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Biopolyurethane/Diethylhexyl Phthalate Hybrid Plasticizer for Flexible Polyvinyl Chloride

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Abstract: Worldwide concerns on the endocrine disruption of phthalate derivatives have sparked extensive research on its alternatives. One of the most prominent use of phthalate derivatives are on the plasticization of polyvinyl chloride (PVC). Therefore, numerous carboxyl acids and their derivates have been studied as candidates for PVC plasticizer. Elastomeric polyurethanes have been extensively studied as solid-state plasticizer to induce flexibility to otherwise rigid PVC. In this research, bio-based polyurethane (BPU) elastomers and phthalate hybrid plasticizer was used for the fabrication of flexible PVC. Even though half the amount of phthalate plasticizer was replaced with BPU the PVC with the hybrid plasticizer showed strain at break of 320.5 %. The of BPU reduced phthalate use by increasing the flexibility of PVC and reduced the migration of phthalate plasticizer.

Keywords: Polyvinyl chloride, Bio-based polyurethane, Plasticizer, Migration, Diethylhexyl phthalate

Introduction

Polyvinyl chloride (PVC) is used in various areas of industries because of its good chemical resistance, mechanical properties, and processing properties. In the PVC industry various additives are used to enhance processability and performance of the PVC compounds. The apparent polarity arising from the polarized carbon-chlorine bond in the PVC structure allows various additives to be incorporated via electrostatic interactions. Plasticizers are one of the most important additive in PVC compounding due its ability to easily enhance flexibility, workability and distensibility of PVC [1]. Diethylhexyl phthalate (DEHP), with its economic efficiency and good compatibility with PVC is one of the most prominently used plasticizer.

Unfortunately, various studies have shown possibilities of phthalate derivatives as potential endocrine disruptors which produces a negative effect in the liver and reproductive organs of mammals [2-5]. These potential dangers of phthalate derived plasticizers provide a major hindrance to the use of PVC in commercial products. Various nations have already prohibited the use of phthalate containing products from their use in child related products. However flexible PVC products contains up to 40 wt% of plasticizers depending on its application. Plasticizers inside the flexible PVC products may not cause harm to humans, however most plasticizers are low molecular weight chemicals bound to the PVC chain by comparably weak physical bonds such as van der Waals forces and dipole-dipole interactions, which have high possibilities of migration in to the human body. In addition, the external forces can cause the weakening of these interactions and bring out an enormous falling-off in the quality of PVC products [6-8]. As a result, various attempts have been made to reduce phthalate migration such as increasing barrier properties of PVC or using alternative plasticizers.

Many researches have shown that the use of thermoplastic polyurethane elastomers as a solid-state plasticizer for PVC is a valuable solution to replace the use of phthalate derivatives such as DEHP [1,5,9,10]. Thermoplastic polyurethanes are excellent candidates as solid-state plasticizers due to its low temperature flexibility and melt processability. Moreover, the structure of polyurethane is easily manipulatable by the high reactive isocyanate chemistry allowing a wide selection of polyurethanes with various mechanical properties [11-15]. Also, it is worthy of note that a new series of polyurethanes using plant oil derived polyols such as castor oil, soybean oil, palm oil, and rapeseed oil are promising biofriendly materials [16,17].

In our previous research biopolyurethane (BPU) was synthesized using castor oil and polycaprolactone (PCL) diol [18,19]. Utilizing this BPU a hybrid plasticizer was prepared to tackle the health concerns involved with flexible PVC. By the hybridization of BPU and DEHP, low-temperature flexibility and elongation at break was enhanced by the soft segments of BPU and thermal stability was reinforced by the aromatic hard segments [20]. The BPU plasticized PVC were compounded using a conventional twin-screw extruder. High-performance liquid chromatography (HPLC) technique was used for the plasticizer migration tests due to its inherent separation ability of low molecular weight plasticizers [21-23]. By this quantitative inspection of the plasticizer migration, a more accurate investigation can be made. Easily acquirable household solvents were used as media for the HPLC plasticizer migration test [24,25]. The use of BPU/DEHP hybrid plasticizer on flexible PVC showed high possibilities of reducing phthalate migration and enhanced mechanical properties.

