Application of poly(butylenes succinate) as migration resistant plasticizer for poly(vinyl chloride)

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Abstract. The bio-based and biodegradable polyester poly (butylene succinate) (PBS) was successfully used as alternative plasticizers to modify poly (vinyl chloride) (PVC) in this work. The mechanical properties and plasticizing effect were estimated by the tensile strength, bending strength, bending modulus, hardness and the elongation at break of the PVC/PBS blends. And the migration stability of the PBS was investigated. It was showed that the migration-resistant property of PVC plasticized with PBS was greatly superior to that with dioctyl phthalate (DOP). Further, compatibility and dispersion of PBS in the matrix were excellent, indicating that the environmentally friendly PBS can be used as an alternative plasticizer to remove the potential health risks of migrating out phthalates during applications.
Keywords: poly(butylene succinate); poly(vinyl chloride); plasticizer; migration resistant.

1 Introduction

Over the past few years,interest in developing and using sustainable plasticizers for modification of poly(vinyl chloride) (PVC) to impart flexibility to this polymer, as alternatives to petroleum-derived plasticizers, has been increased[1-5]. Phthalate esters are widely used as poly (vinyl chloride) (PVC) plasticizers,while their possible health and environmental impacts have been a subject of debate for years. The toxicity of phthalates was studied by researchers as early as in 1940s [5]. Since 1990s, adverse effects of phthalates on liver, heart, kidneys, lungs, and other organs have been concluded and caused public concerns [6]. In Taiwan in May 2011, a “plasticizer event” happened. DOP migrated from food packaging to foods. Taiwan has began to limit the phthalate plasticizer used in food packing, medical devices, toys, and plastic products which have contacted human body directly[7-11]. There is further concern because the European Chemicals Agency put phthalates on the candidate list of Substances of Very High oncern in October 2008[12].

To solve these problems, a series of recent publications reported the synthesis and possible application of PVC plasticizers, derived from renewable resources such as epoxidized soybean oil (ESO)[13], dialkyl furan-2,5-dicarboxylates, epoxidized fattyacid esters(EFAE)[14], poly(glutaric acid-glyceryl monooleate) (PGAGMO)[15], hyperbranched poly(E-caprolactone)[16], oligomeric isosorbide esters[17], diester based on castor oil fatty acid[18] and so on. Choi and Kwak[16] reported the use of hyperbranched poly (e-caprolactone) (HPCL) as an alternative for DEHP, and found that HPCL showed a similar plasticizing efficiency than DEHP, but had much better migration resistance. Bo Yin, Nina Aminlashgari[19] studied the plasticizing effects of three glucose hexanoate esters as

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biobased PVC plasticizers (GHs), which showed good miscibility with PVC and better mechanical properties of the GH blends.

Poly(butylene succinate) (PBS) is a typical aliphatic polyester, which has drawn considerable attention at home and abroad due to its biodegradability, nontoxicity and economy. In this study, PBS was used as a plasticizer of PVC, and its plasticizing effects on PVC were studied. To the best of our knowledge, there have been no studies of PBS polyester plasticizers or used PBS as the plasticizer of PVC.

2 Experimental

2.1 Materials

Poly(vinyl chloride) (PVC) was purchased from Inner Mongolia Junzheng energy Chemical Co.,Ltd. Poly(butylene succinate) (PBS) was purchased from Mitsubishi Chem- ical Corporation. Dioctyl phthalate (DOP) was purchased from TianJin Ke Deng Chemi -cal Reagent Co.,Ltd. Ca/Zn composite stabilizer was purchased from Xiamen Green Chemical Industry Co.,Ltd. All the chemicals involved in this work were used as received. The properties of PBS and PVC were given in Table 1.

Table 1. The properties of PBS and PVC

	PVC	**PBS**
Number-average molecular weight	52502	61129
Tensile strength(MPa)	63.17	38.60
Elongation at break(%)	22.53	270.31
Bending strength(MPa)	78.24	19.32
Bending modulus(MPa)	3027.75	588.04
Hardness	14D	59D

2.2 Preparation of sample

The sample formula is as follows: Ca/Zn composite stabilizer (5phr), plasticizer (PBS or DOP) (10phr, 20phr, 30phr, 40phr, 50phr, 60phr), poly(viny chloride) (PVC) (100phr). First, PVC powder, plasticizer, and thermal stabilizers were mixed using a mechanical mixer at room temperature (RT) for 5 min. The mixture was plasticized on a two-roll mill at a constant temperature (130ºC), then molded in a compression molding machine at 170ºC for 5 min and cooled for 3 min under pressure of 10 MPa into sheets of (2±0.1,4±0.1) mm thickness for structure characterization and property measurement. All samples were slightly decomposed, possibly due to thermal stabilizer.

