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Using an Inhibitor to Prevent Plasticizer Migration from Polyurethane Matrix to EPDM Based Substrate

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Abstract The loss of adhesion between the propellant and insulator is one of the most important problems in solid propellant motors due to migration of plasticizer to interface of propellant and insulator. In this work, the polyurethane (PU) binder containing DOP plasticizer was used as a polymeric matrix and β -cyclodextrin (β -CD) was applied as inhibitor agent to prevent plasticizer migration from the PU matrix into the ethylene propylene diene monomer (EPDM) substrate. To increase the compatibility of β -CD and PU matrix, a derivative of β -CD has been synthesized using toluene diisocyanate (β -CD-TDI). The synthesized derivative was characterized by MALDI-MS and FTIR-ATR analyses. FTIR-ATR results confirmed the formation of bonding between β -CD and the polymeric network while the MALDI-MS results showed that the synthesized derivative contained two β -CD and 7 TDI molecules bonded to β -CD. Investigation of the mechanical properties of PU modified by β -CD-TDI showed a decrease in tensile strength and an increase in elongation at break with increasing β -CD-TDI content. DMTA results showed a decrement in crosslinking density by increasing the β -CD-TDI content. Also, to investigate plasticizer migration, extraction of the DOP plasticizer from samples was performed using dichloromethane solvent and its concentration was measured by gas chromatography. The results of migration evaluation after four months showed that using β -CD as an inhibitor agent in the PU binder could prevent the migration of plasticizer to EPDM substrate.

Keywords Plasticizer migration; β -Cyclodextrin; Polyurethane

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INTRODUCTION

In space rocket motors, a solid composite propellant is used to generate high temperature and gas velocity during the combustion. To protect the motor chamber against the produced heat, rubbery insulator is utilized in the internal wall of the combustion chamber.^[1] Modern composite propellants are loaded with solid as high as 85 wt%–90 wt% which leads to high viscosity of composition that makes casting difficult.^[2] In order to improve the rheological properties of the propellant composition and reduce its viscosity, plasticizers are applied.^[3] When a plasticizer is added to the polymer premix, the viscosity reduces considerably by its penetration inside the polymer matrix; the cohesive forces between polymers reduces, and the free volume increases.^[3,4] The plasticizers are not chemically bonded to binder and tend to migrate from propellant to insulator layer due to its concentration gradient.^[1] Such migration is one of the main phenomena of aging during the storage period. The plasticizer migration can affect chemical and mechanical properties of the insulator and propellant, ballistic properties of the propellant, and adhesion between insulator and pro-

pellant.^[5] Therefore, the prevention of plasticizer migration from propellant to insulator is a vital issue that should be considered. In the case of plasticizer migration, some researches have been published about the migration phenomenon while the reduction of migration has been rarely investigated.^[6] For example, ballistic anomalies due to the plasticizer migration have been studied by Probst.^[5] In that work, it has been stated that the composite propellant is conically burned because of plasticizer migration, which affects ballistic properties. When plasticizer migrates from propellant into the insulator, the solid loading fraction increases in the adjacent of insulator which leads to a higher burning rate and further affects the ballistic properties. Another work can be referred to the published study by Gottlieb, in which the migration of plasticizer between bonded propellant interfaces has been studied.^[7] This work shows that the plasticizer migration has a direct influence on the tensile strength.^[7] In the most relevant work about reduction of plasticizer migration, two different adhesive liners have been prepared and utilized to prevent plasticizer migration to insulator.^[1] One of the liners was utilized as barrier coat against migration and caused a decline in plasticizer migration.^[1] Plasticizer migration into the insulator depends on plasticizer concentration, temperature, and solubility parameters of polymer and plasticizer.^[5] To prevent plasticizer

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migration, different methods have been proposed by researchers, among which using barrier coat between propellant and insulator and modification of propellant bulk by different inhibitors have been considered.^[1,8] Phthalate plasticizers used in solid propellant are also widely utilized in poly(vinyl chloride) (PVC) polymer. So the plasticizer migration has also been discussed in PVC polymer that finds wide applications in medical fields.^[9] By considering the widespread use of PVC, many new studies have been published in the field of plasticizer migration reduction for this polymer.^[10,11] In the latest work on this issue, cyclodextrin (β -CD) has been utilized as an inhibitor against plasticizer migration.^[11,12] β -CD molecule is a cyclic molecule consisting of seven glucose units. It has a relatively hydrophobic interior cavity and hydrophilic exterior, and the cavity can act as hosts for guest molecules with appropriate size and polarity.^[12] Several published works have recently used CD and its derivatives as inhibitors against phthalate plasticizers migration in PVC polymeric bulk.^[13]