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Experimental

Materials

Castor oil (Yakuri Pure Chemical Co., Ltd.), polycaprolactone diol (PCL diol) (M_n=2,000 g/mol, OH-value 51-63 mg KOH/g) (Sigma Aldrich), and 1, 4-butanediol (BD) (M_w=90.12 g/mol, OH-value 1,246 mg KOH/g) hybrid polyols were used for the biopolyurethane synthesis. 4, 4'-diphenylmethane diisocyanate (MDI) was bought from Sigma Aldrich Co., LLC, Korea and kept refrigerated before use. Micro-suspension PVC (KH-60) was from Hanwha Chemical Co., Ltd., Korea. with polymerization degree of 1700±100. Primary plasticizer DEHP was purchased from Samchun Pure Chemical Co., Ltd., Korea. Epoxidized soybean oil (ESO) (Figure 1) supplied by Songwon Industrial Co., Ltd., Korea was used as lubricant and chlorine radical collecting heat stabilizer. Zinc stearate and calcium stearate were purchased from Sigma Aldrich Co., LLC, Korea and were used as synergetic heat stabilizers [26].

The olive oil used for the medium in the plasticizer migration test was purchased from CJ Co., Ltd., Korea. The special grade of hydrochloric acid (HCL) was supplied by Samchun Pure Chemical Co. Ltd., Korea. The sodium hydroxide was from Junsei Chemical Co., Ltd., Korea. The acentonitrile and methanol were purchased from Sigma Aldrich Co., LLC, Korea.

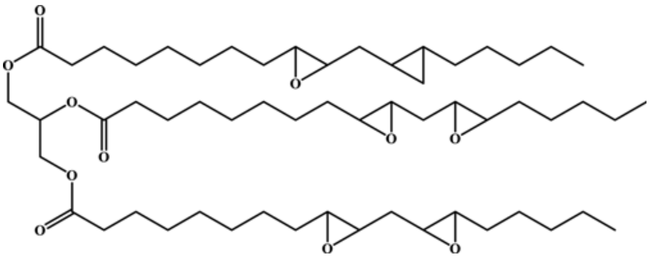

Figure 1. Chemical structure of epoxidized soybean oil.

Biopolyurethane Synthesis

The polyurethane for PVC plasticization was synthesized according to our previous research using the ratio shown in Table 1 [19]. Preparation of BPU was conducted in a four-neck round bottom reactor at normal pressure equipped with a mechanical stirrer, nitrogen inlet and outlet. Castor oil and PCL diol were melted at 80 °C for 1 h in the reactor under vigorous stirring in nitrogen purged atmosphere. Then the total amount of MDI added in three portions over the 1 h of reaction time interval. DMF solution was subsequently added to the reactor to control the viscosity increase due to BPU crosslinking.

Preparation of BPU/DEHP Plasticized PVC

The PVC plastisol was prepared by stirring the composition ratio descripted in Table 2. Half the amount of DEHP in 60 phr (per hundred resin) plasticized PVC was replaced with BPU to investigate the effect of the BPU/DEHP hybrid plasticizer. Zinc, calcium stearates were added as heat stabilizers [26]. ESO was added as a secondary plasticizer and heat stabilizer. The BPU was added to the PVC/DEHP plastisol before the melt compounding process. The mixture was then melt compounded using a co-rotating twin screw extruder (BA-19, Bautek) at 170 °C. In addition, the screw speed has been changed while melt blending as it is known that screw speed is independent of the blends [1].

Characterization

Fourier transform infrared (FTIR) spectra of BPU/DEHP plasticized PVC were recorded over the wavenumber range of 600 to 4000 cm^{-1} using a Nicolet 760 MAGNa-IR spectrometer equipped with a single reflection attenuated total reflectance (ATR) system. Dynamic mechanical thermal analysis (DMA) was conducted with a Mettler Toledo

Table 1. Composition of synthesized BPU

Sample	Polyols				Chain extender		Isocyanate	
	Castor oil		PCL diol		1,4-butane diol		MDI	
BPU	1.592 g	0.002 mol	95 g	0.047 mol	4.506 g	0.05 mol	25.025 g	0.1 mol

Table 2. Composition of the plasticized PVC

Component	BPU0	BPU3	BPU5	BPU7
PVC resin	58.8 (100)	69.9 (100)	69.0 (100)	68.0 (100)
DEHP	35.3 (60)	21.0 (30)	20.7 (30)	20.4 (30)
Zinc stearate	1.8 (3)	2.1 (3)	2.1 (3)	2.0 (3)
Calcium stearate	1.2 (2)	1.4 (2)	1.4 (2)	1.4 (2)
Epoxidized soybean oil	2.9 (5)	3.5 (5)	3.4 (5)	3.4 (5)
BPU	0	2.1 (3)	3.4 (5)	4.8 (7)

*in weight % (per hundred resin).

