Nanobrush Structured Oligo(ε-caprolactone) as a Novel Plasticizer for the Manufacture of Eco-friendly Poly(vinyl chloride)

Woo Hyuk Choi* and Seung-Yeop Kwak**

Department of Materials Science and Engineering, Seoul National University,
599 Gwanak-ro, Gwanakgu, Seoul 151-744, Korea
*korean1616@yahoo.co.kr, **sykwak@snu.ac.kr

ABSTRACT

Nanobrush structured oligo(ε-caprolactone) (nb-OCL), which has excellent mobility and many carbonyl groups interacted with poly(vinyl chloride) (PVC) chain, was synthesized as a alternative plasticizer for endocrine-disrupting di(2-ethylhexyl) phthalate (DEHP) which migrated from PVC. The flexible PVC, which was plasticized by nb-OCL using solution blending, was evaluated plasticizer efficiencies by the lowering of glass transition temperature and the enhancement in percentage elongation at break. In addition, plasticizer migration tests were carried out three different conditions which are contact with a liquid media, other solid substrates, and atmosphere. Through this investigation, we found that PVC/nb-OCL had flexibility as high as PVC/DEHP, and that there was no plasticizer migration even under harsh condition at the extractability and exudability tests, while DEHP was migrated from PVC. Finally, nb-OCL can be used as a novel plasticizer for eco-friendly flexible PVC.

Keywords: oligo(ε-caprolactone), alternative plasticizer, eco-friendly, poly(vinyl chloride)

1 INTRODUCTION

The flexible PVC is a rubbery polymeric material that is widely used, particularly in military, construction, biomedical, baby-care, and food packaging applications. For the manufacture of the flexible PVC, phthalates such as DEHP are the most commonly used plasticizers for better processability during processing and greater flexibility in end use. According to the information recently reported, the phthalates still hold almost 90% of the world's plasticizer market. There have been, however, many studied on toxicity as an endocrine disruptor of DEHP which migrated from flexible PVC [1]. Plasticizer migration raises enormous concerns, mainly plasticizer toxicity and deterioration of PVC properties. As a result of these concerns about phthalates, many countries have introduced regulations on the use of phthalates in flexible PVC.

To solve these problems, several approaches have been studied, but they are incomplete [2]. One approach is low molecular weight plasticizers that impart flexibility to PVC as high as DEHP, but they still undergo plasticizer migration. Another approach is surface treatment that has been shown to successfully inhibit plasticizer migration but deteriorate the physicochemical properties of the PVC products. The other approach is blending PVC with polymeric plasticizers seems to be one of the better approaches, but they impart insufficient flexibility to PVC.

In this study, we focused on oligo(ε-caprolactone) (OCL) and nanobrush structure, since OCL is well known as a non-toxic material and very high miscibility with PVC, and nanobrush structure has excellent mobility with many carbonyl groups interacted with PVC chain and a properly high molecular weight to prevent plasticizer migration from PVC. Therefore, the main objective of this study is to investigate the development of nb-OCL as an eco-friendly plasticizer which has high flexibility without plasticizer migration from PVC.

2 EXPERIMENTAL

2.1 Materials

ε-caprolactone (CL, Alfa Aesar, 99%), dipentaerythritol (DPTOL, Sigma-Aldrich, technical grade), tin(II) 2-ethylhexanoate ($Sn(Oct)_2$, Sigma-Aldrich, 95%), methanol (MeOH, Daejung Chemicals & Metals, 99.5%), di(2-ethylhexyl) phthalate (DEHP, Junsei chemical, 99%) was purchased. Straight poly(vinyl chloride) (PVC) resin, P-1000, was provided by Hanwha Chemical Co. Ltd., Korea. The thermal stabilizer, MT-800, was supplied by Songwon Co., Ltd., Korea. All chemicals were used as received without any further purification except DPTOL which was dried at 120 °C for several hours.