In this work, a new derivative of β -CD-TDI was synthesized and utilized to reduce dioctyl phthalate (DOP) plasticizer migration from PU-based network to ethylene propylene diene monomer (EPDM)-based substrate. The synthesized inhibitor agent (β -CD-TDI) was characterized and then chemically bonded to HTPB-based PU binder. Afterwards, the effect of synthesized inhibitor on mechanical properties of the PU binder was evaluated. Finally, the migration of DOP from PU binder to EPDM substrate was assessed during four months.

EXPERIMENTAL

Materials and Methods

Hydroxyl-terminated polybutadiene (HTPB) (60% *trans*, 20% *cis*, 20% vinyl, MW = 2900 g/mol) as diol, 2,4-toluene diisocyanate (TDI) (MW = 174.2 g/mol, purity = 95%) as curing agent, castor oil (CO) (Meq. = 355 g/equiv.) as cross-linking agent, and ferric acetyl-acetonate (FeAA) (purity = 99%) as curing catalyst were utilized to prepare PU binder. Dioctyl phthalate (DOP) (MW = 390.6 g/mol) was applied as plasticizer and β -cyclodextrin (β -CD) ($C_{42}H_{70}O_{35}$, MW = 1134.98 g/mol) was utilized as an inhibitor during plasticizer migration. Dimethylacetamide and dichloromethane with GC-grad were applied as solvents.

In order to characterize the synthesized derivative of β -CD-TDI, matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) (ABCIES 4800 MALDI-TOF) and Fourier-transform infrared spectroscopy-attenuated total reflection FTIR-ATR (Thermo Nicolet 6700) were performed. Dynamic mechanical thermal analysis (DMTA) (Mettler-Toledo-Switzerland) was applied to determine the crosslinking density. Evaluation of the mechanical properties of prepared samples was carried out by tensile test (Hegewald and Peschke Inspekt 50) and hardness (Rex 1600 shore A) analyses. Determination of DOP concentration in samples was conducted by gas chromatography (GC) analysis (Shimadzu 2010 GC-Plus FID-Detector). Vacuum equipped mechanical stirrer (Lenze) was applied for mixing the polymer composition.

Synthesis of β -CD-TDI

Due to the polar structure of β -CD, it cannot be well dispersed but becomes coagulated in the HTPB pre-polymer. In order to properly operate β -CD as an inhibitor agent, it should be dissolved in the pre-polymer and linked chemically to the binder network; otherwise the β -CD itself may migrate to the interface of binder and EPDM substrate. To this aim, TDI was used to modify β -CD. A TDI molecule has two isocyanate groups ($N=C=O$), one of which can bond to β -CD and the other can bond to the polymer network after adding to the pre-polymer. To perform this synthesis, some solvents were tested and by considering solubility of β -CD, TDI, and pre-polymer, DMAc was selected to synthesize the β -CD-TDI. Hence, a certain amount of β -CD was firstly dissolved in DMAc and then used for stoichiometric calculations with four TDI molecules bonded to one β -CD molecule. By considering the functionality of one for TDI (with the aim of reacting one of the isocyanate groups), a certain amount of TDI was added to the solution. The solution was heated at 45 °C with stirring for 20 min, and then the synthesized β -CD-TDI in DMAc was utilized to prepare PU binder.

Synthesis of PU Binder Containing β -CD-TDI

According to the stoichiometric calculations and the R-value of 1.05, 104 g of HTPB, 24.8 g of TDI, and 1.98 g of DOP plasticizer were added to the mechanical agitator tank and mixed under vacuum at 50 °C for 5 min; then 5.7 g of castor oil was added and stirring continuously for 30 min. Afterwards, the solution of the prepared β -CD-TDI was added to the pre-polymer and stirred for 10 min under vacuum at 50 °C. It should be noted that under the vacuum condition, a large amount of the used solvent was evaporated. In the next stage, 52.5 g of castor oil was poured into the mixture and well mixed for 10 min at 50 °C. Finally, the prepared compound was cast on cured EPDM substrate sheet in a Teflon lined rectangular cubic mold with the dimension of 10 cm $\times$ 5 cm $\times$ 2 cm. The prepared sample was cured at 60 °C for 2 days. Finally, the sample was released from the mold at the end of the curing process and kept at 50 °C. Schematic view of the prepared sample is demonstrated in Fig. 1.