DMA/SDTA861E dynamic mechanical analyzer over the temperature range from -40 to 100 °C at 3 K/min of heating rate with 1 Hz of single frequency oscillation mode using at least five samples of dimensions 5 mm×2.5 mm. The mechanical properties were investigated using Instron 4465 universal testing machine (UTM) equipped with a 10 N load cell according to the ASTM D638 standard. Tensile tests were conducted with an elongation speed of 10 mm/min at room temperature and at least five samples were tested. The thermal stability was observed by thermogravimetric analysis (TGA) using a PerkinElmer Pyrsis 1 thermogravimetric analyzer under nitrogen atmosphere with a flow rate of 20 m*l*/min. The temperature was raised from 25 to 600 °C at 10 °C/min heating rate. The chemicals emitted during thermal degradation of the plasticized PVC/BPU samples were analyzed using PerkinElmer TGA Pyris 1 Clarus 680 GC/Clarus SQ8T MS.

HPLC was conducted to investigate DEHP migration of the prepared samples. A Waters Symmetry C18 5 μm (4.6 mm×150 mm column) was used as the HPLC column. All the samples were prepared by migrating DEHP from compression molded film in to different surrounding media in glass vials to prevent contamination. The HPLC results were obtained after migrating DEHP from the BPU/DEHP plasticized PVC in to the selected medium at 37 °C for 24 h, 72 h, and 1 week. The total amount of each migrated samples injected into the HPLC was 10 μ*l*. The flow rate was 0.6 m*l*/min with 60 % of acetonitrile and 40 % of methanol. The detection wavelength was 228 nm. The mediums used to detect DEHP migration of the samples were olive oil, deionized water, and pH 13, pH 1 with acid-base titrated medium with NaOH and HCl. Extra pure grade (>99 %) of DEHP was used to obtain standard curves in the HPLC migration test.

Results and Discussion

Biopolyurethane Synthesis

FTIR spectroscopy was performed to confirm the successful synthesis of BPU. The obtained spectra in Figure 2. shows the characteristic transmittance expected of conventional polyurethanes. C-N stretching and N-H out-of-plane bending bands were detected as a combined band at 1529 cm^{-1}. Ester C=O stretching band was detected at 1718 cm^{-1}, C-H stretching vibrations of urethane bonds were observed at 2864 cm^{-1} and 2942 cm^{-1}, and the N-H stretching band was detected at 3320 cm^{-1}. The spectra showed no transmittance bands relating to free -NCO group indicating the completion of polyurethane synthesis [19].

Plasticizer Compatibility of BPU/DEHP Plasticized PVC

The BPU/DEHP plasticized PVCs exhibited yellow characteristics and showed optical transparency indicating that the blends did not contain two phase ranges of different refractive indexes [27]. FTIR spectroscopy confirmed that the chemical structures of the PVC and BPU were retained

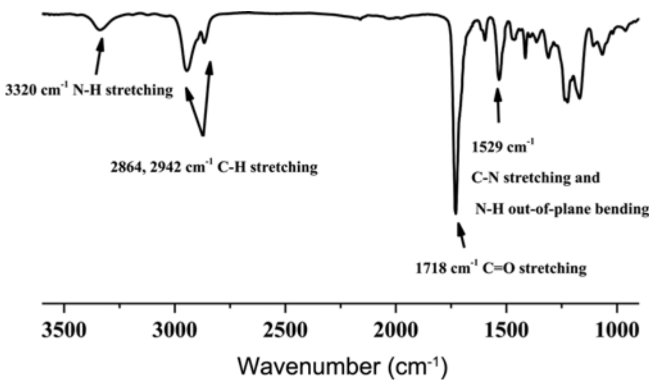

Figure 2. FTIR spectrum of the synthesized BPU.