2.2 Polymerization of Nanobrush Structured oligo(ε-caprolactone)

nb-OCL was prepared by ring-opening polymerization of CL which was initiated with DPTOL as a multifunctional initiating core in the presence of catalytic amount of $Sn(Oct)_2$ (Figure 1). Brush number was accomplished by DPTOL having 6 hydroxyl groups, and brush length were controlled by CL-to-hydroxyl group molar ratio which was $[CL]_0/[-OH]_0 = 5$ [3]. The basic reaction procedure of the nb-OCL is as follows. 200 mmol of CL and 6.67 mmol of DPTOL were put into the reaction flask, which was followed by the three repeated session of evacuation and nitrogen purging processes. The flask was then immersed

into an oil bath stabilized at 160 °C with vigorous stirring for 30 min, where the DPTOL was dissolved in CL medium forming a homogeneous mixture. Since then, the oil bath was adjusted to 110 °C, and certain amount of the catalyst, $Sn(Oct)_2$, was added to the flask. After 36 h polymerization under a stream of nitrogen, the reaction mixture was cooled to room temperature and poured dropwise into an excess of cold MeOH. The precipitates were washed with MeOH for several times and dried at room temperature in a vacuum.

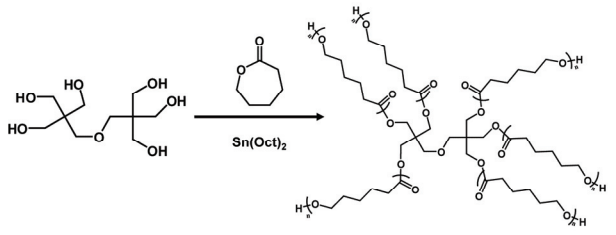

Figure 1: Polymerization of nb-OCL.

The polymerization of nb-OCL was monitored with Fourier-transform infrared (FT-IR) spectroscopy using Perkin-Elmer GX IR spectrophotometer with a spectral resolution of 4 cm^{-1} in the range 4000 ~ 400 cm^{-1}. All samples were prepared with compression-molding, and potassium bromide (KBr) powder was used as the sample matrix and reference material. The brush length of nb-OCL was confirmed with 600 MHz high resolution ^1H nuclear magnetic resonance (NMR) spectroscopy using a Bruker Avance 600 with chloroform-*d* ($CDCl_3$-*d*) as the solvent. In addition, the number-average molecular weight of nb-OCL was measured by ^1H NMR end-group analysis ($M_{n,\ NMR}$) and matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry ($M_{n,\ MALDI}$) using Applied Biosystems Voyager-DE STR Biospectrometry Workstation with dithranol/THF as the matrix solution.

2.3 Preparation of the Flexible PVC

PVC/nb-OCL was prepared by solution blending using THF as a solvent [4]. In order to compare the plasticization efficiency and plasticizer migration, neat PVC and PVC/DEHP were also prepared by solution blending. The formulations of the flexible PVC are 100 parts per hundred (phr) of PVC resin, 60 phr of plasticizer and 2 phr of the thermal stabilizer. The solution blending procedure of the flexible PVC was as follows. PVC resin and nb-OCL or DEHP were separately dissolved in THF until the solution becomes homogenous. After that, THF solvent was slowly removed being subject to heating at 60 °C oven for 24 h in order to completely remove all the residual solvent. Finally, the transparent PVC/nb-OCL film was obtained.

The plasticization efficiencies of the PVC/nb-OCL were evaluated by the lowering of the glass transition temperatures, T_g, and the enhancement in percentage elongation at break, %EB. T_g of the flexible PVC samples were determined with Netzsch DSC 200 F3 Maia differential scanning calorimetry (DSC) at a heating rate of 10 °C/min in the temperature range −110 ~ 140 °C under a stream of nitrogen. Moreover, %EB of the flexibility PVC samples were measured by tensile test performed with Instron-5543 universal testing machine (UTM). The tests were conducted at a strain rate of 20 mm/min using a 100 N static load cell. The test samples had dumbbells shape with a width of 9.5 mm and a thickness of 0.5 mm in accord with the American Standard Testing Method (ASTM) D-638.

