American Journal of Biomedical Science and Engineering
2015; 1(1): 9-19
Published online January 30, 2015 (http://www.aascit.org/journal/ajbse)

AASCIT American Association for Science and Technology

Keywords
Plasticizer,
DEHCH,
Plasticizing System,
Properties

Received: January 18, 2015
Revised: January 28, 2015
Accepted: January 29, 2015

Synthesis and Application of a New Environmental Friendly Plasticizer

Long Zhang, Jing Zhang, Xuejia Ding*, Jieke Zhu, Yanqin Liu, Yifeng Fan, Yongzhen Wu, Yongfei Wei

Beijing Laboratory of Biomedical Materials, Beijing, China

Email address
dingxj2011@126.com (Xuejia Ding)

Citation
Long Zhang, Xuejia Ding, Yuanhui Ou, Jieke Zhu, Yanqin Liu. Synthesis and Application of a New Environmental Friendly Plasticizer. *American Journal of Biomedical Science and Engineering*. Vol. 1, No. 1, 2015, pp. 9-19.

Abstract
In this article, di(2-ethylhexyl)-1,2-cyclohexane dicarboxylate (DEHCH) was synthesized via esterification between hexahydrophthalic anhydride (HHPA) and iso-octanol by using concentrated sulfuric acid as a catalyst. Polyvinyl chloride (PVC) compounds after addition of the synthesized plasticizer DEHCH presented similar plasticizing performance with diethylhexyl phthalate (DEHP), di(isononyl)-1,2-cyclohexane dicarboxylate (DINCH), Trioctyl trimellitate,1,2,4-benzenetricarboxylic acid tris(2-ethylhexyl) ester (TOTM) and Acetyl tributyl citrate (ATBC). As demonstrated by comparisons of the results of mechanical properties, transparency, and volatilization and migration tests obtained for plasticized PVC compounds. We also investigate a variety of plasticizer composite plasticizing performance of the product, blending of DEHCH and TOTM and blending of DEHCH with ATBC to plasticizing the PVC. DEHCH can also be considered as an alternative plasticizer for DEHP.

1. Introduction

Polyvinyl chloride (PVC) is a versatile thermoplastic resin plastic. Because of the large amount of polar atoms of chlorine, PVC has amorphous structure, which gives excellent mechanical properties, abrasion resistance, flame resistance, chemical resistance and other characteristics of the material. Influenced by strong polarity chlorine atom, PVC is a hard polymer. In order to enlarge the application field of PVC, a plasticizer may be added to soften the PVC. PVC plasticizers can inserts in the PVC molecular chain, secondary valence bond between the molecular chains can be reduced, so that it is easy to slide and to reduce the interfacial energy between the PVC and the plasticizer, thereby reducing the glass transition temperature, soften temperature and melt temperature, etc. Thus, improve the pressing flexibility of PVC, to achieve plasticized purposes [1].

PVC has wide application sectors such as food packaging, medical materials, children toys, and tubing systems. Phthalate plasticizers are the most commonly used plasticizers worldwide for their desirable properties of a plasticizer, such as minimal interaction with resins at room temperature, produce highly elastic compounds with reasonable cold strength, satisfactory insulation for cables, and low cost. However, in the last decade, adverse health effects of phthalates have been thoroughly investigated and discussed. In 1982, the National Cancer Institute had prove the dioctyl phthalate (DOP) can make tooth animals suffer from liver cancer, make injuries to human body especially for a greater role in the growth and development of infants and children. US Food and Drug Administration (FDA) and some European countries have forbidden its use for food packaging, medical materials, and children toys. The potential toxicity to human health has caused increasing attention of manufacturers and consumers, and many researchers have been driven to find non-toxic and biodegradable plasticizers to replace traditional plasticizers in recent years[3].

In 2002, BASF made a market introduction of di(isononyl)-1,2-cyclohexane dicarboxylate (DINCH) as an alternative plasticizer, which is similar to those of phthalic acid esters plasticizer with even better comprehensive performance and use value, and biodegradable, non-toxic, environmental protection is the most suitable substitute for phthalates. And it has been applied to sensitive products such as medical devices, toys and food packaging. However, BASF's DINCH is obtained by hydrogenating the di(isononyl) phthalate under high temperature and high pressure, and it is a little expensive.

In this study, di(2-ethylhexyl)-1,2-cyclohexane dicarboxylate (DEHCH), was synthesized by esterification between iso-octanol and cis-cyclohexane-1,2-dicarboxylic anhydride, also called hexahydrophthalic anhydride (HHPA). The key research of this study focuses on the mix of the plasticizer DEHCH, DINCH citric acid esters plasticizer, trimellitic acid plasticizers.

2. Experimental

2.1. Materials

Cis-cyclohexane-1,2-dicarboxylic anhydride (HHPA, purity>98%) was obtained from Henan Puyang Huicheng chemical Co., Ltd. Isooctane and concentrated sulfuric acid were analytical grade from Beijing Chemical Works (Beijing, China). DEHP was obtained from Beijing Huaying Chemical Co. (Beijing, China), while DINCH was obtained from BASF (Beijing, China). Acetyl tributyl citrate (ATBC) was obtained from Guangzhou Jierui Chemical Technology Co., Ltd (Beijing, China). Trioctyl trimellitate, 1, 2, 4-benzenetricarboxylic acid tris (2-ethylhexyl) ester (TOTM) was obtained from Shandong Kexing Chemical (Beijing, China). The epoxy soybean oil was obtained from Shandong Liangshan Guangzhou Hongtai Epoxy Soybean Oil Co., Ltd (Beijing, China). PVC resin S-65 (K65) in powder form was obtained from Formosa Plastics Industry Co. (Ningbo, China).

2.2. Synthesis of DEHCH

Weighed amounts of HHPA and isooctane were firstly added to a flask with a reflux condenser, a water segregator, a nitrogen catheter, and an electric stirring apparatus. The mixture was heated to a certain temperature and concentrated sulfuric acid was added[2]. The reaction was then carried out for a certain time. The solution obtained was placed into a separator funnel and then neutralized with 2% sodium hydroxide solution until acid number (mg KOH/ g) was lower than 0.1. Then the organic solution was washed by 80 ^{o}C water for twice. Finally the organic solution was separated from water phase and then it was added with sodium sulfate to draw water residue and was further evaporated. Conversion of HHPA was determined by the following simplified expression:

$$\mathrm{C} = \left(1 - \frac{A_{\mathrm{m}}}{A}\right) \times 100\%$$

Where C was the conversion of HHPA, A was the acid number of the mixture of HHPA and isooctane, Am was the acid numbers of the crude reaction mixture.

2.3. Characterization of DEHCH

The obtained ester was characterized by analyzing their functional groups using Fourier Transform Infrared Spectroscopy (FTIR, Tensor27) from Bruker (Beijing, China), and their proton peaks using ^{1}H-NMR (AV600 Spectrometer) from Bruker (Beijing, China) in $CDCl_3$.

2.4. Plasticization of PVC Resin

The synthesized plasticizer DEHCH, mix of DINCH, ATBC and TOTM, which according to the certain proportion, were incorporated into PVC compounds in order to evaluate its plasticizing performance compared with DEHP and DINCH.

2.5. Preparation

PVC compounds were prepared using a high-speed mixer according to the procedure described by Wadey[3]. The 100 phr (per hundred resin) PVC resin was added to the mix and heated to 50 ^{o}C at 1500 rpm. The speed was reduced to 750 rpm and 50 phr plasticizer was added. The rotar speed was again increased to 1500 rpm. Then 2 phr Ca/Zn stabilizer was added and the mixer speed was increased to 2500 rpm until the temperature reached 120 ^{o}C. The dry blend was then cooled in the cooling mixer and bagged at 30 ^{o}C. The dry blends were milled on a two-roll mill for 5 min and then banded at 165 ^{o}C. The milled sheets were pressed to a thickness of 2mm for 5 min at 180 ^{o}C to ensure the ultimate physical properties would be developed.

