

Viscoelastic Behavior of PVC Plastisol with Cyclodextrin Derivative and Anti-Migration of Plasticizers in Flexible PVC

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ABSTRACT

Rheological analysis can be a particularly useful tool for studying poly(vinyl chloride) (PVC) plastisol manufacturing processes. In this study, two kinds of conventional plasticizer, di-isononyl phthalate (DINP) and di-isononyl cyclohexene-4,5-dicarboxylate (Neocizer), incorporating cyclodextrin derivative (CD-*d*) were mechanically mixed with PVC resin to prepare PVC plastisols. CD-*d* was prepared to improve the ability of anti-migration in plasticizers by the modification. In order to investigate the influence of CD-*d* on the rheological behavior of PVC plastisols, the viscoelastic measurements were utilized to continuously monitor the change of the storage modulus, G' , and loss modulus, G'' , as a function of temperature by means of a parallel-plate rotational rheometer. The results showed that completion of gelation was slightly delayed and storage modulus decreased with addition of CD-*d* in the PVC matrix. FE-SEM was also used to observe the particulate structure of PVC plastisols at various stages of gelation and fusion. Subsequently, prepared PVC plastisol was converted to the flexible PVC by heating briefly to the fusion temperature and then cooling. Migration test of resulting flexible PVC were additionally carried out according to ISO 3826:1993(E) method. It was found that the addition of CD-*d* decreases the levels of plasticizer from the flexible PVC by almost 40%.

INTRODUCTION

Generally, the flexible PVC products are fabricated through the pre-mixture in a liquid form, *i.e.* plastisol, which is a suspension of fine PVC particles dispersed in a plasticizer.¹ The plastisol is converted to the final product by heating briefly to the fusion temperature and then cooling. Therefore, the processability requirements in PVC plastisol processing emphasize the viscoelastic behavior such gelation and fusion of plastisol. Previously a method of characterizing the progress of gelation and fusion continuously over the temperature range of interest by using viscoelastic measurements has been developed.² It is necessary to determine whether changes in the processing conditions of PVC plastisol were needed for use in industrial application.

Cyclodextrins are composed of six (α -), seven (β -), eight (γ -) or more α -(1,4)-linked glucose units forming a toroidal shape with a hydrophobic cavity. The average diameters of cavities are 0.45 nm for α -CD, 0.65 nm for β -CD, and 0.83 nm for γ -CD.³ Primary and secondary hydroxyl groups available for modification are present on the smaller and larger rims, respectively, marking the external surface hydrophilic. CDs are capable of forming inclusion complex with a variety of small molecules of the appropriate size and polarity through the influences of non-covalent interaction (*e.g.* van der Waals force and hydrophobic interaction).⁴

Specifically, β -CD has some applications in a wide range of fields and especially environmental protection by using their ability such as formation of inclusion complex which is able to effectively immobilize toxic compounds.⁵

In this work, DINP and Neocizer as a plasticizer, incorporating CD-*d* were mechanically mixed with emulsion grade PVC resin to prepare PVC plastisols. CD-*d* was prepared to improve the ability of anti-migration of DINP and Neocizer by the modification. It was necessary to determine whether changes in the processing conditions of PVC plastisol were needed for use in industrial application. In order to investigate the influence of CD-*d* on the rheological behavior of PVC plastisols, the viscoelastic measurements were utilized to continuously monitor the change of the storage modulus, G' , and loss modulus, G'' , as a function of temperature. FE-SEM was also used to observe the morphological change of PVC plastisols at various stages of gelation and fusion. In addition, plasticizer migration tests were carried out for the flexible PVC according to the ISO 3826:1993(E) test method,⁶ and the quantity of migrated plasticizers was then determined with gas chromatography.

EXPERIMENTAL

Materials

β -CD was obtained from Tokyo Chemical Industry Co., LTD. and dried in a vacuum oven at 60 °C for 7 days before its use. Benzoyl chloride and anhydrous pyridine were purchased from Sigma-Aldrich (stated purity $\geq 99\%$). DINP and Neocizer were kindly provided by Aekyung Petrochemical Co., Ltd., Korea (Fig. 1). Emulsion grade PVC resin, LG PB1752, was kindly provided by LG Chem. Ltd., Korea. Epoxidized soybean oil (ESO) was purchased from Yakuri pure chemicals Co., Ltd., Japan. Thermal stabilizer, MT-800, was supplied by Songwon Co., Ltd., Korea.

