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Effects of Poly(butylene succinate) and Calcium Carbonate on the Physical Properties of Plasticized Poly(vinyl chloride)

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Abstract

In this studypoly(butylene succinate) (PBS) , a polymeric plasticizer, was partially replaced a conventional plasticizer, diisononyl phthalate (DINP) to avoid the plasticizer loss from poly(vinyl chloride) (PVC) overtime for various service conditions and to obtain a long-term plasticizer retention in the flexible PVC products. The plasticized PVC samples were prepared by melt mixing on a two roll mill, followed by compression molding. The mechanical properties (tensile properties, tear strength and hardness), thermal stability and morphology of the 20/20 phr (parts by weight per hundred parts of resin) DINP/PBS-plasticized PVC were evaluated and compared with those of the 40 phr DINP-plasticized PVC. The tensile strength, Young's modulus, tear strength, hardness and thermal stability were found to be improved, while the elongation at break was decreased as a result of the partial replacement of DINP with PBS in the plasticized PVC. Moreover, the DINP/PBS-plasticized PVC composites filled with varied loadings of $CaCO_3$ (2.5, 5, 7.5 and 10 phr) showed an increase in the elongation at break, Young's modulus and thermal stability in a dose-dependent manner, while the tensile strength, tear strength and hardness were unaffected by the increasing amount of $CaCO_3$. The morphology of the composites observed by scanning electron microscopy showed a number of voids on the fractured surface of the plasticized PVC due to the pulling out $CaCO_3$ particles, caused by the low interfacial adhesion between filler and polymer.

Keywords : Poly(vinyl chloride), Diisononyl phthalate, Poly(butylene succinate), Calcium carbonate, Physical properties
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Introduction

Commercial applications of poly(vinyl chloride) (PVC) generally require the inclusion of particular additives such as plasticizers, heat stabilizers, lubricants and fillers to obtain PVC compounds with desired properties and variety of applications. Plasticizers are commonly used to enhance flexibility, softness, toughness, workability, pliability or distensibility, while fillers are used to reduce cost or to improve certain characteristics such as strength, stiffness, abrasion resistance, dimensional stability, thermal stability or mold shrinkage(1-3). Conventional plasticizers such as di-2-ethylhexyl phthalate (DEHP), diisodecyl phthalate (DIDP) and diisononyl phthalate (DINP) are a typically high boiling point organic liquid that can reduce the glass transition temperature (T_g) of PVC by increasing mobility of polymer chains, inducing somehow an enhancement of the impact resistance and elongation at break(4,3). However, PVCs plasticized with the low molecular weight phthalate compounds always have an application limit for many purposes, due to the migration and leaching of these plasticizers over time in various service conditions(4-6). These phenomena lead to a serious change in the mechanical properties of the end-products and a noticeable shrinkage. The plasticizer migration also provides some adverse effects on human and environment due to the toxicity of the phthalates(4,5,7-9). To avoid the plasticizer loss but at the same time retain the possibilities of plasticized PVC, the compatible and non-toxic polymeric plasticizers are being used to substitute the low molecular plasticizers. This is due to the fact that polymeric plasticizers exhibit low volatility and low migration at high temperature(1,6,8). It has been reported that ethylene vinyl acetate copolymer(1), polyesterurethane(5), ethylene acrylic copolymer(6), nitrile rubber(10,11) poly(1,2-propylene glycol adipate)(7), thermoplastic polyurethane(12,13), poly(ε-caprolactone)(14,15), poly (butylene adipate-co-terephthalate)(16), epoxidized natural rubber(11,17), carboxylated nitrile rubber(11) and chlorinated polyethylene(18) were used to replace or partially replace the conventional plasticizers to obtain long-term plasticizer retention in the flexible PVC products. However, polymeric plasticizers usually have lower plasticizing effect than conventional plasticizers, plus they are too expensive to use alone. Thus, flexible

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PVC products may be obtained replacement of the conventional both technically and economically by partial plasticizers with polymeric plasticizers.