2.6. Mechanical Properties

Tensile strength, percentage tensile elongation at break (ultimate elongation), and the modulus at 100 % elongation were determined at 25 ^{o}C using a universal testing machine (LR30K, Ametek Co., England) according to Chinese standard GB/ T1040–2008, and the tensile speed was 50 mm/min. Hardness was also determined at 25 ^{o}C using a shore durometer (XY-1, Shanghai Chemical Machinery Factory, China) according to Chinese standard GB/T531–1999. Impact strength was determined at -40 ^{o}C using a resilimpactor (Ceast Co., Italy) according to Chinese standard GB/T1843–2008.

2.7. Transparency

Transmittances of PVC compounds were measured by using aphotometer (WGT-S, Shanghai Precision & Scientific Instrument Co., China) according to Chinese standard GB/T2410-2008. The samples had substantially plane-parallel surfaces free of dust or internal voids with 1 mm thickness.

2.8. Volatility Tests

The volatilization loss of the plasticizer from PVC compounds was determined according to ISO176–2005. Samples (in triplicate) were weighted and hanged in metal containers at 100 °C in which laid some activated carbon. After 24 h the samples were taken out and cooled to room temperature. The weights of cooled samples were measured and average percentage weight losses were determined.

2.9. Migration Stability Tests

Migration of the plasticizer from PVC compound samples was carried out in three different solvents (water, ethanol, and petroleum ether) at 25 °C. Samples (in triplicate) were weighed and kept in 150 ml of each solvent for 48 h, and then dried in a drying oven at 40 °C for 48 h. The weights of the dried samples were measured and average percentage weight losses were determined.

3. Results and Discussion

3.1. Characterization of the Synthesized Ester

Table 1. *Meteorological chromatography and mass spectrometry*

Serial number	Retention time/min	Compound name	Molecular formula	Molecular weight	Relative mass fraction/%	The main mass-to-charge ratio
1	25.43	Trans-DEHCH	$C_{24}H_{44}O_4$	396.61	0.32	15,29,43,57,71,81,113,26,155,173,183,201,223,238,267,285,339, 367,396
2	25.5	Cis-DEHCH	$C_{24}H_{44}O_4$	396.61	99.68	15,29,43,57,71,81,113,26,155,173,183,201,223,238,267,285,339, 367,396

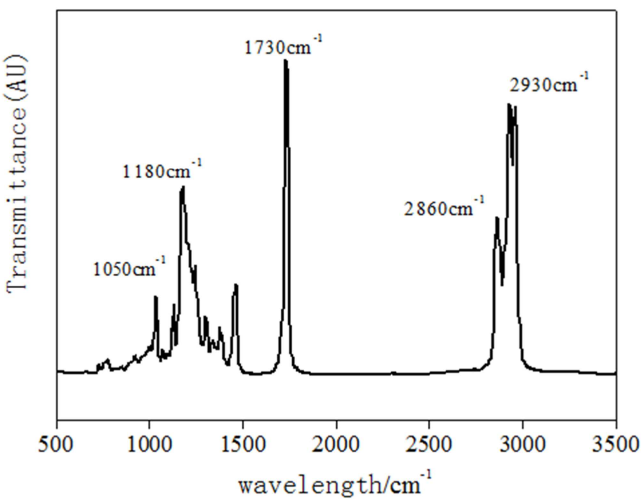


Figure 1. *FTIR spectrum of DEHCH.*

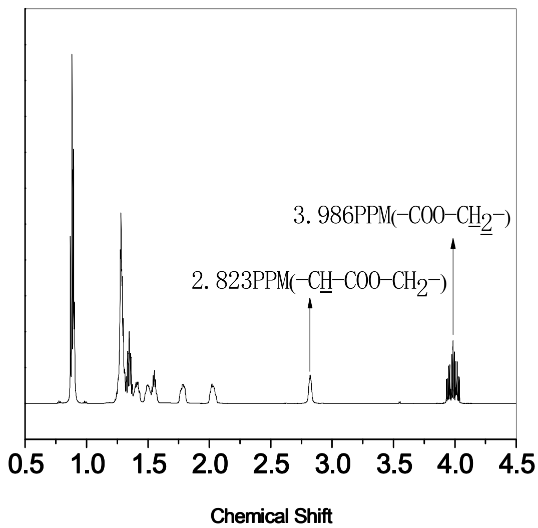


Figure 2. *^{1}H-NMR spectrum of DEHCH*

FTIR data showed that there was a shift of C=O absorption band from 1709 to 1730 cm^{-1} as shown in Figure 1, which indicated that C=O of an hydride had been transformed into that of ester. The absorption peak at 1180 cm^{-1} was attributed to C–O–C, and the alkane angular deformation (CH_2) was mainly at 2930 and 2860 cm^{-1}.The absorption band regarding to OH angular deformation at 3445 cm^{-1} was disappeared[7].

As shown in Figure 2, the obtained ^{1}H-NMR spectra presented the characteristic appearance of R–$COOCH_2$–R at 3.986 ppm and disappearance of HO–CH_2–R at 3.50 ppm.

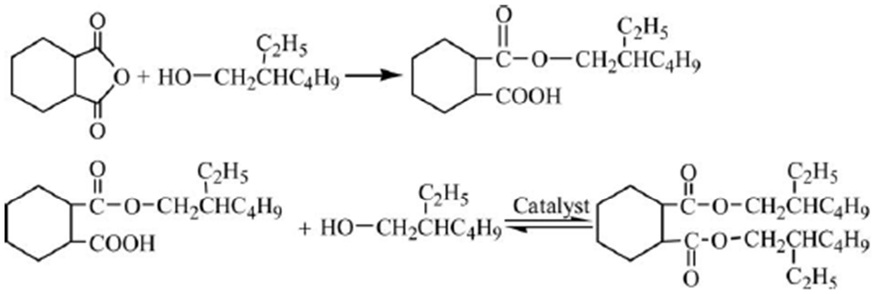
The result of meteorological chromatography and mass spectrometry are shown in Table 1, which indicate that the product only had a compound with two optical isomers, the structure of the cis content is 0.32 %, the content of trans structure is 99.68%, all the above indicated that the product had been successfully synthesized.

3.2. DEHCH

3.2.1. Optimization of Synthesized Ester

According to the Segura[4], the alkyl moiety 8 carbon atoms with the best safety performance, led us to the final decision to use 2-ethylhexyl alcohol and isooctanol with anhydride synthesis.

Di(2-ethylhexyl)-1,2-cyclohexane dicarboxylate (DEHCH) was synthesized via esterification between hexahydrophthalic anhydride(HHPA) and iso-octanol by using concentrated sulfuric acid as a catalyst. Like esterification of phthalic anhydride with alcohol, this reaction also takes place in two steps as shown in Scheme 1. The first stage is so rapid that it can be carried out in the absence of catalyst[5]. However, esterification of the second carboxylic group is very slow and needs to be facilitated by acid catalyst and the resulting water must be removed from the reaction mixture. So the reaction equilibrium and conversion of HHPA could be changed by controlling variables such as reaction temperature, time, catalyst content, and feed molar ratio[6].