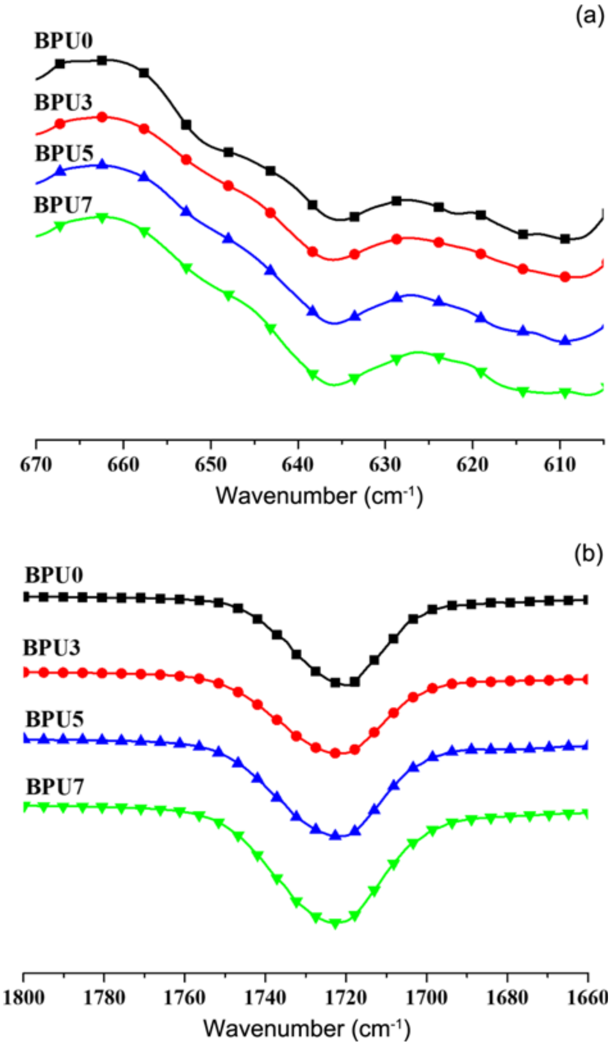

Figure 3. Scale expanded FTIR (a) C-Cl atactic stretching and (b) C=O stretching vibration spectra of BPU/DEHP plasticized PVCs.

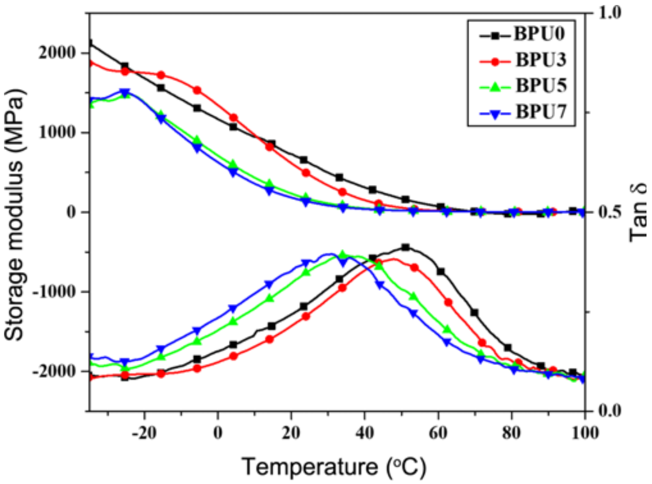

Figure 4. Storage modulus and tan δ as a function of temperature for the BPU/DEHP plasticized PVCs.

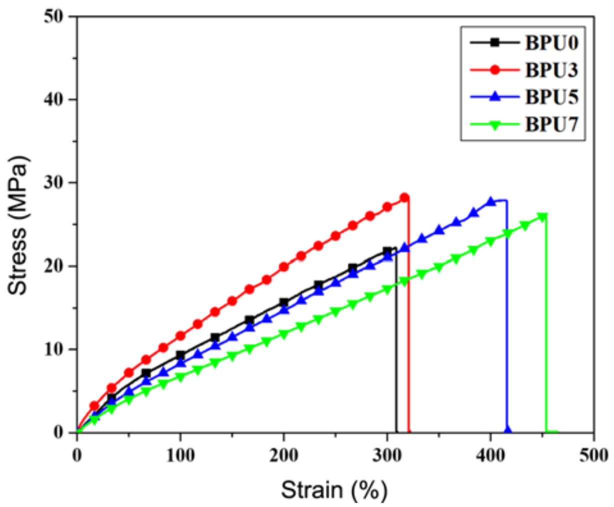

Figure 5. Stress-strain curves of BPU/DEHP plasticized PVCs.