The present work explored the possibility of partial replacement of DINP, a low molecular plasticizer by poly(butylene succinate) (PBS), a biodegradable macromolecular plasticizer. PBS is a highly flexible aliphatic polyester ($T_g \sim$ -40 to -10°C) with no adverse effects on the environment(19-21). According to the specific bonds between the carbonyl groups in PBS and the α-hydrogens in PVC, PBS has a good compatibility with PVC. The mechanical properties (tensile properties, tear strength and hardness), morphology and thermal stability of the PVC plasticized with 40 phr (parts by weight per hundred parts of resin) of DINP and 20/20 phr of DINP/PBS blend were investigated and compared. Moreover, the DINP/PBS-plasticized PVC was further filled with varied loadings of a micro-sized calcium carbonate ($CaCO_3$), which is a common mineral filler used in the PVC formulation. Since $CaCO_3$ is one of the hydrogen chloride (HCl) scavengers(22-24), it is expected to improve not only the mechanical properties but also the thermal stability of the plasticized PVC by trapping the HCl generated in heating or burning of the chlorine containing resin. Finally, the prepared environmentally friendly plasticized PVC composites were also characterized for their mechanical properties, morphology and thermal stability.

Materials and Experimental Procedures

Materials

PVC resin of a suspension grade with a K-value of 66, the conventional plasticizer DINP, the heat stabilizer calcium/zinc stearate, the lubricant stearic acid, and the ultrafine $CaCO_3$ with particle size of about 4.7 μm were all kindly donated by Thai Nam Plastic (Public) Company (Samutsakorn, Thailand). PBS (GSPla) manufactured by Mitsubishi Chemical Corporation (Tokyo, Japan) was provided by National Metal and Materials Technology Center (Pathumthani, Thailand). All materials were used as received without further purification.

Specimen Preparation

The PVC compounds were prepared by mixing the PVC powder with the required amounts of DINP, PBS, $CaCO_3$, Ca/Zn stearate and stearic acid, as shown in Table 1. The melt mixing was performed on a two-roll mill (CR-OH-820) at 165°C for 5 minutes. The batch mixed compound was subsequently fabricated into a 14 cm × 10 cm × 0.3 cm sheet by compression molding (Lab Tech Engineering LP-S-50) at 165°C for 5 minutes at a pressure of 150 kg/cm^2. The sheet was then cut into the desired specimen shape and size for further testing.

Table 1. Sample composition.

Sample	PVC (phr)	DINP (phr)	PBS (phr)	$CaCO_3$ (phr)	Ca/Zn stearate (phr)	Stearic acid (phr)
A	100	40	-	-	2	0.2
B	100	20	20	-	2	0.2
C	100	20	20	2.5	2	0.2
D	100	20	20	5	2	0.2
E	100	20	20	7.5	2	0.2
F	100	20	20	10	2	0.2

Characterization

The tensile test was conducted at an ambient temperature according to ASTM D638 standard Type IV using a Lloyd LR100K computerized universal testing machine with a 10 kN load cell. The standard dumbbell-shaped sample was extended at a strain rate of 50 mm/min. Tear strength was measured according to ASTM D1004 on a cresent-shaped sample with the same testing machine at a strain rate of 50 mm/min. For each formulation, at least five specimens were tested to obtain the average and standard deviation. The hardness was measured according to ASTM D2240 using a durometer (MS-ES-2530, Shore Instrument & Mfg. Co.) and expressed as Shore D hardness.

The morphology of tensile fractured surface was observed by a scanning electron microscope (SEM, Jeol JSM-6480LV) at an accelerated voltage of 15 kV and a magnification of 500×. The fractured surface was coated with a thin layer of gold to form a conductive layer before observation.

