at various ASA contents: (●) PVC, (■) PVC/ASA 90:10wt%, (◆) PVC/ASA 80:20wt%, (▲) PVC/ASA 70:30wt%, (▼) PVC/ASA 60:40wt%, (○) PVC/ASA 50:50wt%, (□) ASA.

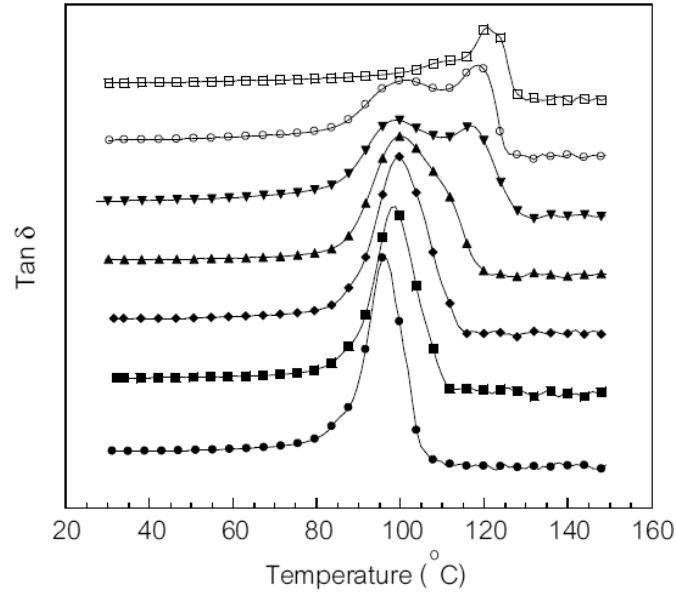


Fig. 5. Loss tangent of PVC/ASA blends at various ASA contents: (●) PVC, (■) PVC/ASA 90:10wt%, (◆) PVC/ASA 80:20wt%, (▲) PVC/ASA 70:30wt%, (▼) PVC/ASA 60:40wt%, (○) PVC/ASA 50:50wt%, (□) ASA.

In Fig. 6, the $T_{g,s}$ from DMA experimental of the PVC/ASA blends are depicted. From the figure, the $T_{g,1}$ was found to increase from 96°C to 102°C with the increase of ASA content in range of 0 wt% to 50 wt% while $T_{g,2}$ was found to shift to lower temperature from 121°C at the blend composition of 100 wt% of ASA to 112°C at that of 30 wt% of ASA. The possible reason for increasing in $T_{g,1}$ about 2-6°C is due to some part that is SAN (styrene-acrylonitrile) of ASA segment will disperse into PVC's domain and the incorporation of ASA chains into PVC chains might provide an enhanced interfacial adhesion between the PVC and ASA domains, while decreasing of $T_{g,2}$ about 2-9°C with the increase PVC content (or the decrease of ASA content). This behavior shows some part of PVC segment can disperse into ASA's domain that is to say the partial miscibility between a ASA rich phase, composed of ASA and PVC, and a PVC-rich phase, composed of PVC and ASA. Thus, the decrease in $T_{g,2}$ is more pronounced than that of $T_{g,1}$.

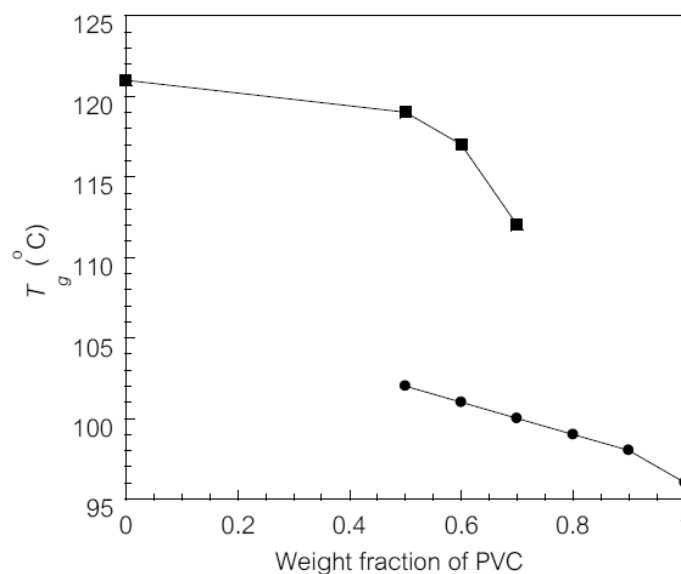


Fig. 6. Effect of blend composition on the $T_{g,1}$ (PVC) (●) and $T_{g,2}$ (ASA) (■) in the PVC/ASA blends.