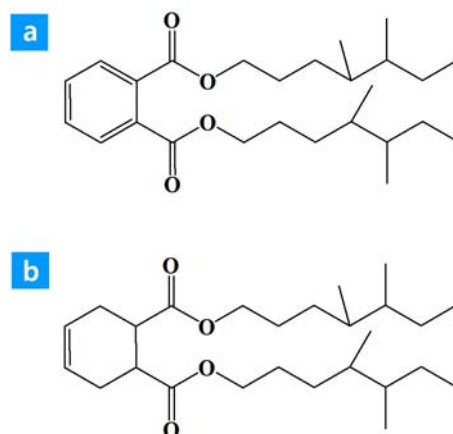
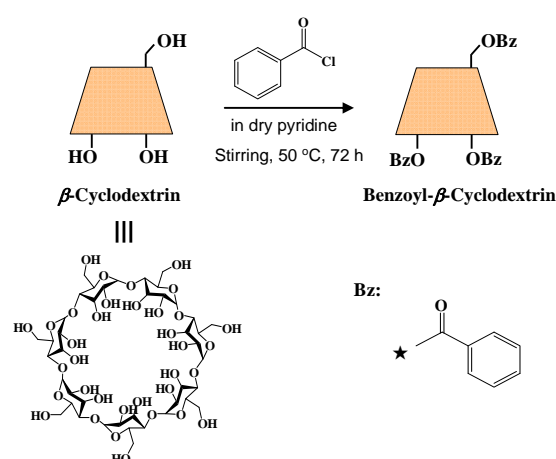


Figure 1. Chemical structure of (a) DINP and (b) Neocizer.

Preparation of cyclodextrin derivative (CD-*d*) nanoparticles

β -CD was modified with benzoyl chloride, resulting in CD-*d* (Scheme 1). 11.35 g (10 mmol) of purified and dried β -CD was stirred into 240 ml anhydrous pyridine and then 160 ml benzoyl chloride (1.44 mol) was added. The solution was stirred at 50 °C for 72 h. At the end of the reaction, the bright pink solution was varied to orange-brown solution with some precipitate. The resulting mixture was evaporated at 50 °C under reduced pressure until about half volume. The thick solution was cooled in an ice-bath, and 500 ml of



Scheme 1. Preparation of CD-*d* as a migration restrainer.

anhydrous methanol was added very slowly with stirring. The plentiful white precipitate was filtered off, and the crude product was resuspended in methanol. The white powders in methanol were filtered out and washed several times with distilled water and methanol by turns. Finally, the product was dried in a vacuum oven and ground to fine white powders.⁷

Rheological observation of PVC plastisols with CD-*d*

The PVC plastisols were composed of dried emulsion PVC, DINP or Neocizer (70 parts per hundred resin (phr)), epoxidized soybean oil (ESO) (3 phr), thermal stabilizer (2 phr), and CD-*d* (10 phr). All materials were mixed for a day with mechanical mixer of a two-blade propeller for homogenization. After completion of the mixing, air bubbles in plastisols were removed in a vacuum and the resulting plastisols were aged for two weeks before their use. The rheological behavior of PVC plastisols was examined for investigation of the influence of CD-*d* and the determination of their processing condition. The parallel-plate rotational rheometer, Rheometer AR2000 (TA instruments Inc.), was used in the dynamic oscillatory mode with a controlled heating rate. The 40 mm diameter parallel discs were used with a gap setting of 1 mm. The frequency of oscillation and shear strain amplitude were maintained to be 10 Hz and 2.5%, respectively. The measurement temperature was controlled from 25 to 200 °C with a programmed increase rate of 5 °C min⁻¹.