2.3 Characterizations

Tensile properties were measured using a Z wick/Roell Tensile Tester (Germany) at RT, according to GB/T 1040.1–2006 (China) with a testing speed of 50 mm min^{-1}. The Shore D hardness test was carried out using a Shore rubber hardness tester (Shanghai Liuling Instrument Factory), according to GB/T 2411-2008 (China), performed at 15s per sample.

Surface and cross-section of PVC blends were investigated by using a JSM-6700F scanning electron microscopic (SEM) instrument (JEOL, Japan), distanced at 8mm, operated at 12kv and sputtered with gold at the surface and cross-section of all samples.

Chemical resistance test of the plasticizer from samples was characterized. To appraise migration stability, the liquids selected as tap water, alcohol, glycerol, petroleum ether, cyclohexane. The

samples were immersed in 100 mL of the liquids with dimension 10×10×1mm^3 at room temperature for 48 hours. Periodically, the sheets were removed and dried for measurement of weight loss.

3 Results and discussion

3.1Mechanical properties

Plasticizer plays an important role in the mechanical properties of PVC blends. Hence, evaluation of tensile strength, elongation at break, bending strength and bending modulus was a good effective way to study the effect of plasticizers. The mechanical properties data of PVC blends was given in Figures 1. The results showed that with the increasing content of PBS, the tensile strength, bending strength and bending modulus decreased concurrently from 45.05MPa to 28.57MPa, 75.16MPa to 16.21MPa, 2924.13MPa to 836.57MPa, respectively. While the elongation at break increased from 35.75% to 262%. It illustrated that PBS could improve the flexibility of PVC sheets effectively. Usually, it was believed that the improvement of its mechanical properties about the blends is due to the decrease of viscosity [15, 18]. PBS could better interact with the PVC molecule to reduce physical crosslinking points of the chlorine atoms in the PVC molecular chains, shield the polymer chains from interacting with each other and increase the chain segmental motion in PVC. PBS would be conductive to thermoplastic processing of PVC blends.

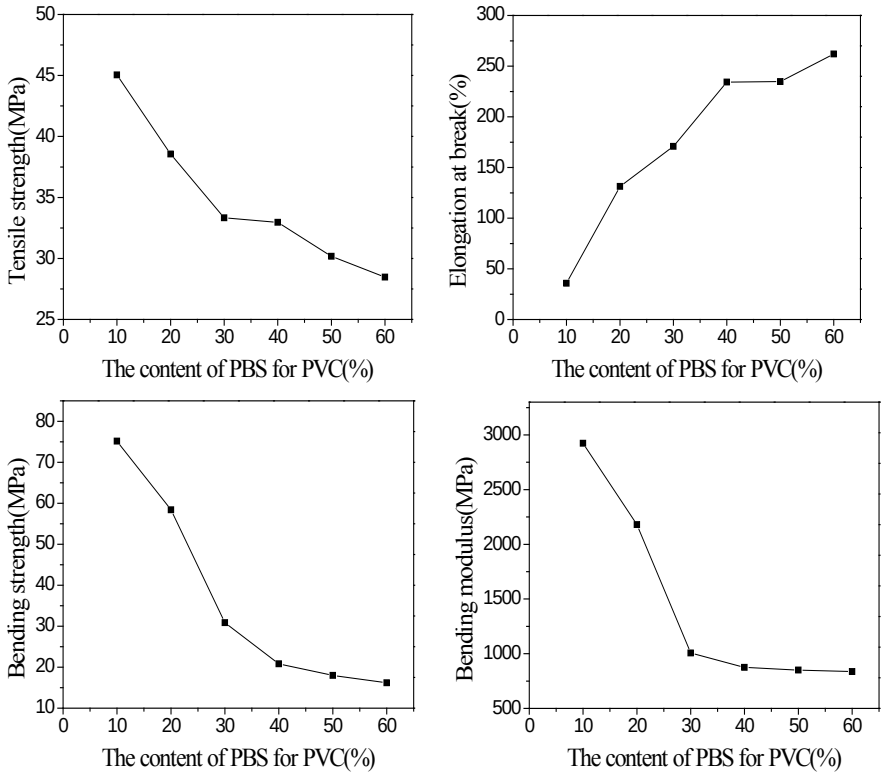

Figure 1. Mechanical properties of PVC/PBS

3.2 Hardness test

The plasticizing effect was inferred from hardness measurements, since the hardness of a material is reflective of its flexibility. The hardness data of all the samples was given in Figure 2.With the

increase in the content of PBS, the hardness of PBS/PVC sheets decreased concurrently from 71D to 50D. It is consistent with the common rule that plasticizer can decrease the hardness of PVC. The decrement of hardness indicated that the ductility of PVC was mildly improved. It was because that PBS could interact with the PVC molecule and facilitate the mobility of PVC chain segment.