Scheme 1. *Esterification between HHPA and iso-octanol.*

3.2.2. Reproducible Experiments at the Optimal Condition

Through the single variable test method, which in turn change acid glycol ratio, reaction temperature, reaction time and catalyst dosage, the optimal condition of synthesizing DEHCH via esterification was as followed: the molar ratio of isooctane-to-HHPA was 2.4 : 1, concentrated sulfuric acid content was 0.5 % of HHPA weight, and reaction temperature and time were respectively 170 °C and 1.5 h. There was not big difference between the conversions of HHPA of each time. The average conversion was 98.32%, and the standard deviation was 0.11%, which indicated that the optimal condition was reliable.

3.3. Properties of PVC Resin Plasticized by Pure DEHCH

To evaluate the plasticizing performance of synthesized DEHCH, the properties of PVC compound, which were separately plasticized with DEHCH and DINCH, DEHCH and ATBC, DEHCH and TOTM, were compared by analyzing mechanical properties, transparency, volatility, and migration stability[7].

3.3.1. DEHCH Content on the Properties of PVC

Plasticizing effect of plasticizer is through its solvation effects. When added to the polymer molecules, plasticizer would increase the distance between molecules, lower molecular inter-atomic forces and increase the mobility of molecular chain, so as to reduce the glass transition temperature (Tg), and soften the polymer. As shown in Figure 3 and Figure 4, with the increase of dosage of DEHCH, tensile strength and 100 % stretch modulus decrease at the same time, while the elongation at break increased gradually, compared with the pure PVC resin tensile strength (45.4 MPa) and elongation at break (22.8 %), DEHCH plasticized PVC resin obviously decrease the tensile strength, and elongation at break increase significantly, which show that the material has good plasticity and elasticity. As shown in Figure 5, the brittle temperature of PVC resin is gradually decreased with the increase of DEHCH. As the Tg of pure PVC is 93.5 °C, it can be seen that joining DEHCH significantly decreases the Tg of PVC, thus PVC has good low temperature performance.

Table 2. *DEHCH formula of plasticized PVC materials*

Component	Content /phr
PVC	100
DEHCH	30-70
Calcium zinc stabilizer	1.8

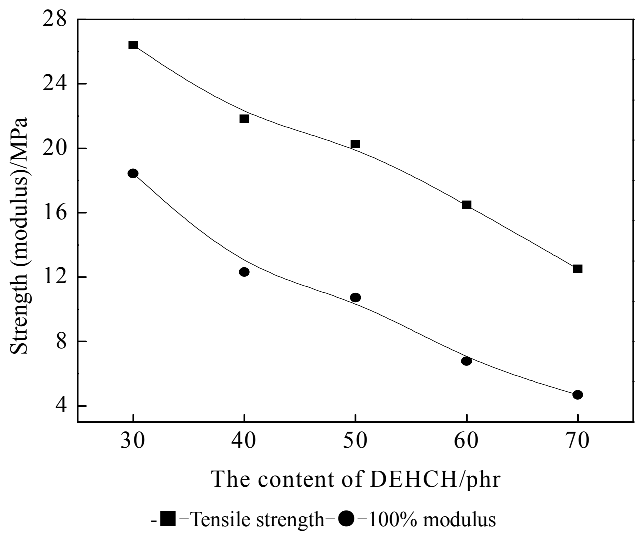


Figure 3. *Effects of DEHCH content on tensile strength and 100% modulus*

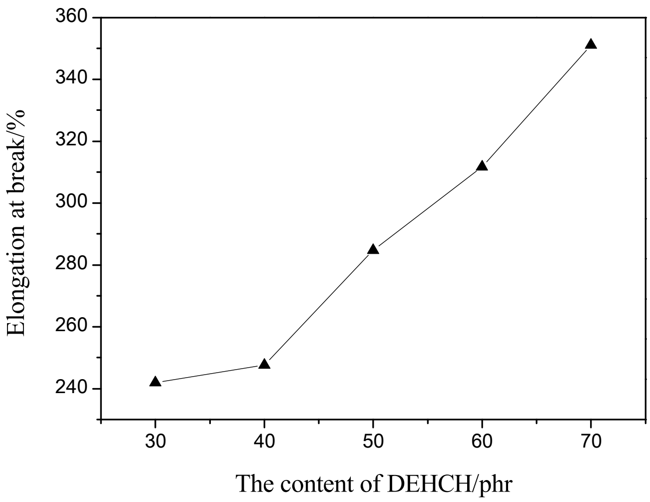


Figure 4. *Effect of DEHCH content on elongation at break*

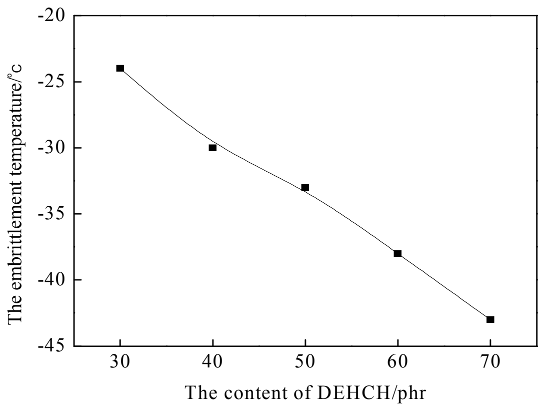


Figure 5. *Effect of DEHCH content on brittle temperature*

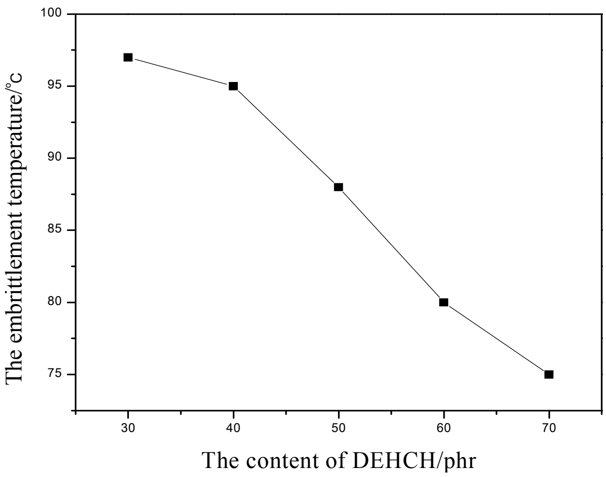


Figure 6. *Effect of DEHCH content on hardness*

3.3.2. Transparency

Since PVC is a transparent polymer, a study of transparency is a necessary method for investigating the plasticizing performance of plasticizers. The transparency of the PVC compounds is shown in Figure 7.Along with the increase of the content of DEHCH, the light transmittance of PVC is slightly lower, and the haze of PVC is slightly higher, the overall changes little. It shows that with the plasticizer content changes, the transparency of PVC change little[8-14].

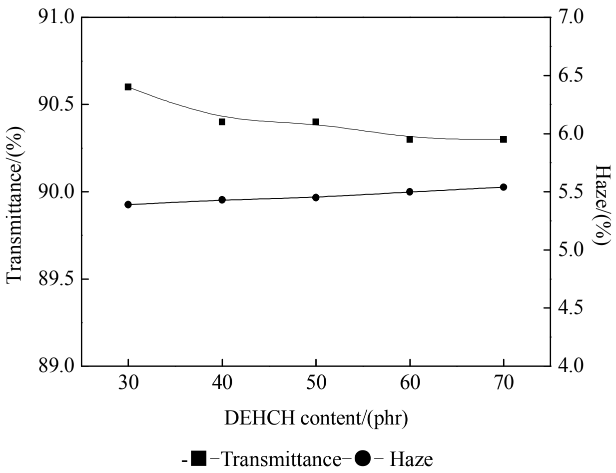


Figure 7. *Effect of DEHCH content on Light transmittance and Haze*

3.3.3. Volatility Tests

After using in high temperature environment for a long time, small molecules of plasticizer will migrate to the surface evaporates from inside the PVC material, which influence the stability of PVC material performance. From Figure 6, with the increase of DEHCH, the mass loss is bigger under high temperature. According to ISO176-2005, mass loss less than 0.81% for a low volatile, less than 3.83% for medium volatile, so according to the volatile of the DEHCH, it should be carefully used in the fields of wire and cable, etc[15-17].