Migration tests

First of all, the plasticized PVC sheets were fabricated in size of 30×30×2 mm. The PVC sheets (*i.e.* PVC/DINP, PVC/DINP-CD, PVC/Neo, and PVC/Neo-CD) were rinsed with distilled water to remove the dusts and impurities on the surface. Leaching test was carried out for reference of ISO 3926:1993(E) test method. Distilled water

and ethanol were mixed to prepare the leaching solution. The ratio of distilled water and ethanol was set to 123.77:100 (v/v) at 25 °C. Each prepared sheet was soaked into the 100 ml leaching solution. The testing temperature was kept at 37 ± 1 °C and the samples remained for 7 days without shaking. The standard solutions were prepared before the measurements. The solution 1 was made by dissolving 1 g of plasticizers (DINP and Neocizer) in 100 ml ethanol. The solution 2 was made by diluting 10 ml of the solution 1 to 100 ml ethanol. The following procedures are below. The standard solutions and leached plasticizers were analyzed by gas chromatography (GC). Quantitative analysis of leached plasticizers was performed on a Hewlett Packard model 6890 Series II Plus gas chromatograph.

RESULTS and DISCUSSION

Modification of β -CD and dispersion of CD-*d* in plasticizers

Fig.1 shows the ¹H NMR spectra of neat β -CD, benzoyl chloride, and CD-*d*. ¹H NMR spectroscopy gave additional evidence of modification and determined degree of substitution (DS). The spectrum of CD-*d* showed that peaks of hydroxyl groups of β -CD disappeared and involved peaks

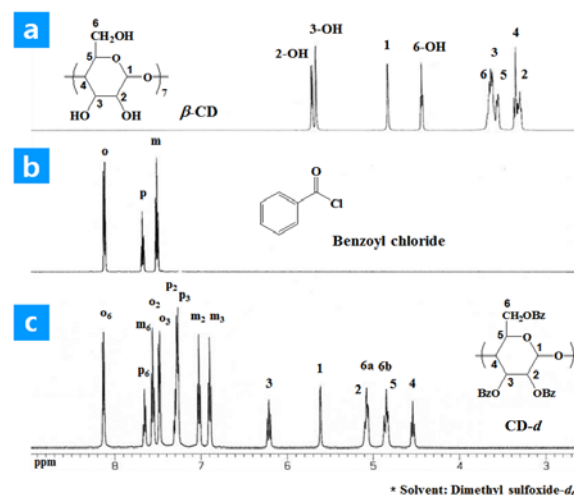


Figure 2. ¹H NMR spectra of (a) β -CD, (b) benzoyl chloride, and (c) CD-*d*.

attributed to protons of benzoyl group (*i.e.* 2,3,6-COC₆H₅ at 6.9~8.1 ppm) substituted for the three hydroxyl groups of β -CD. Each proton (*i.e.* 3-*H* triplet at 6.2 ppm, 1-*H* doublet at 5.6 ppm, 2-*H* doublet of doublets at 5.1 ppm, 5-, 6_a-, 6_b-*H*, at 4.8~5.0 ppm and 4-*H* triplet at 4.5 ppm, respectively) of a glucose unit was detected and the peaks shifted to downfield by modification. The number of benzoyl groups, *x*, substituted to hydroxyl groups of a glucose unit (*i.e.* one of primary and two of secondary hydroxyl group) is simply determined from the areas of relative peaks in the ¹H NMR spectrum. The value of DS was calculated to be approximately 2.91/3.00, which confirms the successful modification of neat β -CD into