3.4. Heat Resistance Measurement of PVC/ASA Blends

The effects of ASA contents ranging from 0 wt% to 50 wt% on heat distortion temperature (HDT) and vicat softening temperature of PVC/ASA blends were also measured and are shown in Fig. 7. From the results, the HDT of the neat PVC and ASA were determined to be 64°C and 77°C, respectively while the vicat softening temperatures of the neat PVC was approximately 77°C and of ASA was about 91°C. In addition, the PVC/ASA blends showed HDT and vicat softening temperatures between the values of the two starting polymers and a linear relationship with the amount of ASA added. The results, therefore, imply improved thermal and dimensional stability of the blend with the presence of the ASA in the PVC. This behavior was suggested that the component with higher glass transition temperature (T_g) as the dispersed phase, then the HDT and vicat softening temperatures of the blend follow the rule of mixture relationship.

Due to higher T_g of SAN (ca. 100°C) in ASA matrix, diffusion of the SAN component into the PVC domain can improve thermal properties of the blends and provided the blends with wider service temperature than that of the neat PVC. The addition the ASA, having greater T_g than that of the PVC, as an impact modifier for PVC thus provided further improvement on the HDT and vicat softening temperature of the blend following the rule of mixture. However, in the opposite case such as those using impact modifier with lower T_g , the HDT was found to decrease substantially with the amount of the modifier i.e. poly(phenylene sulfide)/nylon66 blends [32].

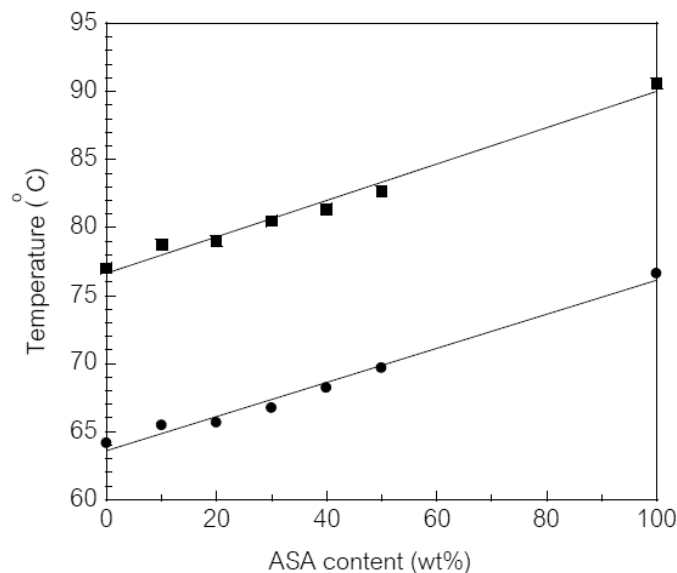


Fig. 7. HDT and vicat softening temperature of PVC/ASA blends at various ASA contents: (●) HDT, (■) vicat softening temperature.

3.5. Water Absorption and Contact Angle Measurement

It is well known to many researchers that water absorption, the tendency of plastics to absorb moisture, can significantly alter some key mechanical, electrical, or optical properties. After water absorption, materials may be dissolved, leached, plasticized, swelled, or show deterioration in mechanical properties. As shown in Fig. 8, percentage of water absorption calculated by weight difference between the samples immersed in water and the dry samples using the following Eq. (1) as a function of time (t) of PVC, ASA, and their PVC blends at varied contents of 0 wt% to 50 wt% of ASA was performed up to the saturation state.

$$M(t) = \left(\frac{w_t - w_0}{w_0} \right) \times 100 \quad (1)$$

where $M(t)$ is the percentage of water content absorbed by each sample, w_0 is its initial weight, and w_t is its weight after water absorption at a certain point of time (t).

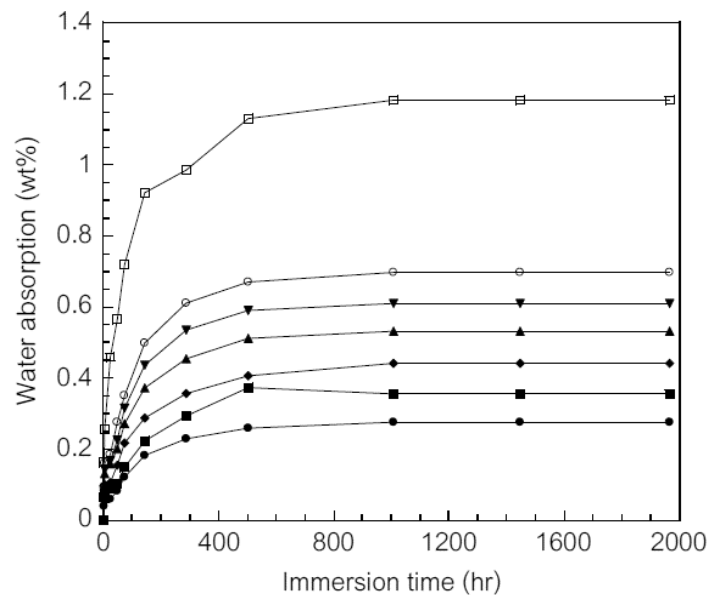


Fig. 8. Water absorption of PVC/ASA blends at various ASA contents: (●) PVC, (■) PVC/ASA 90:10wt%, (◆) PVC/ASA 80:20wt%, (▲) PVC/ASA 70:30 wt%, (▼) PVC/ASA 60:40wt%, (○) PVC/ASA 50:50wt%, (□) ASA.