Table 3. Mechanical properties of the plasticized PVC systems

Sample	Tensile strength (MPa)	Strain at break (%)	Tensile modulus (MPa)
BPU0	22.2±1.2	307.7±15.2	12.5±0.2
BPU3	30.0±1.2	320.5±31.2	14.1±0.9
BPU5	27.0±0.5	415.5±22.9	9.3±0.2
BPU7	25.4±1.1	453.7±19.8	7.8±0.4

after blending, as all the characteristic bonds were observed that those of PVC and BPU respectively. The interaction between DEHP plasticized PVC and synthesized BPU was investigated by analyzing the characteristic C-Cl atactic and C=O stretching vibration band in Figure 3. As the BPU content increases, the C-Cl atactic stretching vibration band shifted to the lower wavenumber and C=O stretching vibration band shifts were also observed. This corresponds to the stretching vibrations of plasticizer C=O groups and C-Cl bonds. These shifts are an indication of possible interactions between components of the BPU and DEHP plasticized PVC [28]. These results indicate that the increasing BPU content enhances the interaction between DEHP plasticized PVC and synthesized BPU [29,30].

Optical transparency confirmed the apparent homogeneity of the blends, however to confirm that the blends are chemically homogenous the presence of a single transition temperature was investigated. The confirmed glass transition temperature (Tg) of neat PVC by DSC was 83.05 °C and the Tg of the synthesized BPU was -3.68 °C. According to the tan δ curve in Figure 4, the blended films exhibited a single peak showing that the blended polymer was homogeneous. This gives evidence that the components of the blended PVC show some compatibility with each other [28,30,31]. Furthermore, as the BPU content increases, the tan δ peak shifted to a lower temperature indicating that the addition of BPU increases the flexibility of the plasticized PVC. This result can be supported by the storage modulus curve also shown in Figure 4, where increasing BPU content lowers the modulus.

Mechanical Properties

The representative stress-strain curves of the BPU/DEHP plasticized PVCs are shown in Figure 5. The apparent stress-strain curves imply that adding a small amount of BPU can increase both the stress and strain at break making the plasticized PVC more flexible and tough. The specific Young's moduli, tensile strengths, and strain at breaks for the plasticized PVCs are listed in Table 3. Youngs modulus and tensile strength of the BPU plasticized PVCs show an initial increase with BPU3. This result is in contradiction to the storage moduli values in Figure 3. where the storage modulus of BPU0 is higher than BPU3. The discrepancy between the two data can be attributed to the branched structure of BPU. Although the low storage modulus of BPU [19] lowers the storage modulus of PVC, the good interfacial adhesion between the branched BPU and PVC resulted as the toughened behavior under elongational deformation. However, with the increase in the BPU content the tensile strength and modulus both decreases. From past reports it is well known that the mechanical properties of plasticized PVC depend on the degree of dipolar interactions in the system. Therefore, the decrease in the tensile strength and modulus seems to result from the interruption between dipolar interaction of PVC by BPU acting as specific barriers in the plasticized PVC system [1]. BPU3 shows 320.5 % strain at break which is higher than BPU0. This result shows that even though DEHP was reduced by 50 %, BPU3 showed characteristics of plasticized PVC. Furthermore, the strain at break increases with the increase in BPU content, giving proof that BPU can act as a plasticizer in PVC systems. This can be attributed to the highly flexible nature of BPU prepared by the given proportion of hard and soft segments [19].

Thermal Degradation and Detection of Gaseous Emission

PVC is known to thermally decompose in a two-step process. The first step of decomposition occurs at around 220 to 350 °C with a significant dehydrochlorination. This causes the release of HCl by the breakage of the conjugated double bonds which are relatively weak. The second step occurs at around 450 to 500 °C by the pyrolysis of linear and cyclic hydrocarbons [26,32-36]. On the other hand, for the decomposition of polyurethanes, the first step occurs around above 200 °C which is due to the urethane bond pyrolysis. At around 150 °C, the urethane bonds repeatedly separate and recombine. However, the urethane bonds suffer from irreversible decomposition over 200 °C. The second step at 470 °C, comes from the degradation of castor oil [19,20,37].