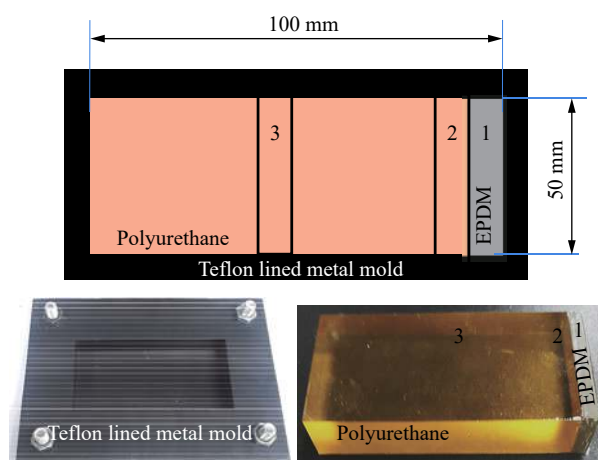


Fig. 1 Schematic of the prepared sample as well as related utilized mold

Plasticizer Migration Analysis

Given that the plasticizer is not chemically bonded to the binder, extraction of the plasticizer can mainly be used for monitoring plasticizer concentration. Based on literature, dichloromethane was used as the extraction solvent and GC was used to determine DOP concentration.^[14] To this aim, classic extraction was utilized where a piece of the prepared sample kept at 50 °C was severed after specified time and placed into 10 mL of dichloromethane for 24 h at room temperature. The chromatographic analysis was performed on GC (Shimadzu 2010 GC-Plus) equipped with flame ionization detector (FID) using a column of RTX-1 dimethyl polysiloxane with internal diameter of 0.25 mm and length of 30 m. The temperature of injector and detector was 260 and 300 °C, respectively. The temperature of column was programmed at 85 °C (hold time of 0.1 min), from 85 °C to 90 °C (hold time of 1 min) with the rate of 0.5 °C/min, from 90 °C to 200 °C (hold time of 0.1 min) with the rate of 10 °C/min, and from 200 °C to 260 °C (hold time of 5 min) with the rate of 2 °C/min. Helium was used as the carrier gas with a flow rate of 1 mL/min and 1 μ L of the sample was injected.^[1,13] In order to accurately measure the DOP concentration using GC, dibutyl phthalate (DBP) was used as the internal standard that is a known amount of compound that should be similar to the analyte. In this method, the obtained signal from the analyte is compared with that from the standard as a response factor ($R = C_A/C_{IS}$). The response factor is used to prepare calibration curve by plotting the response factor as a function of the analyte concentration.

RESULTS AND DISCUSSION

After synthesizing and characterizing the modified β -CD-TDI, some samples with different contents of β -CD-TDI were prepared and their mechanical properties such as tensile strength, elongation, and hardness were studied. DMTA analysis was also performed to evaluate crosslinking density. Finally, the performance of the modified β -CD-TDI in reducing the migration of DOP plasticizer was assessed. The results are presented and discussed in the following section.

FTIR-ATR Analysis

FTIR-ATR analysis was performed to confirm the reaction between TDI and β -CD as well as to evaluate the formation of a linkage between the modified β -CD with polymeric network. The FTIR-ATR spectra of β -CD, TDI, HTPB, and the sample containing all three materials are presented in Fig. 2. The band at 3300 cm^{-1} related to the hydroxyl groups of β -CD has been reduced in the CD-TDI-HTPB sample, indicating that the hydroxyl groups of β -CD have been reacted with the isocyanate group of TDI. The bands at 1600–1700 cm^{-1} can be attributed to the stretching modes of C=O and the band located at 1530 cm^{-1} is related to C–N bond. The band in the range of 2000–2300 cm^{-1} related to N=C=O group has disappeared in the CD-TDI-HTPB sample, indicating the formation of urethane bond. Also, the bands in the range of 1100–1150 cm^{-1} can be related to C–OH stretches and C–O–C antisymmetric stretches in the prepared sample, confirming the existence of β -CD in the polymer structure.^[13,15]