From Fig. 8, the water absorption at 24 hr of PVC was found to be only about 0.06 wt% while that of the blends was found to increase from 0.09 wt% to 0.18 wt% with an increase of ASA. Furthermore, the neat ASA exhibited a higher water absorption value, at 24 hr immersion, of about 0.40 wt% due to the presence of a highly polar moiety of an acrylonitrile component in ASA. The phenomenon was also confirmed by contact angle measurement. The contact angle data of the PVC/ASA blends was very corresponsive to the water absorption value of the blends. The neat PVC, having lower water absorption than that of the neat ASA, showed higher contact angle of about 98° while the neat ASA provided a contact angle of about 88°. Moreover, the PVC/ASA blends by adding of ASA contents from 10 wt% to 50 wt% showed a contact angle of about 97°, 96°, 95°, 94°, and 93°, respectively. As previously reported [33], for laminated plastics, the factor influencing the contact angle is the affinity of the surface for water. If the material is a strongly hydrophilic solid, the water droplet can spread out on the solid surface and the contact angle will approach 0°. Moderate hydrophilic solids have a contact angle up to 90°, while the contact angle of water on the hydrophobic solid is typically larger than 90°. Thus, the stronger affinity to water of ASA thus rendered the observed increase in water absorption in the PVC/ASA blends with the amount of the ASA. Furthermore, to predict of water absorption behavior, the diffusion mechanism of the PVC/ASA blends was analyzed following Eq. (2):

$$\log \frac{M_t}{M_\infty} = \log k + n \log t \quad (2)$$

where M_t is the amount of water absorbed for given time (t), M_∞ is the amount of water absorbed after infinite time or at saturation level, k and n is coefficient. Normally, classifications of the diffusion mechanism in a glassy polymer are concerned with the relative rates of mobility of the penetrant and of the polymer segments. The classifications are (I) Fickian diffusion, in which the rate of diffusion is much less than that of the polymer segment mobility. Sorption mechanism is independent on swelling kinetics. Equilibrium is reached in relatively short time as the rate of absorption is initially high, (II) the other extreme of diffusion mechanism known as Case II or super Case II that rate of diffusion and penetrant mobility are much higher compared to other relaxation mechanism. Sorption mechanism is a strong function of swelling kinetics, and (III) Non-Fickian or anomalous diffusion, occurs when the penetrant mobility and segmental relaxation mechanism are comparable. Case I and Case II can be viewed as two extremes of diffusion processes with anomalous diffusion lying between them [34]. Plotting experimental data into Eq. (2) gave a value of $n = 0.28-0.31$, which is close to the Fickian diffusion. Therefore, the diffusion properties of polymer materials modeled using the Fick's second law can be evaluated by water absorbed of pre-dried sample immersed in water by finding the slope of the first part of the water absorbed curve versus square root of time by using the following Eq. (3). The coefficient of diffusion (D) defined as the slope of the normalised water absorption versus \sqrt{t} and shows the form:

$$D = \pi \left(\frac{kh}{4M_{\infty}} \right)^2 \sqrt{t} \quad (3)$$

where k is the initial slope of a curve of $M(t)$ against \sqrt{t} , M_{∞} is the amount of water absorbed after infinite time or at saturation level and h is the thickness of the samples.

From the equation, the initial slope of each relationship (not present) defined to k value of the PVC/ASA blends at various ASA contents were presented in Table 1. Then, the coefficient diffusion (D) calculated using Eq. (3) of each sample with thickness (h) equals to 3.2 mm of all blend samples was also reported in Table 1. From the table, we can see that the coefficient of diffusion for room temperature (25°C) water-immersed samples was found to increase with an increase in ASA content. Higher ASA content of the PVC/ASA blend samples, as would be expected, contains a greater diffusivity due to higher acrylonitrile content in ASA.

Table 1. Water absorption of PVC/ASA blends immersed in distilled water at room temperature (25°C).