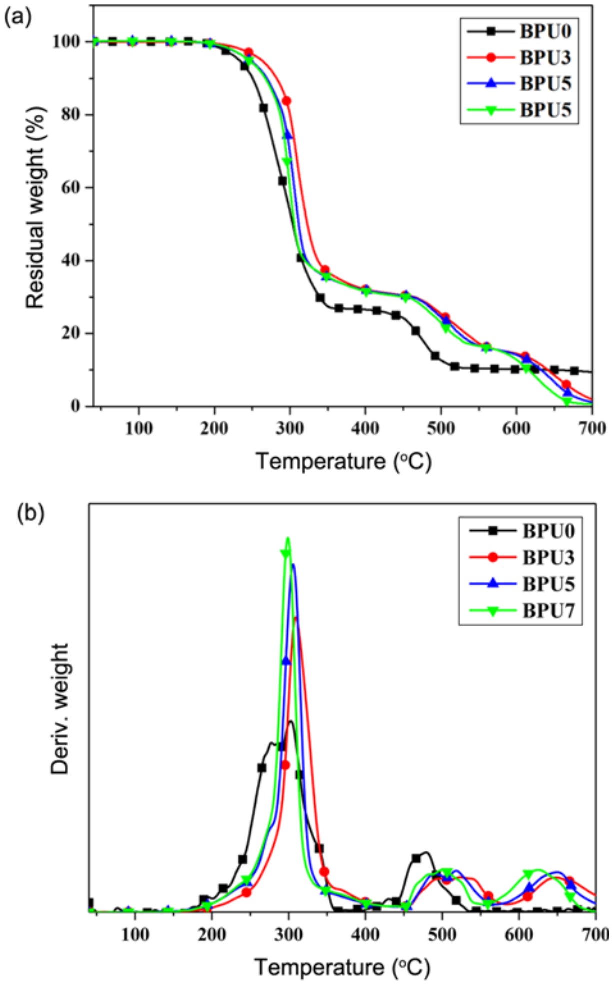

Figure 6. TGA thermograms (a) and derivative curves (b) of BPU/DEHP plasticized PVCs.

The thermal degradation behavior of the prepared plasticized PVCs was analyzed by TGA as shown in Figure 6. and Table 4. The TGA thermogram shows typical features of plasticized PVC degradation. The samples with added BPU showed degradation at elevated temperatures compared to PVC plasticized solely by DEHP. This thermal feature can be related to the higher degradation temperature of the solid-

Table 4. Thermal degradation parameters of the plasticized PVC systems

Sample	$T_{\rm i}$ (°C)[a]	T_{75} (°C)[b]	$T_{\rm max1}$ (°C)[c]	$T_{\rm max2}$ (°C)[d]
BPU0	197.5	439.7	302.8	479.1
BPU3	221.0	501.9	310.4	523.6
BPU5	205.2	496.7	305.8	518.2
BPU7	207.8	489.5	298.1	499.6

[a]The initial thermal degradation temperature ($T_{\rm i}$) at 1 % weight reduction. [b](T_{75}) at 75 % weight reduction. [c]the decomposition temperature at maximum rate of the primary weight loss, and [d]the decomposition temperature at maximum rate of the secondary weight loss.