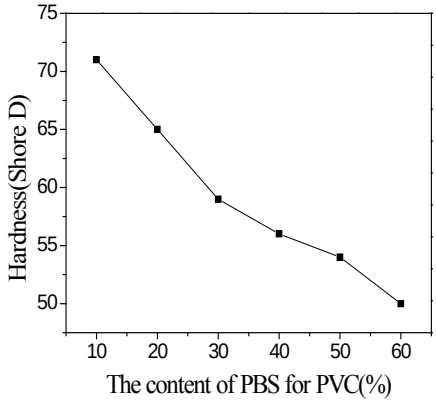

Figure 2. Surface hardness of PVC films

3.3 Scanning electron microscopy

The plasticizing effects can be observed by SEM micrographs about fractured surfaces of the sample obtained from the mechanical tests and hardness test. The value of magnification is 3000. The cross-section and surface of PVC blend were shown in Fig3. In Fig3 (a) and (b), it can be seen from the SEM imagesthat the surface of plasticized PVC films with 30 phr PBS and 40 phr PBS was homogeneous and smooth(red circle part). It indicated that the good compatibility between PBS and PVC could effectively restrain the release of plasticizer from the products and improve the flexibility of products. By means of the phase morphology, revealed in the Fig3 (c) and (d) about PVC/PBS blends etched in THMS(red circle part), itappeared that PBS was evenly dispersed in PVC matrix and intimately surrounded with PVC continuous phase.

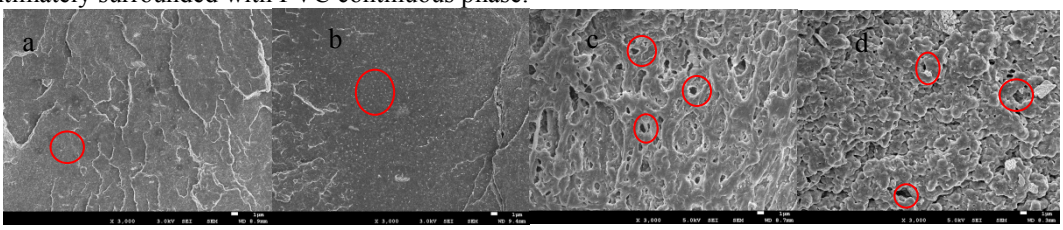

Figure 3. SEM images of various cured PVC/PBS blends of unetched and etched (15 min in THMS) fracture surfaces.(a)PVC/PBS(100/30) unetched, (b)PVC/PBS(100/40) unetched(c)PVC/PBS(100/30) etched, (d)PVC/PBS(100/40) etched

3.4 Chemical resistance test

The migration of plasticizer in solvents was evaluated and expressed in terms of the percentage weight loss after immersion in solvents. The weight loss of the PVC samples by exudation was shown in Figure 4. In order to compare with PBS, PVC/DOP sheets were prepared with 50 phr DOP. In tap water, glycerol, petroleum ether, alcohol and cyclohexane, 0.25 wt.%, 1 wt.%, 28.52 wt.%, 11.99 wt.%, and 28.06 wt.% of the plasticizer were found to migrate out from the PVC/DOP samples, respectively. However, in PVC/PBS samples, there was less than 0.22 wt.%,0.21 wt.% and 0.54 wt.% or even no PBS migration. The reason mainly had two aspects: (1) compared with DOP, high molecular weight of polyester plasticizer PBS could make it hard to migrate from the PVC[16]; (2) the

entanglements between PBS and PVC chains were more stronger than the low molecular weight DOP. As discussed above, PBS had stronger interactions with PVC and lower weight loss in organic solvent. Altogether the results indicate that the PBS have large potential as green PVC plasticizers and they could be a promising option to overcome the environmental problems caused by phthalate plasticizers.

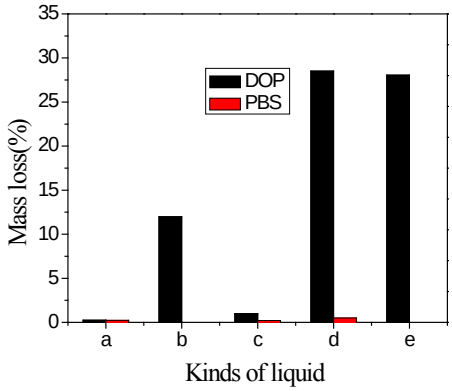

Figure 4. Migration degree of the plasticized PVC samples in different solvent. (a) tap water, (b) glycerol, (c)petroleum ether, (d)alcohol, (e) cyclohexane

4 Conclusion

In this work, the properties of PVC blends plasticized with PBS were investigated. The addition of PBS to PVC was found to significantly improve the flexibilitys, performed by decreasing the tensile strength, bending strength, bending modulus, hardness and increasing the elongation at break. The SEM images (red circle part) indicated that compatibility and dispersion of PBS in the matrix were excellent. The percentage weight loss≤(0.6wt.%) showed PBS had a good interfacial ad hesion and stronger interactions with PVC.

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