The thermal stability was measured using a thermogravimetric analyzer (TGA, Mettler Toledo, TGA/SDTA 851^e), operating under a N_2 atmosphere at a heating rate of 20°C/min within the temperature range of 50-800°C.

Results and Discussion

Mechanical Properties

The mechanical properties including tensile strength, Young's modulus, elongation at break, tear strength and hardness are summarized in Table 2. It is evident that the tensile strength of PVC plasticized with 20/20 phr DINP/PBS (Sample B) was higher than that plasticized with only DINP (Sample A) by about 1.13-fold. This is owing to the high molecular weight of PBS as well as the chain entanglement between PBS and PVC molecules that caused an increase in the tensile strength of the plasticized PVC. Moreover, the 20/20 DINP/PBS-plasticized PVC composites filled with varied loadings of $CaCO_3$ (2.5, 5, 7.5 and 10 phr; Samples C to H) exhibited similar or slightly increased tensile strength (1.05-fold at 10 phr of $CaCO_3$) as compared with the unfilled one (Sample B). From the Table 2, the Young's modulus of Sample B was much higher than that of Sample A (2.72-fold). This influence is attributed to the intermolecular attraction and chain entanglement between PBS and PVC molecules that tended to restrict either PVC or PBS chain mobility. Moreover, as DINP was replaced by PBS, there is less of the more strongly solvating plasticizer in the PVC matrix. As expected, the addition of $CaCO_3$ increased the Young's modulus of the plasticized PVC composites in a dose-dependent manner from 1.54-fold higher at 2.5 phr $CaCO_3$ (Sample C) to 1.65-fold higher at 7.5 phr $CaCO_3$ (Sample E) as compared to the Sample B. This is a consequence of the stiff $CaCO_3$ particles that effectively restricted the mobility and deformability of the polymer chains during tensile loading. In addition, a slight decrease in the Young's modulus beyond 7.5 phr $CaCO_3$ (Sample F) may be due to the self aggregation of $CaCO_3$ in the PVC matrix. It was also found that the partial replacement of DINP by PBS caused a reduction in the elongation at break as a result of the reduced chain mobility as mentioned above and thus the elongation at break of Sample B was lower than that of the Sample A (1.15-fold). However, the high level of elongation at break of plasticized PVC was still retained. Therefore, PBS produced a stiffer material with rather similar ductility as the conventional plasticizer. Moreover, the elongation at break was further increased by the inclusion of $CaCO_3$ in a dose dependent manner (1.01-fold at 7.5 phr to 1.15-fold at 2.5 phr), which was a consequence of the weak interaction between $CaCO_3$ and the polymers that created voids for the matrix to be drawn into the deformation zone and thereby increased the elongation at break. In conclusion, the addition of $CaCO_3$ showed an increase not only the stiffness but also the elongation at break of the composites, whilst the tensile strength remained essentially unaffected.

Table 2 shows that Sample B had higher tear strength than Sample A by about 1.2-fold, indicating that the partial replacement of PBS to DINP was very effective at improving the tear strength of the plasticized PVC, caused by the physical entanglement of PBS and PVC chains as mention above. However, the plasticized PVC containing varied loadings of $CaCO_3$ (Samples C to H) exhibited similar or slightly decreased tear strength compared to the Sample B, suggesting that $CaCO_3$ did not significantly affect the tear strength of these plasticized PVC composites. It was also found that the hardness of Sample B was higher than that of Sample A by about 1.2-fold, due to the restriction in the segmental motion of the PVC molecules by the high molecular weight PBS. Moreover, only a small increase in hardness (1.01- to 1.03-fold) was observed with the inclusion of $CaCO_3$ in the plasticized PVC composites (Samples C to H) compared to the Sample B. This suggested that $CaCO_3$ particles were mostly embedded within the polymer matrix and did not participate in the alteration of surface hardness of the plasticized PVC composites.

Table 2. Mechanical properties of the plasticized PVC samples.