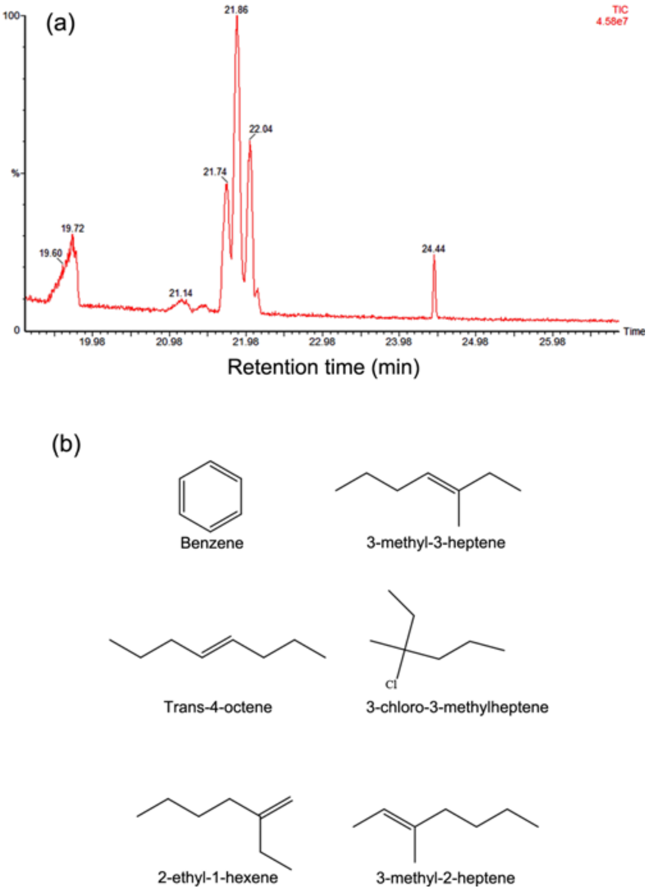

Figure 7. (a) TIC of evolved gases from degradation of BPU3 in nitrogen and (b) schemes of detected molecules during the thermal decomposition.

state urethane plasticizer compared to the liquid state DEHP. In addition, the elevated degradation temperatures could be explained by the interaction between urethane bonds of the BPU and α-hydrogen of the chlorinated polymer as reported by Pielichowski and Hamerton [38]. To further understand the degradation of the hybrid plasticized PVC TGA GC/MS was applied (Figure 7). According to TGA GC/MS analysis, not only dehydrochlorination but also linear and cyclic hydrocarbons were detected for the plasticized PVC. This can be interpreted as the degradation steps did not proceed in separate steps. Expressed differently, the degradation steps stated previously were mainly attributed to the amount of gaseous emission from the samples.

Phthalate Migration by HPLC

DEHP detected after incubation of the plasticized PVC in various media after 24 h, 72 h, and 1 week are shown in Table 5. Among the four conditions, DEHP was detected only in the olive oil medium condition [39]. As BPU content increased from 3 to 5 phr, the amount of DEHP migration decreased. However, the DEHP migration of the samples that contained 7 g of BPU increased more than the one which contained 5 g of BPU. The addition of a 5 part of BPU decreases the plasticizer migration, however, the migration rate increases when the amount of plasticizer exceeds 5 phr. The reduction of the DEHP migration can be explained by the relatively high molecular weight proportion of the BPU which hinders plasticizer migration. It can also be interpreted as the plasticizers were saturated between PVC chains. Therefore, the saturated plasticizers expand to the maximum distance between PVC chains which accelerates the DEHP migration. On the other hand, the largest amount of plasticizer has migrated when the samples were incubated for 72 hours. In the perspective of time, it can be explained as after DEHP molecules gradually permeated into the surrounding media, the surrounding media slowly took possession of the vacant place of PVC chain. By extension, a temporary equilibrium of DEHP concentration in the PVC chain and surrounding medium could be reached due to the counter-diffusion. Therefore, the equilibrium was proceeding between the after 24 h to 72 h and it can be said that the equilibrium state was almost completed due to the decreased DEHP migration [40].

Table 5. DEHP detection by HPLC of plasticized PVC films incubated in different media (ppm)

Sample	Migration media	24 hours	72 hours	1 week
BPU3	Olive oil	1932	4003	6378
	pH 13	0	0	0
	pH 1	0	0	0
	Deionized water	0	0	0
BPU5	Olive oil	1153	3123	5234
	pH 13	0	0	0
	pH 1	0	0	0
	Deionized water	0	0	0
BPU7	Olive oil	1312	3770	7366
	pH 13	0	0	0
	pH 1	0	0	0
	Deionized water	0	0	0

Conclusion

In this research DEHP combined with BPU were used as plasticizers to increase flexibility to PVC. The DEHP/BPU plasticizer reached the desired elongational properties with reduced amounts of DEHP, showing that the BPU successfully acted as plasticizer for PVC. The resultant plasticized PVC showed homogeneous properties by the presence of a single Tg, proving that the enhanced ductility up to 453.7 % was not due to interfacial chain slippage caused by the incompatibility of the BPU and PVC. This result was supported by the increase in tensile strength and modulus, showing physical interactions within the blends. Furthermore, the addition of the BPU to plasticized PVC seems to act as a barrier to the DEHP decreasing the plasticizer migration amount. These results suggest that hybridization of DEHP and BPU as plasticizers can provide a solution to the endocrine disruption problem of DEHP in plasticized PVCs.

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