2.4 Evaluation of Plasticizer Migration

The plasticizer migration tests were carried out three different conditions which are contact with a liquid media (extractability), other solid substrates (exudability), and atmosphere (volatility) under harsh condition to clearly determine the plasticizer migration, in which the films of dimension 20 × 20 × 0.5 mm^3 were used. All plasticizer migration tests were carried out based on the appropriate ASTM. In the extractability test, ASTM D5227-95, the films were immersed in 1 L of n-hexane and stirred at 50 °C for 2 h. In exudability test, ASTM D2199-82, the films were placed between two sheets of unplasticized poly(methyl-methacrylate) (PMMA) and pressed by 10 ton at 50 °C for 72 h. In volatility test, ASTM D1203-94, the films were placed at the center of activated carbon (granular, 4 ~ 14 mesh) at 80 °C for 24 h.

3 RESULT AND DISCUSSION

3.1 General Characterization of Nanobrush Structured Oligo(ε-caprolactone)

In the FT-IR spectrum, which spectrum is not included on this paper, of nb-OCL, five main absorptions are observed; O−H stretching (3600 ~ 3200 cm^{-1}), sp^3 C−H stretch (3000 ~ 2800 cm^{-1}), unconjugated ester C=O (1720 cm^{-1}), ester C−O stretch (1300 ~ 1000 cm^{-1}), and C−C stretch (1100 ~ 1000 cm^{-1}). These results indicate that the successful polymerization of nb-OCL was confirmed qualitatively.

As can be seen in Figure 2, the chemical structure of nb-OCL with 6 brushes was confirmed. Furthermore, the average brush length of nb-OCL, *n*, and $M_{n,\ NMR}$ were calculated from the ratios of the integrated area. The peak assigned to the chain ends (e, δ 3.65) and the peak assigned to the repeating methylene units (a, δ 2.31) in OCL segments were quite distinguishable; therefore, *n* values could be easily calculated from the ratios of the integrated area of these peaks. $M_{n,\ NMR}$ was also calculated from the following equation (1):

$$M_{n,\,NMR} = M_{core} + M_{CL} \times n \quad (1)$$

where M_{core} and M_{CL} are the molecular weight of initiating core (DPTOL) and CL, respectively.

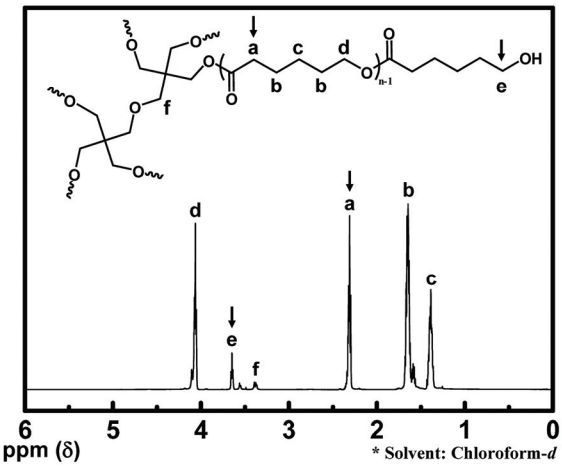

Figure 2: ^{1}H NMR spectrum of nb-OCL.

The molecular weight of nb-OCL was also determined by MALDI-TOF mass spectrometry. In Figure 3, the mass difference between each adjacent peak is 114 m/z (mass-to-charge ratio), which corresponds well with the mass of the CL repeating unit in nb-OCL. For nb-OCL, $M_{n,\,MALDI}$ was found to be in good agreement with $M_{n,\,target}$. Brush length and molecular weight of nb-OCL determined by ^{1}H NMR and MALDI-TOF mass spectrometry were listed in Table 1.