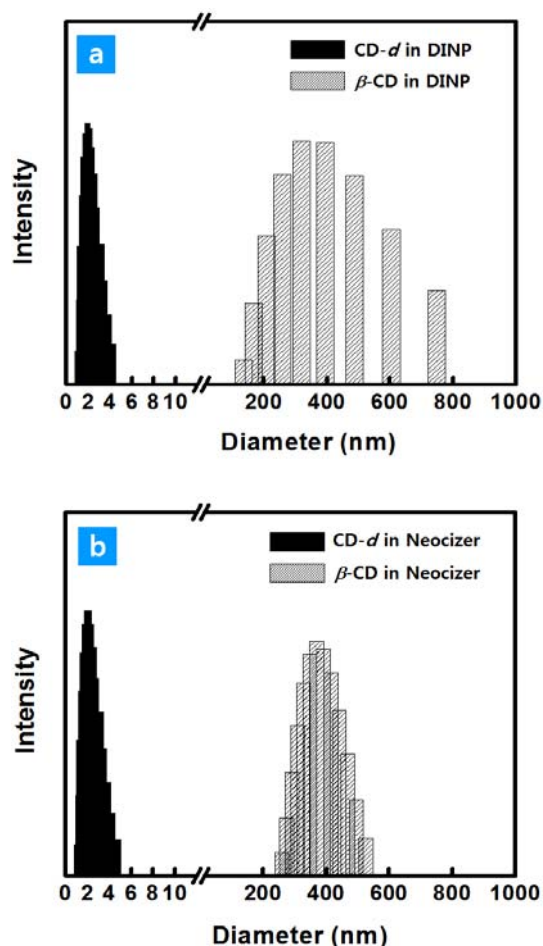


Figure 2. Particle size distributions of CD-*d* (solid black bar) and neat β -CD (shaded gray bar) in (a) DINP and (b) Neocizer.

CD-*d*. Fig. 2 shows the particle size and its distribution of CD-*d* and neat β -CD in both plasticizers. Moving particle in Brownian motion causes a Doppler shift according to changing the wavelength of the incoming light. This change is related to the size of the particle and it is possible to compute the sphere size distribution. This method is based on the intensity of scattered laser light, which is measured by periods and depends on the particle size. Smaller particles diffuse faster than the larger ones. The DLS exhibited nanosized dispersion of CD-*d* in both DINP and Neocizer ($d = 2.1 \pm 0.8$ nm in DINP, $d = 2.3 \pm 0.8$ nm in Neocizer).

Rheological behavior of PVC plastisols

PVC resins obtained by the emulsion polymerization process are usually used in the preparation of plastisols. Generally, the plasticized PVC products are fabricated through the plastisol by heating briefly to the fusion temperature and then cooling.⁸ Therefore, the processability requirements in PVC plastisol processing emphasize the viscoelastic behavior such gelation and fusion of the plastisol. During gelation and fusion important changes such as the elastic and the viscous modulus in rheological magnitudes were observed. Fig. 3(a) was change of G' and G'' of PVC/DINP and PVC/DINP-CD plastisols being recorded as a function of temperature. The viscoelastic behavior obtained from PVC/DINP-CD was similar to that of PVC/DINP. In Fig. 3, G' of all plastisols are plotted together for a better comparison. The maximum of the modulus corresponds to a completion gelation and onset of fusion. The completion of gelation of PVC/DINP-CD plastisols was 158 °C, and exhibited a slightly higher temperature in comparison with PVC/DINP plastisol (150 °C). It is likely to say that the gelation of the PVC plastisols was delayed by the addition of CD-*d* particles which obstruct the absorption of the plasticizer. Moreover, the a little decrease of G' was observed as CD-*d* contents in PVC plastisols increased.