Sample[a]	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	Tear strength (N/mm)	Hardness (Shore D)
A	19.8±0.51	226.8±9.39	49.4±14.83	115.8±6.62	37.4±0.57
B	22.4±0.57	197.7±12.31	134.2±21.79	139.0±5.30	44.6±0.72
C	22.4±0.90	224.6±18.18	206.5±19.73	140.7±4.06	45.0±0.36
D	22.4±0.59	218.1±15.51	206.7±29.03	137.4±3.44	45.0±0.68
E	22.5±0.77	200.6±10.38	221.6±25.03	137.1±3.70	45.4±0.50
F	23.1±0.32	210.4±15.88	207.8±16.19	138.2±3.44	46.0±0.42

[a] Sample codes are from Table 1

SEM Analysis

SEM analysis of the tensile fractured surface revealed that the 40 DINP-plasticized PVC (Sample A) exhibited relatively rough and uneven topography with many low ridges distributed on its fractured surface (Figure 1a), which corresponds to the ductile failure behavior. In comparison, the 20/20 DINP/PBS-plasticized PVC (Sample B) exhibited smoother fractured surface (Figure 1b), suggesting that Sample B had lower ductility than Sample A. A uniform distribution of PBS in PVC matrix was also observed due to the intermolecular adhesion and chain entanglement between PBS and PVC molecules. These observations confirmed that well dispersed PBS restricted the mobility of PVC chains, and thus caused a decrease in the elongation at break and an increase in the Young's modulus and hardness. Moreover, there existed a number of voids on the fractured surface of the plasticized PVC containing varied loadings of $CaCO_3$ (Samples C to H) as shown in Figures 2c-f, due to the debonding of $CaCO_3$ particles from polymer matrix during the tensile deformation. However, the roughness and unevenness of the fractured surfaces could be observed in the composites, indicating that the ductile deformation was still retained. These observations are in agreement with the results of the elongation at break.