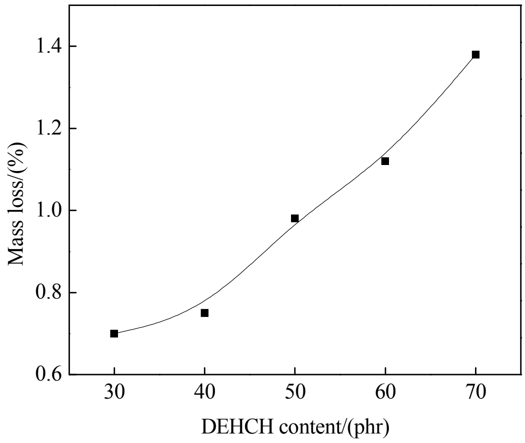


Figure 8. *Effect of DEHCH content on volatility.*

3.3.4. Migration Stability Tests

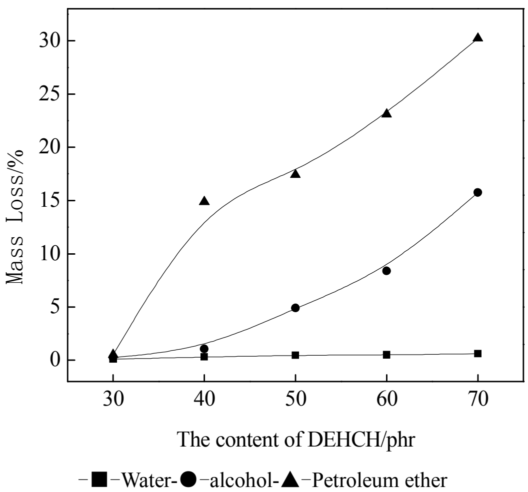


Figure 9. *Effect of DEHCH content on migration stability in solvents*

If a polymeric material comes into contact with liquids (water and solvents), the probability of plasticizer extraction will increase. In the process of using small molecule plasticizer, it will be out of polymer material due to internal migration, when polymer materials are in contact with the solvent phase, migration will increase. It can be seen from Figure 9, the mass loss of DEHCH is small in water, but with the increase of content, mass loss will increase slowly. The mass loss is very big in ethanol and petroleum ether, and with the increase of content, mass loss also increases rapidly, especially in petroleum ether. This is because the DEHCH polarity is small, and it is a hydrophobic material. When the content of DEHCH is 30 phr, the mass loss in various solvents is small, compared with the actual amount to join each formula DEHCH, overall quality loss is not particularly big, it may show the DEHCH has good solvent resistance[18-19].

3.4. Properties of PVC Resin Plasticized by Different Plasticizers

3.4.1. Different Plasticizers Content on the Properties of PVC

Table 3. *The different plasticizers formula of plasticized PVC materials*

Component	Content /phr
PVC	100
Plasticizer	50
Calcium zinc stabilizer	1.8

Plasticizer types include: DEHCH, DINCH, TOTM, ATBC, DEHP.

3.4.2. Mechanical Properties

As can be seen from Table 4, compared with the traditional plasticizer DEHP, the PVC were plasticized by four environmental protection plasticizer, its tensile strength and elongation at break is similar, the PVC which was plasticized with TOTM has a maximum tensile strength of 20.4 MPa, and the elongation at break of maximum is 339%. In addition, it shows from the table that the PVC was plasticized by DINCH, the brittle temperature is lowest, it is -38^{o}C.Their Shaw hardness A is similar.

Table 4. *The Mechanical Properties of the different plasticizer plasticized PVC*

plasticizer	The tensile strength	The elongation at break	100% stretch modulus	brittle temperature	Shaw hardness A
DEHCH	19.2	321	8.7	-33	89
DINCH	19.6	304	10.2	-38	87
TOTM	20.4	339	9.1	-33	88
ATBC	18.9	328	8.8	-27	85
DEHP	19.5	301	10.0	-35	86

3.4.3. The Stability of the Different Plasticizer Plasticized PVC

The stability of the different plasticizer plasticized PVC material performance shown in Table 5.It can be seen from the Table 5, DEHCH and DINCH have the similar volatile and resistance to solvent extraction, but the volatility of DEHCH is higher, this is because the molecular weight of DEHCH is less, and it has low boiling point, the solvent extraction of DEHCH slightly better than DEHP. It can be seen from the Table 5 that the ATBC has the highest volatile, while the TOTM has the lowest volatile.

Table 5. *The stability of the different plasticizer plasticized PVC*

Plasticizer		DEHCH	DINCH	TOTM	ATBC	DEHP
Volatile	Mass loss/%	0.79	0.58	0.27	0.76	0.75
Migration Stability	Water/%	0.47	0.45	0.09	0.79	0.62
	Ethanol/%	4.93	4.85	1.50	2.12	5.81
	Petroleum ether/%	17.42	17.37	16.80	8.76	18.64
	1% of detergent	0.51	0.52	0.13	0.85	0.68

3.4.4. The Transparency of the Different Plasticizer Plasticized PVC

Table 6. *The transparency of plasticized PVC resin by different plasticizers*

Plasticizer	DEHCH	DINCH	TOTM	ATBC	DEHP
Light transmittance/(%)	90.4	90.5	91.8	88.8	89.2
Haze/(%)	5.45	5.76	3.78	8.47	5.62

The transparency performance of plasticized PVC resin by different plasticizers material is shown in Table 6. As can be seen from the Table 6, DEHCH plasticized with PVC light transmittance and fog degrees are similar to DINCH, and better than the transparency of DEHP. In addition, TOTM plasticized PVC has the highest light transmittance and the lowest haze, so it has the best transparency. As compared with other plasticizer, TOTM is optimal compatibility with PVC. And transparency of ATBC plasticized PVC is worst, but it still has very high light transmittance, which also meets the requirements of transparent products.

3.5. DEHCH and DINCH, ESO System

3.5.1. Formula of Plasticized PVC

According to the above optimization formula of the plasticizer and the number of plasticizer used in daily production. Which fixed the number of main plasticizer DEHCH and ATBC to 50 Phr, change the content of DEHCH, to investigate the performance of plasticized PVC. According to Luo Chaoyun et al. [20] According to the best results of epoxy soybean oil (ESO) soften PVC, the content of the ESO chosen five copies. The formula is shown in Table 7.

Table 7. *Formula of plasticized PVC*

Component	Content / phr
PVC	100
Main Plasticizer	50
Calcium zinc stabilizer	1.8
ESO	5

3.5.2. Mechanical Properties

In a fixed DEHCH and DINCH total content of 50, the content of DEHCH effect on the properties of PVC is shown in Figure 10 to 13. The figure shows that as the change of DEHCH content, the tensile strength of the PVC at about 19.2 MPa, 100 % stretch modulus at about 8.4 MPa, elongation at break is around 330%, hardness is controlled in 82 A, change littler, but temperature of embrittlement is increase with the increase of content of DEHCH. It can be seen that without thinking the strength and toughness of the PVC material, join DINCH to plasticized PVC can improve material of low temperature performance.