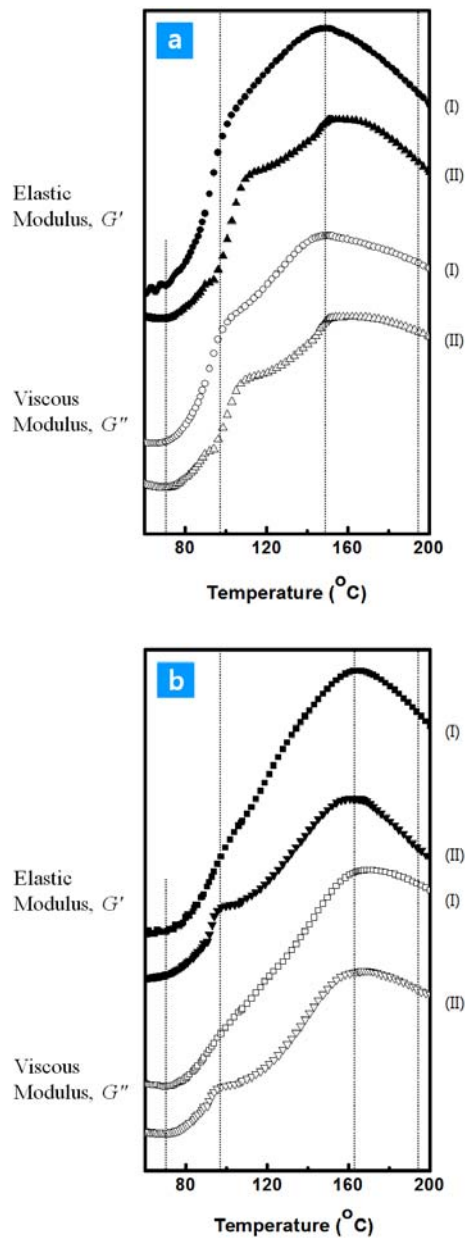
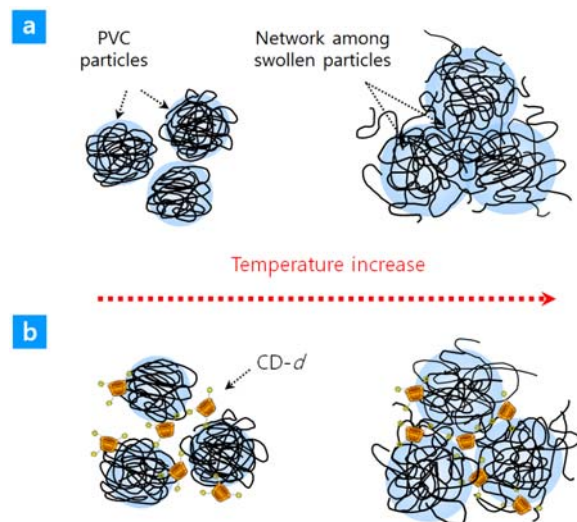


Figure 3. Viscoelastic profile of (a-I) PVC/DINP, (a-II) PVC/DINP-CD, (b-I) PVC/Neo, and (b-II) PVC/Neo-CD plastisol.

It is considered that the formation of entanglement among PVC chains is blocked by CD-*d* particles (Scheme 2). However, the completion of fusion in the viscoelastic data was almost the same point (about 187 °C). Fig. 3(b) was change of G' and G'' of PVC/Neo and PVC/Neo-CD plastisols. The viscoelastic behavior of Neocizer series also showed similar behavior to that of DINP



Scheme 2. Formation of molecular entanglement; (a) neat PVC samples and (b) PVC samples with CD-*d*.

series. However, it was found that the temperatures of completion of gelation in both DINP and Neocizer series were different from each other. When a PVC plastisol is heated, PVC particles are swollen with the plasticizer as the plasticizer is absorbed and the steep increase of both G' and G'' occurs. Simultaneously, the PVC particles become dissolved into the plasticizer from their outer surface, which glues the particles together, and in this stage the G' reaches a maximum with the absorption of all plasticizer by the PVC particles. This is called gelation. Upon further increase in temperature, the swelling and dissolution of more polymers continues and microcrystallites of PVC melt and both G' and G'' begin to drop off. This is called fusion.⁹ The temperature at which fusion is essentially complete is marked by the intersection of both G' and G'' . In addition, during the processing a partial melting of the crystallites in primary PVC particles occurs, allowing the diffusion of the macromolecules through the boundaries and the entanglement of macromolecules. The morphological observation was shown to provide details of structural changes in conjunction with the

behavior of the PVC/DINP and PVC/Neocizer interaction, enabling a qualitative discrimination of the gelation and fusion processes. These results can be also contrasted with and used to interpret the change in viscoelastic behavior. Starting from a two-phase system, solid particles dispersed in liquid, plastisol changes to a one-phase rubbery solid through the gelation and fusion process. Fig. 4 and 5 are the SEM photographs of the PVC/ DINP-CD and PVC/Neo-CD system. All pictures were at