Sample (wt%)	Saturation water absorption M_{∞} (%)	Initial slope of plot between $M(t)$ and \sqrt{t} $k(s^{1/2})$	Diffusion coefficient $D(m^2/s)$
PVC	0.275	0.025	4.631×10^{-12}
PVC/ASA 90:10	0.355	0.034	5.128×10^{-12}
PVC/ASA 80:20	0.441	0.044	5.575×10^{-12}
PVC/ASA 70:30	0.532	0.059	6.882×10^{-12}
PVC/ASA 60:40	0.609	0.064	6.165×10^{-12}
PVC/ABS 50:50	0.697	0.072	5.959×10^{-12}
ASA	1.182	0.114	5.199×10^{-12}

3.6. Natural Weathering Durability of PVC/ASA Blends

PVC without an aid of suitable UV stabilizers is rather sensitive to the weathering action. Its mechanical properties and color are usually changed as a result of ultraviolet irradiation. Especially in the presence of oxygen and moisture, it undergoes a very fast dehydrochlorination and a peroxidation process with the formation of polyenes and subsequent scission of the chains, with the formation of water “washable” products as well as cross-linking [1, 35]. In addition, the un-stabilized PVC suffered a greater change in the color from white to dark grey color owing to the chromophoric group formation of conjugated double bonds i.e., alkene and polyene linkages which can absorb light readily. Photo-degradation might also convert the surface of the un-stabilized PVC to dark-colored surface of lower extensibility owing to polymer chain scission [1].

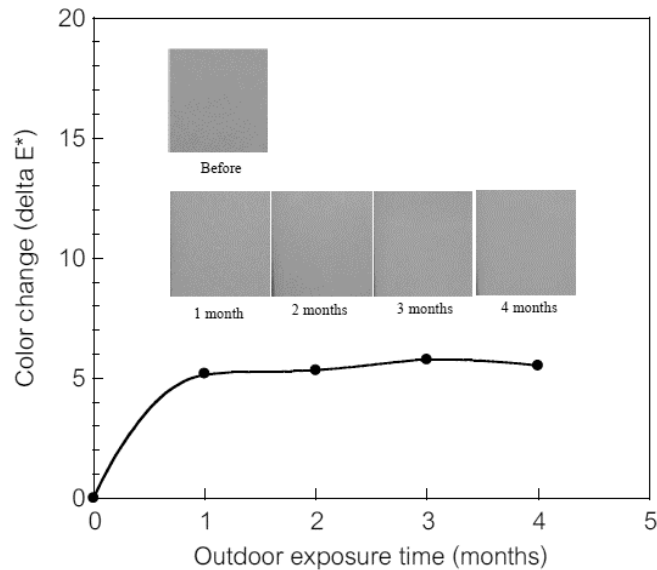


Fig. 9. Color change (ΔE^*) after weathering at various outdoor exposure times: (●) PVC/ASA 50:50wt%.

In this work, the blend formulation with ASA content of 50 wt%, which also provides maximum impact strength as discussed earlier, was selected for natural weathering study. The test was performed in Rayong Province, Thailand, for a time period of up to 120 days (i.e. during December 18th 2010 to April 25th 2011), and the variation of color difference (ΔE^*) as calculated by measuring changes in L^* , a^* , and b^* color values of the samples with a function of time was recorded as depicted in Fig. 9. From the figure, we can see that the incorporation of ASA into PVC greatly imparted substantial color retention of the PVC/ASA blend since the ΔE^* value of the PVC/ASA blend at weight ratio 50/50 was relatively unchanged as a function of the exposure time. The color retention performance of the PVC/ASA blend is due to acrylate rubber in ASA provides resistance to UV radiation and atmospheric oxygen than PVC [22, 36]. Moreover, the visual appearance of the sample surfaces after weathering at various outdoor of the PVC/ASA blend at weight ratio 50/50 observed under the effect of the natural weathering showed negligible change as shown in the inset in Fig. 9. Additionally, no surface crack was observed after this period of natural weathering for the PVC/ASA blend.

4. Conclusions

High impact strength polymer blends between PVC and ASA, as an impact modifier, with improved thermal properties and weathering durability were developed. The effects of the ASA content on mechanical, thermal properties, water absorption, and outdoor weathering stability of the PVC/ASA blends may be summarized as follows. PVC/ASA blends exhibited highest impact strength, i.e. 77.6 kJ m⁻², when ASA content in the blend is about 50 wt%. Tensile and flexural properties of the blends were found to slightly decrease with the ASA content. Glass transition temperature and thermal stability of the blends could be enhanced by the presence of ASA in the blends. The shifting of the two glass transition temperatures of the PVC domain and ASA domain towards each other in the blend suggesting partially miscible nature of these polymers. Furthermore, water absorption of the PVC/ASA blends with ASA increased due to an increase of a highly polar moiety of an acrylonitrile component in ASA. While the water absorption process of these blends at room temperature is found to follow Fickian behavior. Finally, outdoor weathering durability of the blends was substantially enhanced by the ASA addition as confirmed by a negligible color change of the blend samples after outdoor weathering up to 4 months.

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