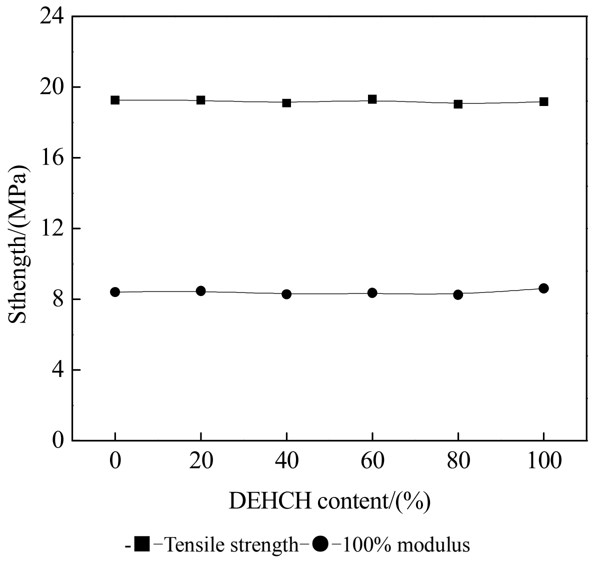


Figure 10. *Effects of DEHCH content on tensile strength and 100% modulus*

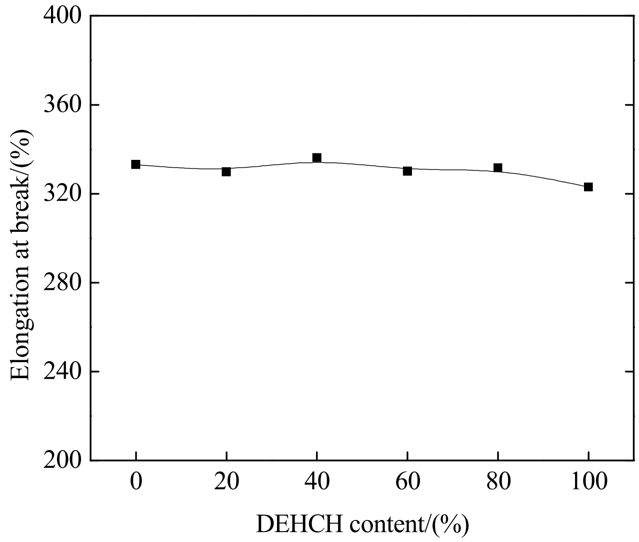


Figure 11. *Effect of DEHCH content on elongation at break*

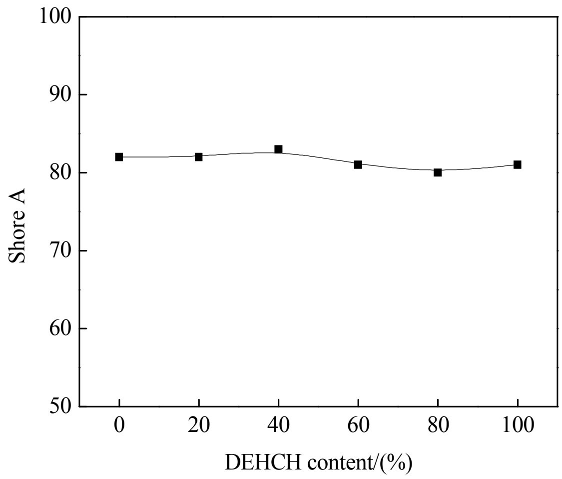


Figure 12. *Effects of DEHCH content on hardness*

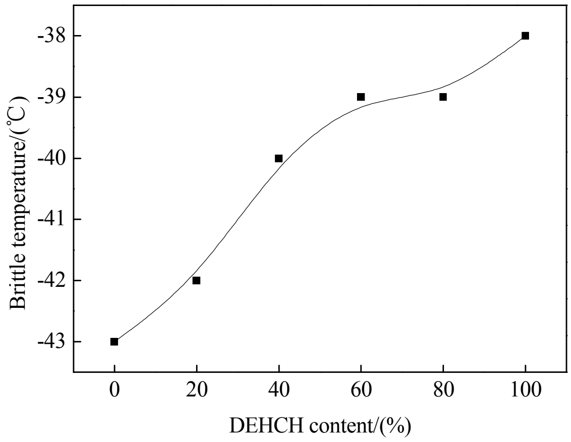


Figure 13. *Effect of DEHCH content on brittle temperature*

3.5.3. Volatility Tests

In a fixed DEHCH and DINCH total dosage of 50, DEHCH percentage of content on the influence of the volatilization of PVC is shown in Figure14.As can be seen from the figure, with the increase of the content of DEHCH, the quality loss PVC under high temperature gradually increased. When content of DEHCH is more than 60%, the Mass loss increased significantly.

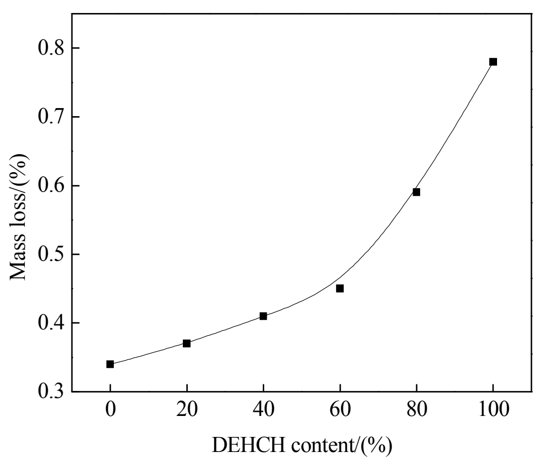


Figure 14. *Effect of DEHCH content on volatility*

3.5.4. Transparency

In a fixed DEHCH and DINCH total dosage of 50, DEHCH percentage of content on the influence of the transparency of PVC is shown in Figure15.It can be seen from the Figure, with the increase of the content of DEHCH, the light transmittance almost unchanged, remain at around 89.6%.With the increase of content of DEHCH, the haze slightly decrease, this is because the haze of DEHCH plasticized with PVC is lower than that of the DINCH, but overall change is very small, at around 6.0%.

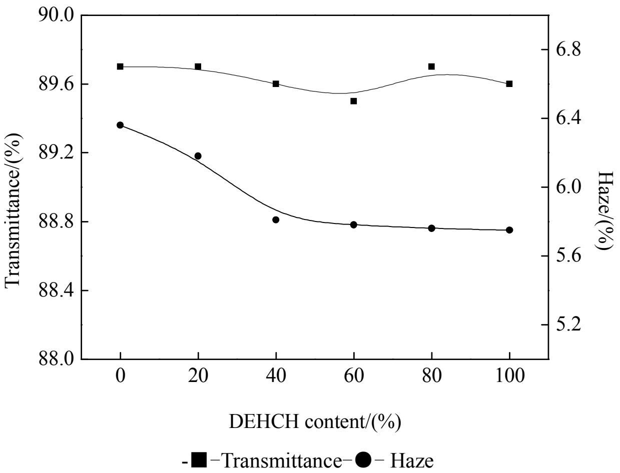


Figure 15. *Effect of DEHCH content on transmittance and haze*

3.6. DEHCH and ATBC, ESO System

3.6.1. Formula of Plasticized PVC

According to the above optimization formula of the plasticizer and the number of plasticizer used in daily production. Which fixed the number of main plasticizer DEHCH and ATBC to 50 Phr, to investigate the performance of plasticized PVC, the formula is shown in Table 8.