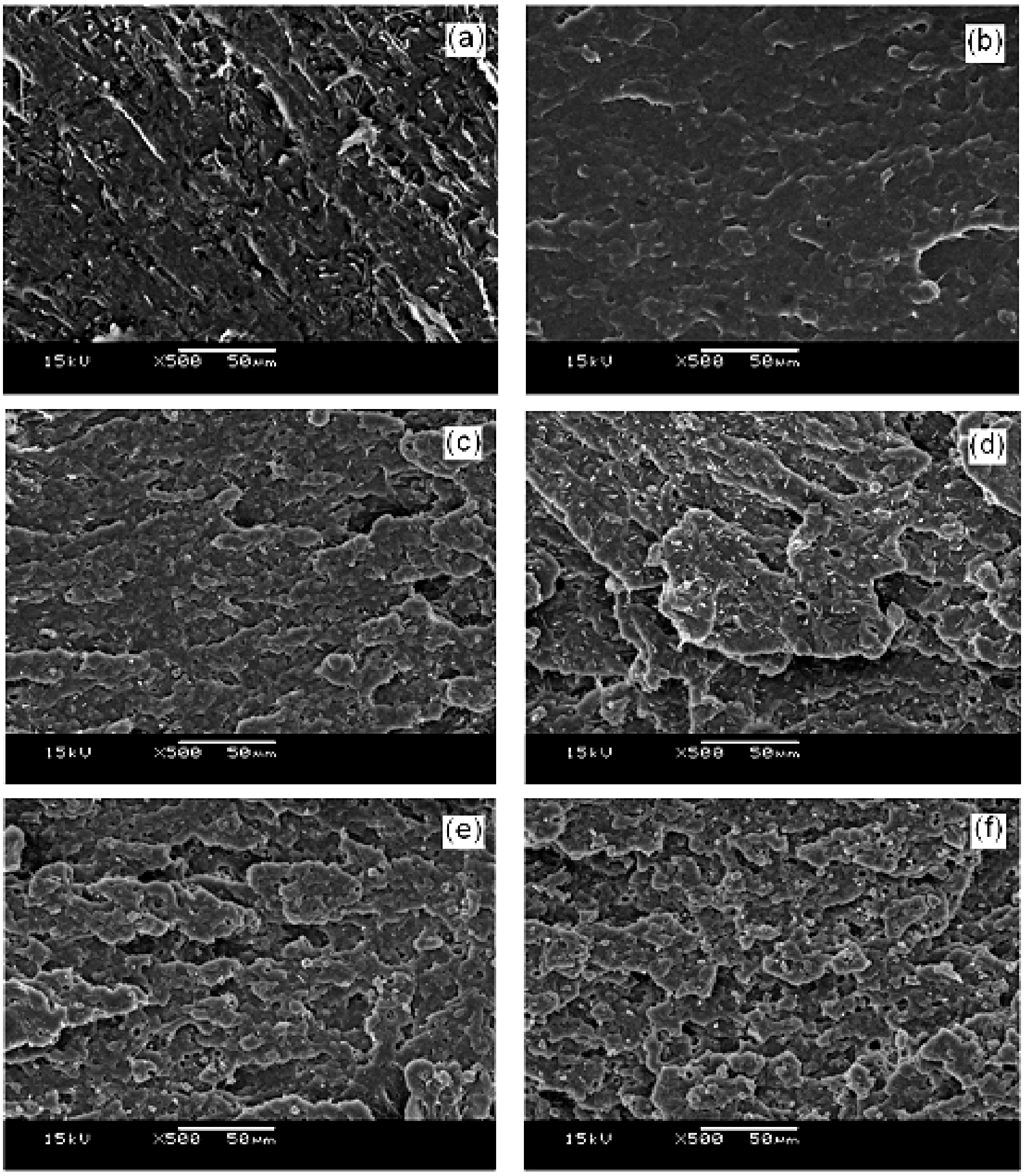

Figure 1. Representative SEM micrographs (500× magnification) of the (a) 40 phr DINP-plasticized PVC and the 20/20 phr DINP/PBS-plasticized PVC filled with (b) 0, (c) 2.5, (d) 5, (e) 7.5 and (f) 10 phr of $CaCO_3$.

Thermogravimetric Analysis (TGA)

TGA was performed to determine the thermal stability of the samples by evaluating the decomposition temperatures and percentage weight loss. Table 3 and Figure 2 summarize temperatures for the onset (T_{onset}), end set ($T_{end\ set}$) and 50% weight loss ($T_{50\%}$) and %char of the samples. It can be observed that all plasticized-PVC samples (Samples A to H) revealed two-stage degradation or two onset temperatures ($T_{onset\ 1}$ and $T_{onset\ 2}$): the first stage mainly involves the phenomenon of dehydrochlorination by eliminating of hydrogen chloride (HCl) molecules and plasticizer volatilization, followed by the formation of conjugated polyene structures along the PVC backbone, while the second stage mainly corresponds to the thermal cracking of the polyene structures to volatile aliphatic and aromatic compounds by the intermolecular cyclization of the conjugated sequences$^{(2,3,5)}$. The results showed that the thermal stability of plasticized PVC increased when DINP was partially replaced with PBS (Sample B) by shifting the T_{onset}, $T_{end\ set}$ and $T_{50\%}$ towards higher temperatures as compared to that plasticized with only DINP (Sample A). This may be explained by the fact that PBS has much higher molecular weight than DINP, and thus there are stronger affinity and entanglement between PBS and PVC molecules, suggesting that the DINP/PBS-plasticized PVC needs greater thermal energy for degradation along with the increase in PBS contents. However, the char formation of Sample B was still very low (1.5 wt%). In addition, the inclusion of $CaCO_3$ into the plasticized PVC (Samples C to H) resulted in an increased thermal stability by shifting the decomposition temperatures towards higher temperatures and increasing the char residue with increasing $CaCO_3$ content. As can be seen, the dehydrochlorination of PVC was considerably delayed for 12-16°C due to the dispersed calcium ions in PVC matrix effectively scavenged the liberated HCl into the form of physically stable calcium chloride, and thus, suppressed the autocatalytic activity of HCl in the dehydrochlorination process. Moreover, the char yield observed at higher $CaCO_3$ loadings likely hindered the diffusivity and permeability of combustible gases into the polymer matrix. Therefore, $CaCO_3$ can be used as a heat-resistant modifier for the plasticized PVC.