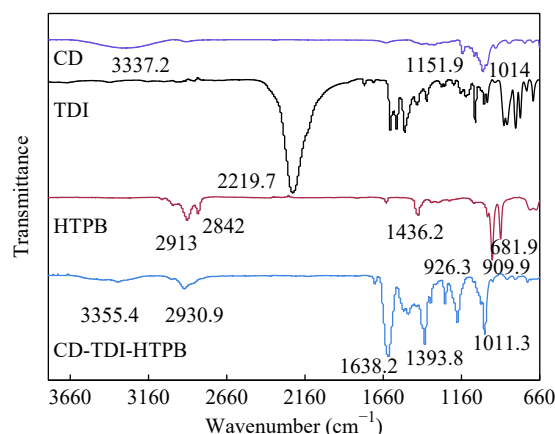


Fig. 2 FTIR-ATR spectra of CD, TDI, HTPB, and PU containing β -CD (CD-TDI-HTPB)

Identification of Synthesized β -CD-TDI

By considering the number of hydroxyl groups in β -CD and the amount of consumed TDI, it is probable to produce different products. MALDI-MS analysis was applied to determine the molecular weight and structure of the synthesized derivative of β -CD-TDI. MALDI-MS result is shown in Fig. 3. As can be seen, there are several signals in the spectrum due to the industrial nature of the consumed precursor and the high sensitivity of MALDI-MS analysis in determining the molecular mass. Here, the molecules were identified after receiving electrical charge by getting H^+ , Na^+ , and K^+ ions. In this method, various products could be made according to the chemical structures of β -CD and TDI. For example, a certain number of TDI molecules can be bonded to a β -CD molecule or a TDI molecule can bridge two β -CD molecules and dimerize or polymerize them. Similarly, different products with several TDIs can be obtained. By investigating the MALDI-MS results, it is concluded that the synthesized products have been charged with ferric ions (Fe^{3+}) contained in the FeAA catalyst and the signals related to these products have appeared in the spectrum (Fig. 3). Some products are also charged with Na^+ and K^+ ions. The signal at $m/z = 1181.64$ is the main product of this process, which consists of two β -CD molecules attached together with a TDI molecule and six TDI molecules bonded to them. The possible chemical structure of this molecule is shown in Fig. 4.