Table 8. *Formula of plasticized PVC*

Component	Content /phr
PVC	100
Main Plasticizer	50
Calcium zinc stabilizer	1.8
ESO	5

3.6.2. Mechanical Properties

In a fixed DEHCH and DINCH total dosage of 50, DEHCH percentage of content on the mechanical properties of PVC is shown in Figure 16 to 19. The figure shows that as the increased of DEHCH content, the tensile strength of the PVC stable at about 19 MPa, 100% stretch modulus increased and elongation at break decreased significantly, a slightly higher hardness, brittle temperature decreased obviously. It shows that DEHCH plasticized with PVC has better elasticity and toughness at low temperature than ATBC plasticized with PVC. In the ATBC plasticized products, add DEHCH can significantly improve the products of low temperature toughness.

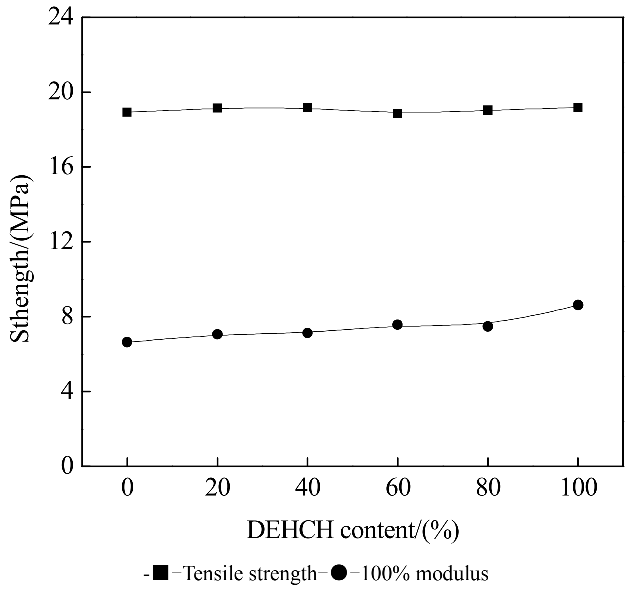


Figure 16. *Effects of DEHCH content on tensile strength and 100% modulus*

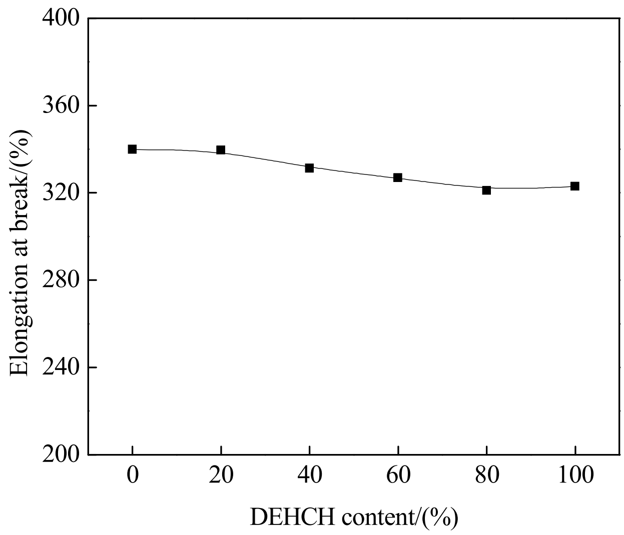


Figure 17. *Effect of DEHCH content on elongation at break*

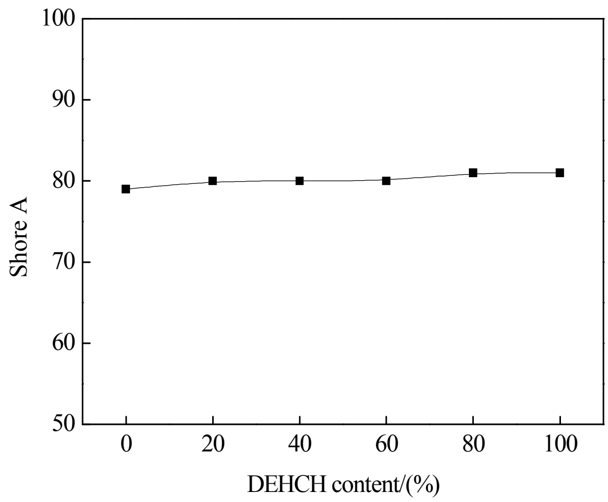


Figure 18. *Effects of DEHCH content on hardness*

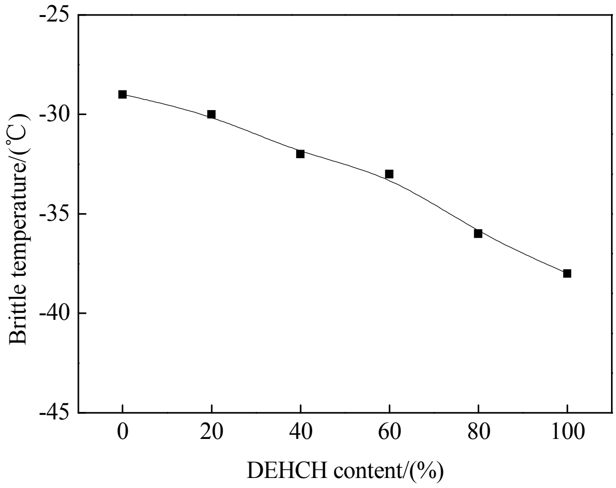


Figure 19. Effect of DEHCH content on brittle temperature

3.6.3. Volatility Tests

In a fixed DEHCH and DINCH total dosage of 50, DEHCH percentage of content on the influence of the volatilization of PVC is shown in Figure 20.It can be seen from the figure, with the increase of the content of DEHCH, the Quality loss PVC under high temperature gradually increased. This is because the ATBC has no benzene or cyclohexane in molecular structure, molecular weight and volume is small, and its high boiling point[21-23].

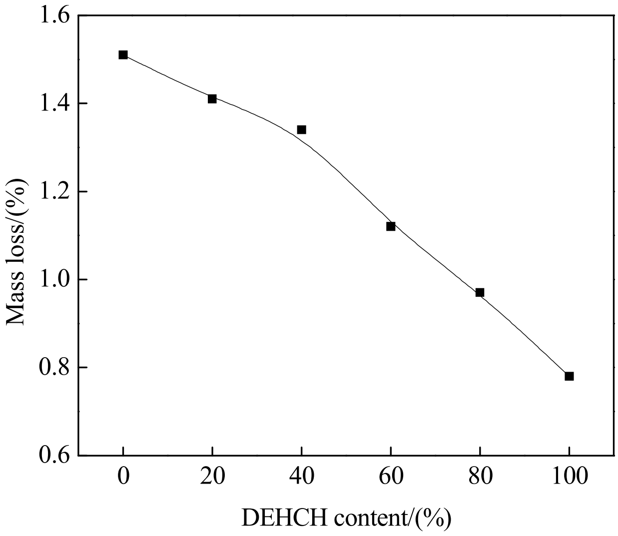


Figure 20. Effect of DEHCH content on volatility

3.6.4. Transparency

In a fixed DEHCH and DINCH total dosage of 50, DEHCH percentage of content on the influence of the transparency of PVC is shown in Figure 21. It can be seen from the figure, with the increase of the content of DEHCH, the Light transmittance increased gradually. With the increase of content of DEHCH, the haze slightly down, This is because DEHCH plasticized with PVC has better transparency than ATBC plasticized with PVC, increase the ATBC plasticizing DEHCH content of a product can improve the transparency of the material.