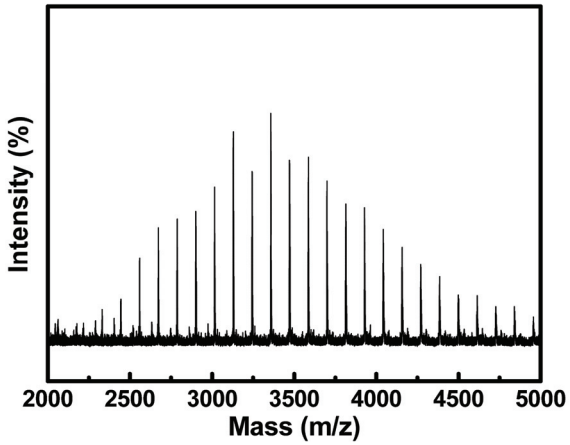

Figure 3: MALDI-TOF mass spectrum of nb-OCL.

Sample	Brush length (n)		Molecular weight (M_n) (g/mol)		
	target	^{1}H NMR	target	MALDI	^{1}H NMR
nb-OCL	5	5.91	3678	3456	4302

Table 1: Brush length and molecular weight of nb-OCL determined by ^{1}H NMR and MALDI-TOF mass spectrometry.

3.2 Plasticization Efficiency of the Flexible PVC

The miscibility of the blend samples is ascertained through the measurement of T_g with DSC, which is one of the most widely used techniques for evaluating blend miscibility on a nanoscale. Figure 4 shows the thermograms of neat PVC, PVC/nb-OCL, and PVC/DEHP, which were recorded during the second heating step. As shown in Figure 4, single T_g is observed for PVC/nb-OCL that indicates complete miscibility.

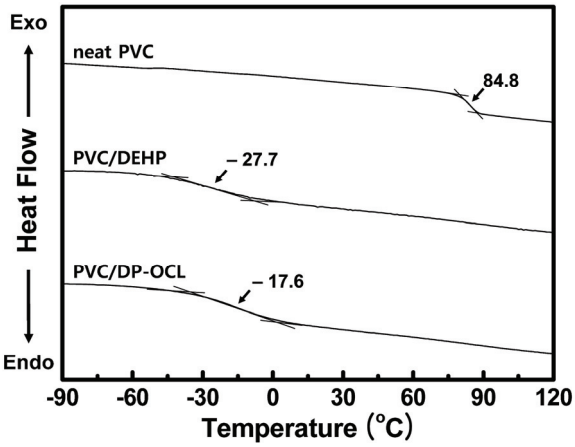

Figure 4: DSC thermograms of the PVC samples.

We adopted two test methods to compare the plasticization efficiencies of nb-OCL and DEHP. One method is related to the lowering of T_g, ΔT_g, and the other to the enhancement in the %EB.

The addition of a plasticizer has the effect of increasing the free volume of the plasticized polymer and thus the lowering T_g. The plasticization efficiency determined by the lowering T_g, $E_{\Delta T_g}$, was calculated from equation (2):

$$E_{\Delta T_g}(\%) = \frac{\Delta T_{g,sample}}{\Delta T_{g,DEHP}} \times 100 \quad (2)$$

The plasticization efficiency at room temperature was estimated by stress-strain curves, which is not shown on this paper, from tensile test using UTM. The plasticization efficiency determined by %EB, $E_{\%EB}$, was calculated from equation (3):

$$E_{\%EB}(\%) = \frac{\Delta \%EB_{sample}}{\Delta \%EB_{DEHP}} \times 100 \quad (3)$$

Plasticization efficiencies of the PVC samples are listed in table 2. These results indicate that nb-OCL can be used as a substitute for DEHP in flexible PVC.

Samples	T_g (°C)	$E_{\Delta T_g}$ (%)	%EB (%)	$E_{\%EB}$ (%)
Neat PVC	84.8	—	15.10	—
PVC/DEHP	– 27.7	100.00	416.13	100.00
PVC/nb-OCL	– 17.6	91.02	267.34	62.90

Table 2: The glass transition temperatures and percentage elongations at break with plasticization efficiencies of the PVC samples.