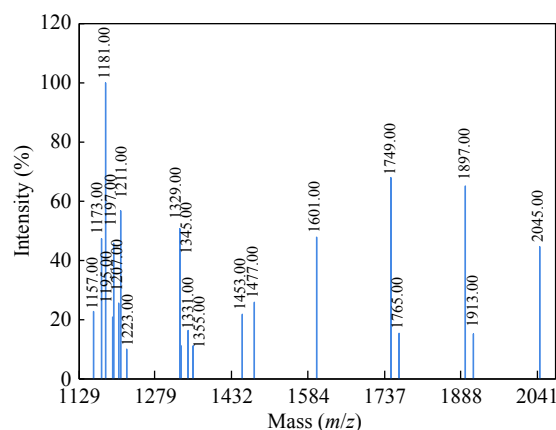


Fig. 3 MALDI-MS analysis for synthesized β -CD-TDI

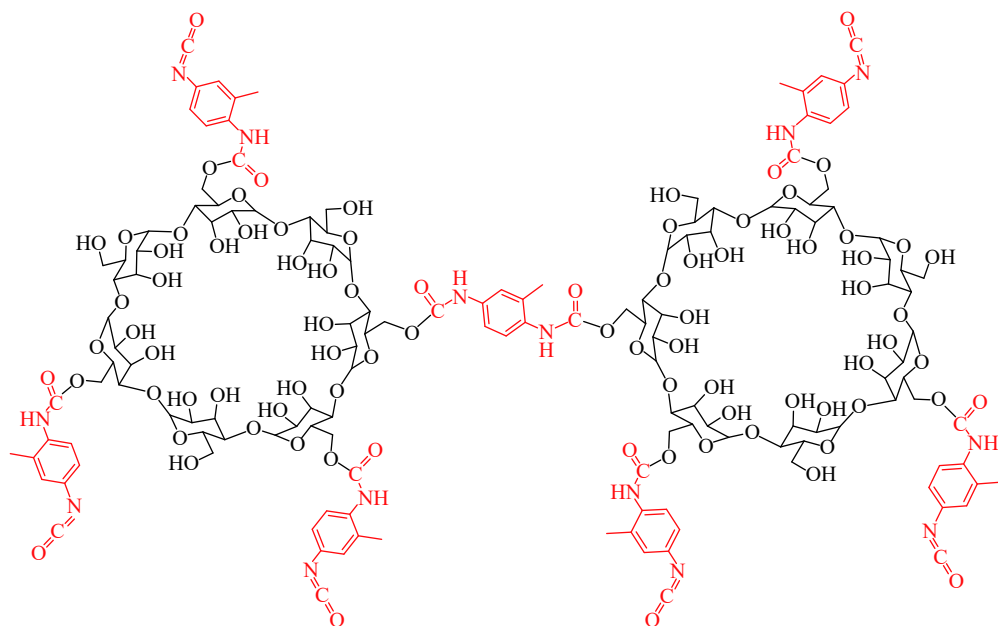


Fig. 4 The probable chemical structure of β -CD-TDI obtained from the MALDI-MS analysis

This molecule, charged by ferric ion, has a mass of 1181.78, which is a difference about 0.14 with the corresponding signal. As shown in Fig. 4, in the structure of the synthesized molecule, one of the isocyanate groups not reacted can be bonded to the polyurethane network. Some of the observed bands are the result of the reaction between isocyanate groups and water during the analysis performance. For example, the signal at 1211.7 is related to the mentioned molecule of which isocyanate groups have reacted with water and the $\text{N}=\text{C}=\text{O}$ group is converted to NCOOH .

Mechanical Properties

Considering that the changes in mechanical properties of the PU binder is probable due to incorporated β -CD, tensile strength, elongation, hardness, and DMTA analyses were performed after synthesis of the PU samples containing different percentages of β -CD. It should be noted that the content of β -CD has been used in the range of 0.25 wt% to 2.8 wt%. The stoichiometry of DOP and β -CD will be equal when 2.8 wt% of β -CD was used. The tensile strength and elongation at break for different samples are shown in Fig. 5. As can be seen from the figure, the tensile strength is decreased with a slight gradient while the elongation percent is increased with increasing the β -CD content. The observed changes could be due to the reduction in crosslinking density and the disrupted network arrangement because the β -CD molecules have a larger size than those of other molecules. This trend has also been observed in a published study about β -CD effect on the crosslinking density of PU.^[16] The change in hardness of the samples by using different amounts of β -CD given in Fig. 6 shows a decreasing trend with increasing β -CD content, which could be due to a reduction in the crosslinking density.

Crosslinking density is the number of chemical bonds which join two polymer chains together per unit volume of polymer. As mentioned, considering large chemical structure of β -CD that contains a large number of hydroxyl

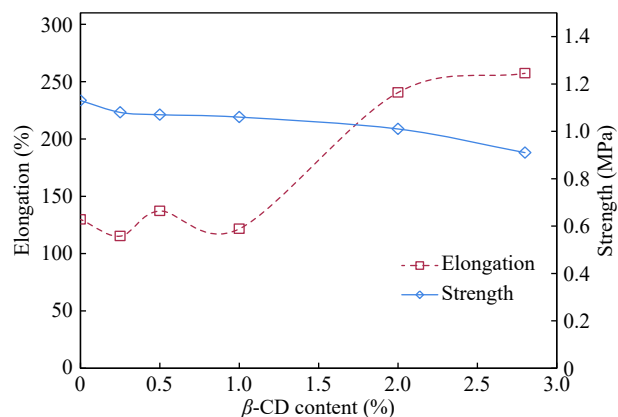


Fig. 5 The effect of β -CD content on tensile strength and elongation at break of the PU binder