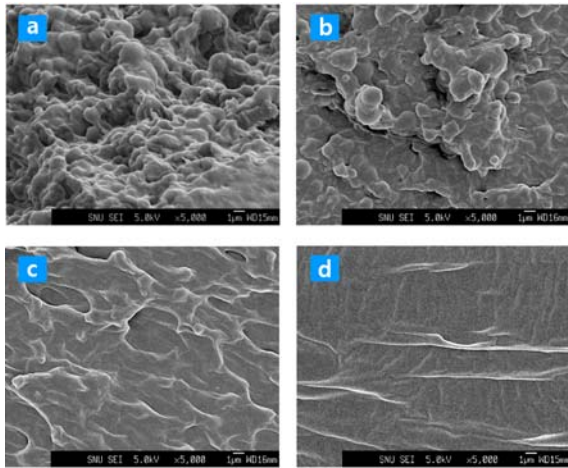


Figure 4. Scanning electron micrographs of PVC/DINP-CD plastisol at (a) 70 °C, (b) 158 °C, (c) 170 °C and (d) 187.

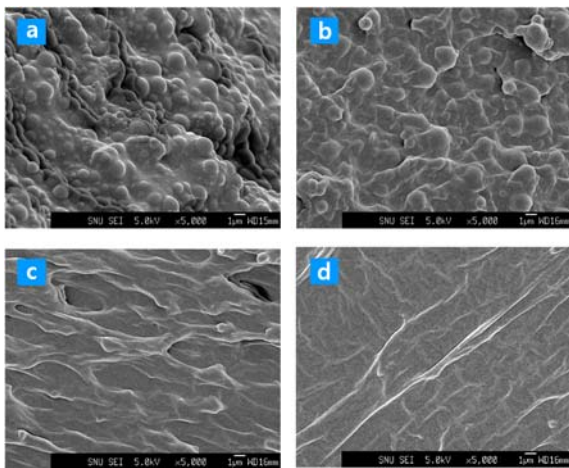


Figure 5. Scanning electron micrographs of PVC/Neo-CD plastisol at (a) 70 °C, (b) 169 °C, (c) 170 °C and (d) 187.

magnification of $\times 5,000$. At 70°C, the particles of PVC are clearly identifiable and the presence of agglomerates is also apparent. At completion of gelation temperature, 158 °C and 169 °C, respectively, only a limited number of particles are identifiable and interparticle boundaries are obscure by knitting together. At 170 °C, the fusion has taken over and the particulate morphology is almost absent. Finally, at 187 °C, the fusion is successfully completed. The fracture surface is continuous and there is no identification of the domain boundaries. During gelation and fusion process, PVC plastisols change from PVC particles in DINP or Neocizer to a uniform mass. Overall, the disappearance of the PVC particulate boundaries increases the homogeneity of the PVC plastisols.

Physical properties of the flexible PVC and anti-migration of plasticizer in flexible PVC

The glass transition temperatures, T_g , were determined from the mid-points of the small endothermic rises in the pre- and post-transition baselines (as listed in Table 1). The addition of plasticizers to PVC resin increases the free volume of the PVC and thus lowers the PVC T_g . The percent plasticization efficiency, $E_{\Delta T_g}$, can be calculated with the following equation:

$$E_{\Delta T_g} (\%) = \frac{\Delta T_{g, \text{PVC/plasticizer-CD}}}{\Delta T_{g, \text{PVC/plasticizer}}} \times 100$$

Table 1. Glass transition temperature (T_g) and percent plasticization efficiency ($E_{\Delta T_g}$).

Data	PVC	PVC/ DINP	PVC/ DINP- CD	PVC/ Neo	PVC/ Neo- CD
T_g (°C) ^a	85.6	-47.3	-44.4	-40.9	-38.8
$E_{\Delta T_g}$ (%) ^b	0	100	97.8	100	98.3

^a Glass transition temperatures.

^b Percent plasticization efficiencies estimated from the lowering of the glass transition temperatures.

where ΔT_g is the reduction in T_g . The calculated $E_{\Delta T_g}$ values are listed in Table 1.

The transmittance and haze of flexible PVC sheets containing CD-*d* are shown in Fig. 6. The introduction of CD-*d* in flexible PVC sheets did not influence the transmittance of the sheets. The reason is that the CD-*d* endowed with hydrophobic benzoyl groups is performed to limit the formation of agglomerates of CD-*d* particles in PVC/DINP-CD and PVC/Neo-CD. In other words, CD-*d* was well-dispersed in the plasticized PVC matrix as nanoscopic level. However, the dispersed CD-*d* particles slightly increased the haze of the sheets because the CD-*d* particles scattered the light in the plasticized PVC matrix.