Table 3. TGA-derived data for the plasticized PVC samples.

Sample[a]	$T_{onset\ 1}$ (°C)	$T_{50\%}$ (°C)	$T_{onset\ 2}$ (°C)	$T_{end\ set}$ (°C)	Char (%)
A	280	317	438	469	0
B	281	324	440	500	1.5
C	293	325	442	500	8.4
D	295	325	443	504	11.4
E	296	325	444	511	13.5
F	297	325	442	514	15.2

[a] Sample codes are from Table 1

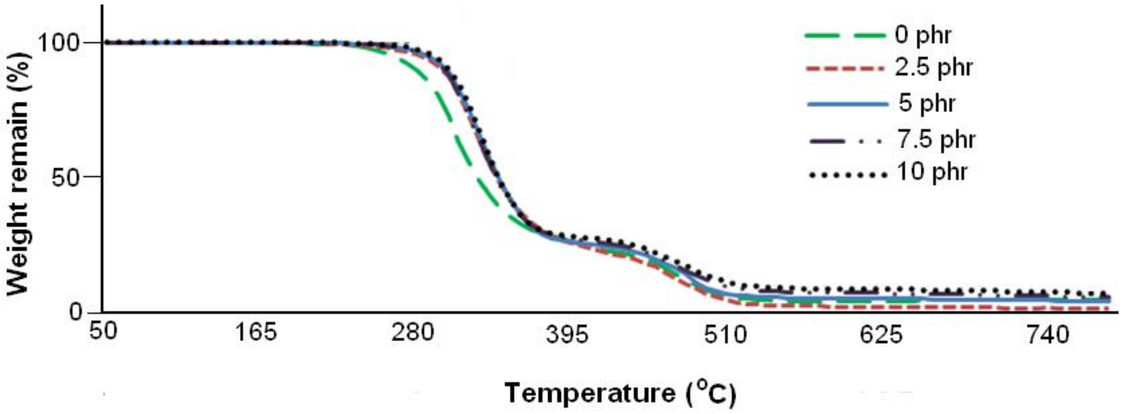

Figure 2. Representative TGA curves of 20/20 phr DINP/PBS-plasticized PVC filled with 0, 2.5, 5, 7.5 and 10 phr of $CaCO_3$.

Conclusions

In this study, flexible PVC was successfully prepared using PBS as a polymeric plasticizer in combination with a conventional plasticizer, DINP at the weight ratio of 20/20 phr. It is evident that the tensile strength, Young's modulus, tear strength, hardness and thermal stability of the DINP/PBS -plasticized PVC were higher than those plasticized with only DINP, due to the high molecular weight of PBS as well as the chain entanglement between PBS and PVC molecules. Even though the elongation at break was deteriorated by the partial replacement of DINP with PBS, but the high level of elongation at break of plasticized PVC was still retained. However, the inclusion of four loadings of $CaCO_3$ (2.5, 5, 7.5 and 10 phr) into the DINP/PBS-plasticized PVC showed an increase in the elongation at break, Young's modulus and thermal stability but an insignificant effect in the tensile strength, tear strength and hardness with the increasing amount of $CaCO_3$. Moreover, there existed a number of voids on the fractured surface of the plasticized PVC due to the pulling out of $CaCO_3$ particles from polymer matrix during the tensile deformation.

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