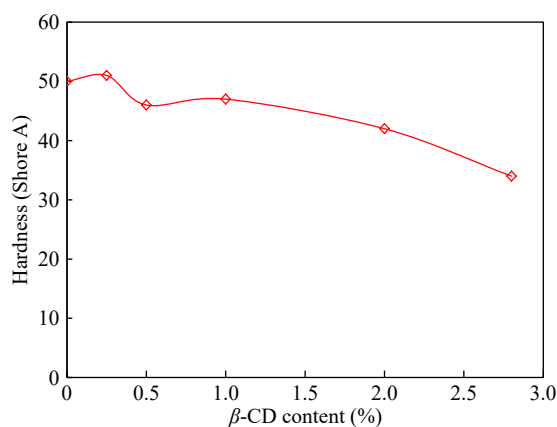


Fig. 6 The effect of β -CD content on hardness of PU binder

groups, its addition in PU compound can affect the crosslinking density. In order to assess the effect of β -CD addition on the crosslinking density of PU, DMTA analysis was performed. The variation of modulus can be related to cross-

linking density.^[17] The storage modulus variations with temperature for samples without β -CD, with 2.0 wt% β -CD, and with 2.8 wt% β -CD are shown in Fig. 7. As can be seen, the storage modulus decreases with the increasing β -CD percentage. As discussed above, inserting β -CD to the binder structure could disrupt the network arrangement and reduce crosslinking density, since the β -CD molecular size is larger than those of other components. It should be noted that the obtained physical properties are acceptable because the reduction of crosslink density is not too much.

Migration Assessment

In order to evaluate DOP migration, DOP concentration was measured by GC analysis after the extraction of DOP plasticizer. For repeatability of results, DBP was selected as

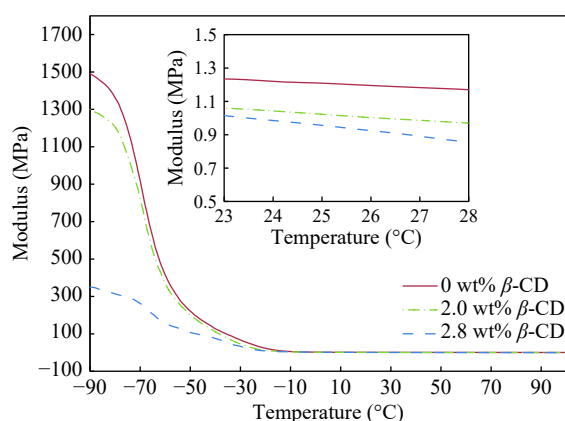


Fig. 7 The effect of β -CD content on storage modulus

internal standard and calibration curve was prepared. To this aim, three samples containing 0 wt%, 2.0 wt%, and 2.8 wt% of β -CD were prepared so that all samples contained one percent plasticizer. The samples were kept at 50 °C and the plasticizer migration from PU binder to EPDM substrate was investigated after 1, 2, and 4 months. The obtained results are presented in Table 1 where the numbers 1, 2, and 3 in the table stand for in the EPDM substrate, adjacent to EPDM, and at a distance of 3 cm from the EPDM with 5 mm thickness, respectively (Fig. 1). Also, the amount of DOP in EPDM substrate is demonstrated in Fig. 8. As can be seen, in the sample without β -CD, the DOP plasticizer could be detected in EPDM, and its content increased with the passing time, which confirms the plasticizer migration from PU binder to EPDM substrate. In the sample containing 2 wt% β -CD, the amount of plasticizer in the EPDM substrate was significantly lower than that in the sample without β -CD which suggested the reduction in plasticizer migration using β -CD. Accordingly, each β -CD can prevent a DOP molecule migration by supramolecular interaction (Fig. 9),^[12,13] so a sample containing 2.8 wt% of β -CD was prepared with the equal stoichiometry of β -CD and plasticizer, of which the detected DOP in EPDM is very low. According to the results, there is a little difference from the regular trend of reduction of plasticizer migration in some samples. This matter could be due to the fact that to investigate DOP migration, the samples were prepared at different time and after a certain time period, DOP concentration was measured in several steps, including extraction of DOP from the samples by dichloromethane for 24 h and analysis of the specimens by