3.3 Plasticizer Migration of the Flexible PVC

To further investigate the applicability of nb-OCL as more eco-friendly plasticizer, plasticizer migration stability of the PVC/nb-OCL sample was verified and compared to that of the PVC/DEHP sample. Plasticizer migration behavior was characterized by measuring the weight loss of the specimens under three different test conditions designed to simulate the environments where flexible PVC products are used. It is noted that the test methods were accelerating the plasticizer migration so that the weight loss during the tests would be large enough to contrast the plasticizer migration of PVC/DEHP with that of PVC/nb-OCL. Each plasticizer migration was determined by measuring the weights of the samples before and after the test as follows equation (4):

$$\text{plasticizer migration}\ (\%) = \frac{W_1 - W_2}{W_1 \times x} \times 100 \qquad (4)$$

where W_1 and W_2 are the weights of plasticizers in the specimens before and after the tests, respectively, and x is weight fraction of plasticizer in the flexible PVC, which is 60/162. There is one assumption that all weight losses during the tests are anticipated to be come from the weight losses of plasticizers, since the PVC can be reasonably considered as stable under the test conditions due to its well-known properties.

The results are shown in Figure 5, in which 80.86, 4.23, and 5.82% of plasticizer in the PVC/DEHP sample were found to have migrated out during the extraction, exudation, and volatility tests, respectively. These results were the averages of the values for three specimens of the same composition. In contrast, there were no weight losses of the plasticizer in the PVC/nb-OCL sample at the solution extractability and the solid exudability tests. The superior plasticizer migration stability of the PVC/nb-OCL is anticipated to the much higher molecular weights of nb-OCL being ca. 3,500 g/mol compared to that of DEHP being 391 g/mol and the many interaction sites between carbonyl groups in nb-OCL and PVC chain.

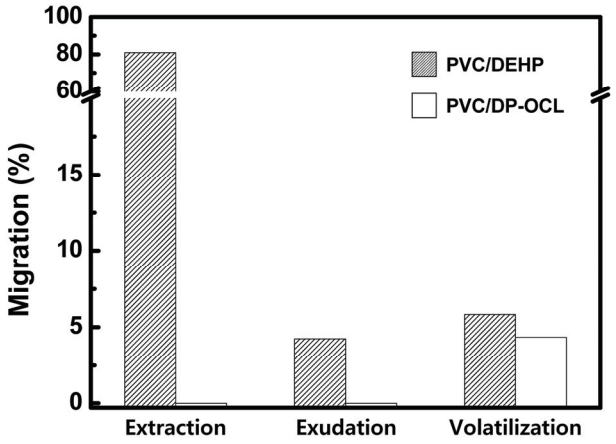

Figure 5: Plasticizer migration for the PVC/DEHP and PVC/nb-OCL.

4 CONCLUSION

In the present study, OCL was chosen because it is well known as a non-toxic material and very high miscibility with PVC. Thus, OCL was polymerized based on nanobrush structure. In order to evaluation of plasticization efficiencies and verification of plasticizer migration, PVC plasticized with nb-OCL was manufactured. From results of evaluation of plasticization efficiency, the PVC/nb-OCL has flexibility as high as the PVC/DEHP. In addition, the PVC/nb-OCL was found that there is no plasticizer migration even under rather harsh conditions at the solution extractability and the solid exudability tests. Therefore, we successfully develop nb-OCL as a novel plasticizer for eco-friendly flexible PVC

REFERENCES

[1] M. Hakkarainen, Adv. Polym. Sci. 211, 159, 2008
[2] J. Choi and S. –Y. Kwak, Environ. Sci. Technol. 41, 3763, 2007
[3] J. Choi, I. –K. Kim, S. –Y. Kwak, Polymer 46, 9725, 2005
[4] D. Wang and C. A. Wilkie, J. Vinyl. Addit. Technol. 8, 238, 2002