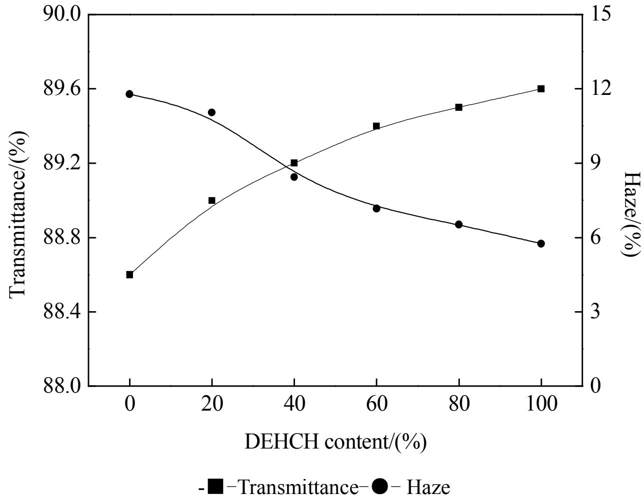


Figure 21. Effect of DEHCH content on transmittance and haze

3.7. DEHCH and TOTM, ESO System

3.7.1. Formula of Plasticized PVC

According to the amount of the plasticizer of PVC soft products commonly, chose to investigate the main plasticizer DEHCH and fixed TOTM total amount to 50, The formula is shown in Table 9.

Table 9. Formula of plasticized PVC

Component	Content /phr
PVC	100
Main Plasticizer	50
Calcium zinc stabilizer	1.8
ESO	5

3.7.2. Mechanical Properties

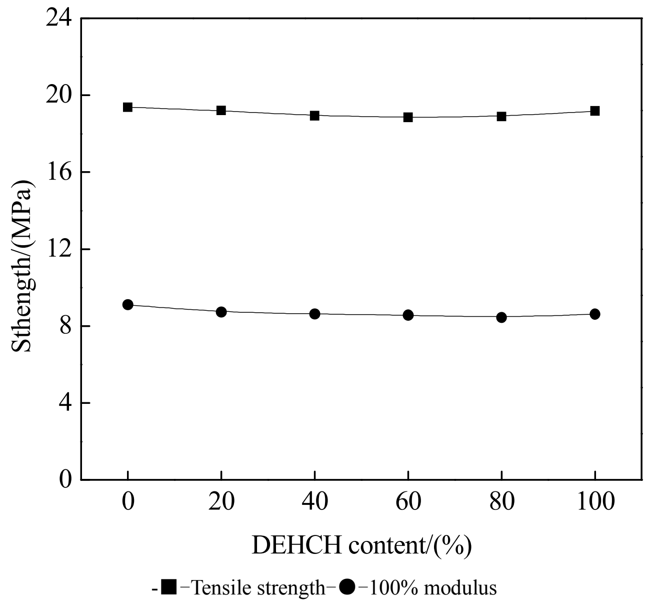


Figure 22. Effects of DEHCH content on tensile strength and 100% modulus

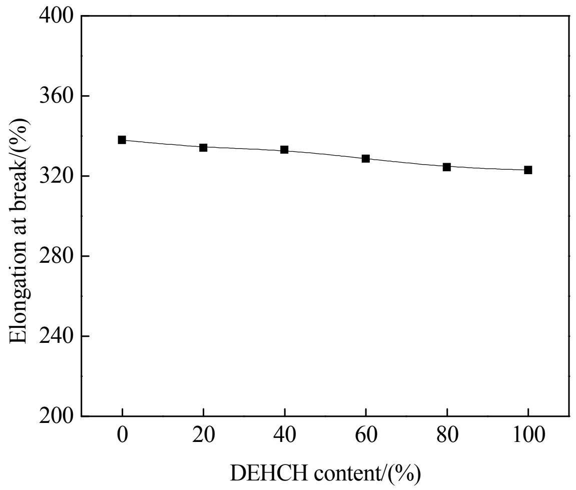


Figure 23. *Effect of DEHCH content on elongation at break*

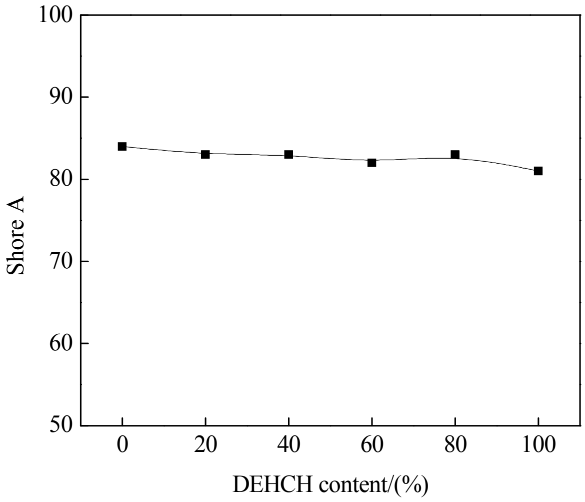


Figure 24. *Effects of DEHCH content on hardness*

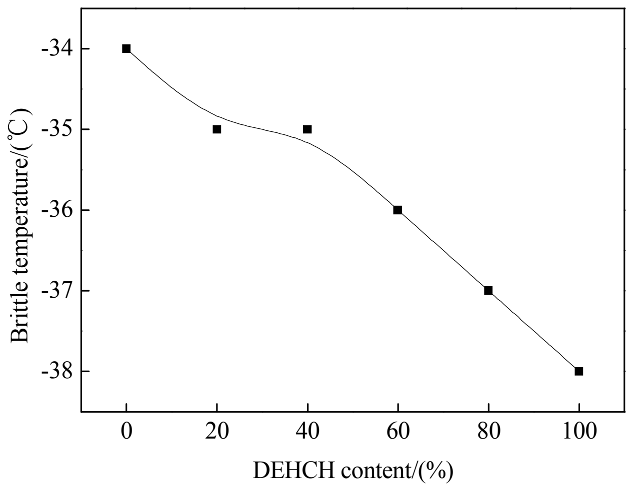


Figure 25. *Effect of DEHCH content on brittle temperature*

In a fixed DEHCH and DINCH total dosage of 50, DEHCH percentage of content on the mechanical properties of PVC is shown in Figure 22 to 25. The figure shows that as the increased of DEHCH content, the tensile strength of the PVC stable at about 19 MPa, 100% stretch modulus dropped from 9.1 MPa to 9.1 MPa, the elongation at break decreased to 322 % from 337 %.This is because the TOTM have stronger polarity, and the compatibility of PVC is better. And hardness dropped from 84 A to 84 A, it can explain that DEHCH is softer than TOTM. On the other hand, with the increase of the content of DEHCH, the brittle temperature gradually decrease, this is because the low temperature toughness of DEHCH is better than TOTM.

3.7.3. Volatility Tests

In a fixed DEHCH and DINCH total content of 50, DEHCH percentage of content on the influence of the volatilization of PVC is shown in Figure 26. It can be seen from the figure, with the increase of the content of DEHCH, the Quality loss PVC under high temperature significant increased. This is because the molecular weight of TOTM is greater than DEHCH, and it is better compatibility with PVC, volatile lower at high temperature. When used in high temperature environment, increase of TOTM content in the products, it can reduce the volatilization loss of products.