The migrated plasticizer of each sample for 1, 3, 5, and 7 days was detected and the sum of its peak areas was compared with the calibration curve of plasticizer concentration. The cumulative amount of migrated plasticizers against time at 37 °C is illustrated in Fig. 7. In the figure, plasticizer leaching mostly dramatically increased at initial stage and slowly increased with the time. After 7 days of leaching, the concentration of leached plasticizer from all plasticized PVC sheets incorporating CD-*d* was lower than that of neat plasticized PVC sheet. Plasticizer on the surface of the PVC sheet diffuses through the interface of sheet and leaching

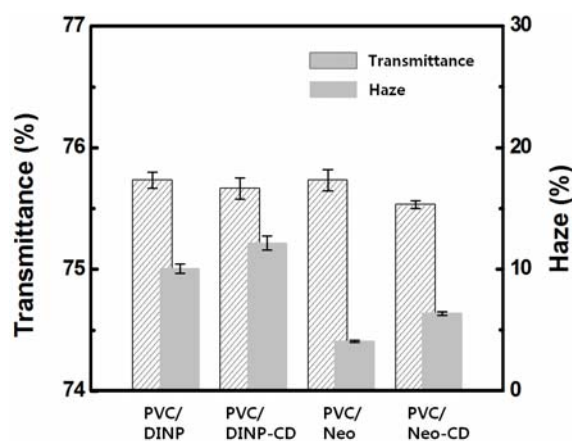


Figure 6. Transmittance and haze of flexible PVC sheets.

solution into the liquid and the vacancies caused by migrated plasticizers are exchanged with leaching solution. The penetrated leaching solution leads to diffusion of plasticizer from the within PVC sheet to the sheet surface by the interaction such as hydrogen bond. Within undergoing the process, CD-*d* prevents the interaction between plasticizer and leaching solution resulting in plasticizer migration. Therefore, CD-*d* acts as a migration restrainer and reduces plasticizer leaching. The reduction efficiency (%) was calculated as:

$$\text{Reduction efficiency (\%)} = \left(1 - \frac{C_{\text{PVC/plasticizer-CD}}}{C_{\text{PVC/plasticizer}}} \right) \times 100$$

where $C_{\text{PVC/plasticizer-CD}}$ and $C_{\text{PVC/plasticizer}}$ are concentration of migrated plasticizer during the migration in PVC/plasticizer-CD and PVC/plasticizer samples, respectively. Reduction efficiency for PVC/DINP-CD and PVC/Neo-CD are 41.6% and 26.8%, respectively. These results indicate that plasticizer leached from plasticizer PVC sheets decreased as the contents of CD-*d* in the sheets increased. In addition, although the numerical reductions of concentration for both leached plasticizers were not very different each other, the reduction efficiency

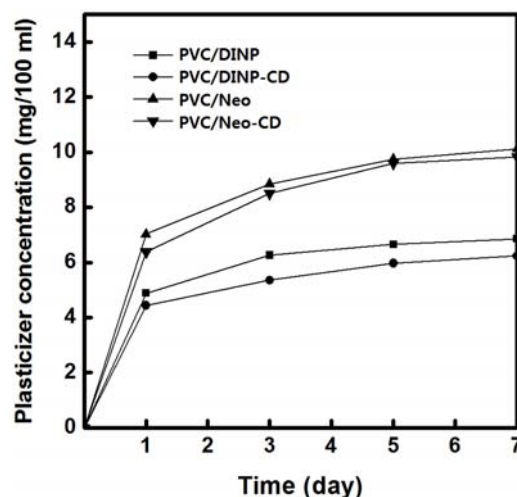


Figure 7. The cumulative amount of migrated plasticizer against time at 37 °C.

for PVC/Neo-CD was slightly smaller than that of PVC/DINP-CD because of the difference between basic concentrations for each sample. DINP (with aromatic ring), more compatible with PVC compared with Neocizer (with aliphatic ring), leached relatively smaller amount than Neocizer.

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