Table 1 The results of DOP analysis in the samples by gas chromatography

Time	Sample*	A_{DOP}	A_{DBP}	A_{DOP}/A_{DBP}	W (g)	C (ppm)
30 days	1 β -CD 0 wt%	53657	147425	0.36	0.68	51.8
	2	131545	72801	1.8	0.57	457.3
	3	1882496	1239362	1.52	0.45	479.4
	1 β -CD 2.0 wt%	1180209	5538329	0.21	0.58	20.1
	2	1775886	1107860	1.6	0.47	486.8
	3	665720	375673	1.77	0.50	510.5
	1 β -CD 2.8 wt%	24624	168517	0.15	0.53	2.2
	2	380070	225266	1.69	0.5	484
	3	1916099	1138114	1.68	0.49	492.7
60 days	1 β -CD 0 wt%	894261	2673089	0.33	0.53	57.8
	2	2849944	1805813	1.58	0.5	449.9
	3	3034129	1729979	1.75	0.5	504.8
	1 β -CD 2.0 wt%	585484	2838781	0.21	0.5	21.2
	2	118233	68182	1.73	0.51	488.8
	3	105585	60474	1.74	0.5	502.3
	1 β -CD 2.8 wt%	376699	2123932	0.18	0.57	10.6
	2	2848336	1870556	1.5	0.45	480.6
	3	2006366	1135811	1.76	0.51	498.7
120 days	1 β -CD 0 wt%	825034	2229703	0.37	0.46	78.6
	2	2201267	1577943	1.4	0.45	436.3
	3	2096218	1318523	1.58	0.45	503
	1 β -CD 2.0 wt%	396864	2468145	0.16	0.47	7.4
	2	2439990	1577173	1.55	0.47	489
	3	1959117	1147411	1.71	0.5	490.3
	1 β -CD 2.8 wt%	380293	2573723	0.15	0.45	3.2
	2	1179676	795351	1.48	0.43	488.6
	3	2813553	1740026	1.6	0.47	491.5

* 1 = EPDM substrate, 2 = Adjacent of EPDM substrate (5 mm thickness), 3 = sample with 3 cm distance from EPDM substrate

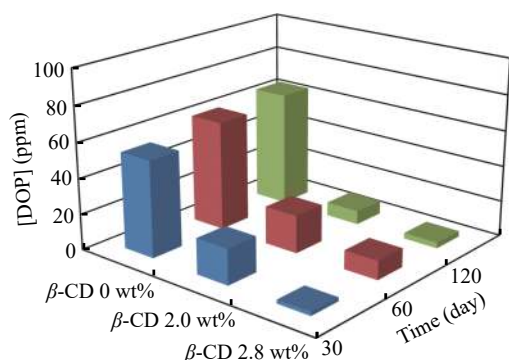


Fig. 8 DOP concentration in EPDM substrate using different amounts of β -CD in binder

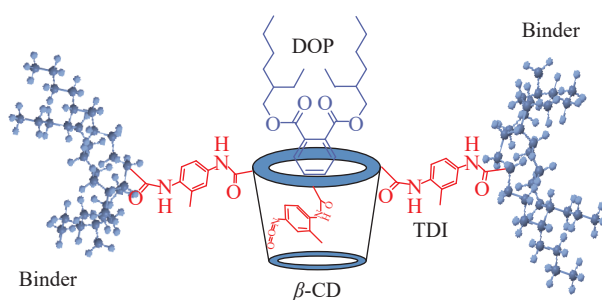


Fig. 9 Prevention of DOP migration by β -CD

GC method using internal standard addition. Considering the multiplicity of the relevant experiments as well as the volatility of dichloromethane as extraction solvent, it is expected to observe this trend. The general trend of the plasticizer migration changes with increasing β -CD content is a descending trend and after four months, the amount of plasticizer identified in the EPDM substrate is very low, which indicates that the plasticizer migration has been prevented by using β -CD during this time.

CONCLUSIONS

In the present study, a derivative of β -CD was synthesized using toluene di-isocyanate (β -CD-TDI) and applied in a PU binder to prevent migration of DOP plasticizer to EPDM based substrate. FTIR-ATR results confirmed the formation of bonding among β -CD, TDI, and polyurethane network. MALDI-MS results showed that the derivative containing two β -CD and 7 TDI molecules bonded to β -CD has been synthesized. The mechanical property assessment showed a decrease in the tensile strength and an increase in the elongation percentage with the increasing β -CD content. DMTA results showed a decrement in crosslinking density with the increasing β -CD amount. Investigation of plasticizer migration after four months showed that the insertion of β -CD into the PU binder prevents the migration of plasticizer to EPDM substrate.

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