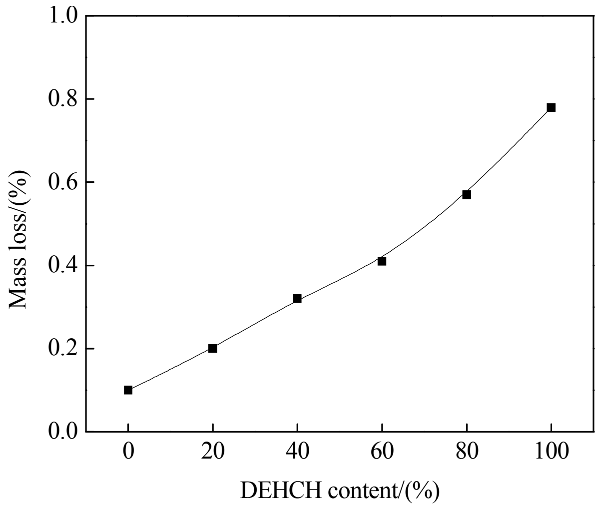


Figure 26. *Effect of DEHCH content on volatility*

3.7.4. Transparency

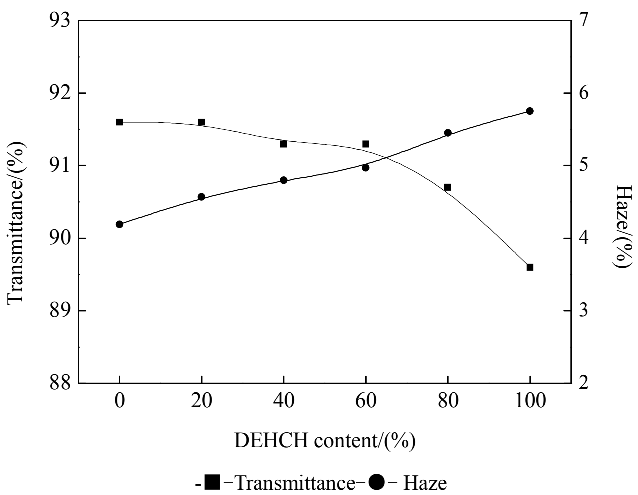


Figure 27. *Effect of DEHCH content on transmittance and haze*

In a fixed DEHCH and DINCH total content of 50, DEHCH percentage of content on the influence of the transparency of PVC is shown in Figure 27. It can be seen from the figure, with the increase of the content of DEHCH, the Light transmittance decreased gradually. With the increase of content of DEHCH, the haze increased gradually, this is because TOTM plasticized with PVC has better transparency than DEHCH plasticized with PVC.

4. Conclusions

From the results we have obtained it can be concluded that:

(1)Di(2-ethylhexyl)-1,2-cyclohexane dicarboxylate (DEHCH) could be synthesized via esterification between hexahydrophthalicanhydride (HHPA) and iso-octanol using concentrated sulfuric acid as a catalyst.

(2) DEHCH can plasticise PVC effectively, DEHCH has similar properties to other plasticizer(DINCH, TOTM, ATBC) performance in the mechanical properties, optical properties, volatile and resistance to solvent extraction, and with DINCH, TOTM, ATBC, it can make up for their shortcomings

(3)DEHCH is a kind of green nontoxic plasticizer could instead of DEHP.

Acknowledgements

The generous financial support of the National supporting project "new plasticizer biomedical materials" Program (2012BAI22B07) gratefully is acknowledged.

References

[1] Wilkes C E, Summers J W. PVC Handbook[M]. Munich: Hanser, 2005.

[2] Hattori Y, Shiraki T. Specific hydrogenated block copolymer composition and process for producing the same: U.S. Patent 4,994,508[P].

[3] Wadey B L. An innovative plasticizer for sensitive applications[J]. Journal of Vinyl and Additive Technology, 2003, 9(4): 172-176.

[4] Segura P A, Kaplan P, Erythropel H C, et al. Comparative Rapid Toxicity Screening of Commercial and Potential “Green” Plasticizers Using Bioluminescent Bacteria[J]. Industrial & Engineering Chemistry Research, 2012, 51(35): 11555-11560

[5] Rahman M, Brazel C S. The plasticizer market: an assessment of traditional plasticizers and research trends to meet new challenges[J]. Progress in Polymer Science, 2004, 29(12): 1223-1248.

[6] Yen T H, Lin-Tan D T, Lin J L. Food safety involving ingestion of foods and beverages prepared with phthalate-plasticizer-containing clouding agents[J]. Journal of the Formosan Medical Association, 2011, 110(11): 671-684.

[7] Daglish A F. STABILIZED VINYLIDENE CHLORIDE: U.S. Patent 2,659,709[P].

[8] Crespo J E, Balart R, Sanchez L, et al. Substitution of di (2 - ethylhexyl) phthalate by di (isononyl) cyclohexane - 1, 2 - dicarboxylate as a plasticizer for industrial vinyl plastisol formulations[J]. Journal of applied polymer science, 2007, 104(2): 1215-1220.

[9] Arabi M, Amini M M, Abedini M, et al. Esterification of phthalic anhydride with 1-butanol and 2-ethylhexanol catalyzed by heteropolyacids[J]. Journal of Molecular Catalysis A: Chemical, 2003, 200(1): 105-110.

[10] Thomas J M, Johnson B F G, Raja R, et al. High-performance nanocatalysts for single-step hydrogenations[J]. Accounts of chemical research, 2003, 36(1): 20-30.

[11] Khajavi S, Jansen J C, Kapteijn F. Application of a sodalite membrane reactor in esterification—Coupling reaction and separation[J]. Catalysis Today, 2010, 156(3): 132-139.

[12] Okamoto Y, Toda C, Ueda K, et al. Transesterification in the microbial degradation of phthalate esters [J]. Journal of Health Science, 2011, 57(3): 293-299.

[13] Wang Q, Storm B K. Separation and analysis of low molecular weight plasticizers in poly (vinyl chloride) tubes[J]. Polymer testing, 2005, 24(3): 290-300.

[14] Sjöberg P, Bondesson U, Gray T J B, et al. Effects of Di-(2-ethylhexyl) Phthalate and Five of its Metabolites on Rat Testis in Vivo and in in Vitro [J]. Actapharmacologicaettoxicologica, 1986, 58 (3): 225-233.

[15] Genay S, Luciani C, Décaudin B, et al. Experimental study on infusion devices containing polyvinyl chloride: to what extent are they di (2-ethylhexyl) phthalate-free [J]. International journal of pharmaceutics, 2011, 412(1): 47-51.

[16] Scott M P, Rahman M, Brazel C S. Application of ionic liquids as low-volatility plasticizers for PMMA[J]. European polymer journal, 2003, 39(10): 1947-1953.

[17] Pollack G M, Buchanan J F, Slaughter R L, et al. Circulating concentrations of di (2-ethylhexyl) phthalate and its de-esterified phthalic acid products following plasticizer exposure in patients receiving hemodialysis[J]. Toxicology and applied pharmacology, 1985, 79(2): 257-267.

[18] Lindström A, Hakkarainen M. Migration resistant polymeric plasticizer for poly (vinyl chloride)[J]. Journal of applied polymer science, 2007, 104(4): 2458-2467.

[19] Jayakrishnan A, Lakshmi S. Immobile plasticizer in flexible PVC [J]. Nature, 1998, 396(6712): 638-638.

[20] Breme F, Buttstaedt J, Emig G. Coating of polymers with titanium-based layers by a novel plasma-assisted chemical vapor deposition process [J]. Thin Solid Films, 2000, 377: 755-759.

[21] Audic J L, Poncin - Epaillard F, Reyx D, et al. Cold plasma surface modification of conventionally and nonconventionally plasticized poly (vinyl chloride)-based flexible films: Global and specific migration of additives into isooctane [J]. Journal of applied polymer science, 2001, 79(8): 1384-1393.

[22] Lakshmi S, Jayakrishnan A. Migration resistant, blood-compatible plasticized polyvinyl chloride for medical and related applications[J]. Artificial organs, 1998, 22(3): 222-229.

[23] Riser G R, Palm W E. A method for determining compatibility parameters of plasticizers for use in PVC through use of torisonalmodulus[J]. Polymer Engineering & Science, 1967, 7(2): 110-114.