

Preparation and Characterization of Carborane Modified Liquid Fluoroelastomers and the investigation of their properties

Juan Li 

Department of Polymer and Composite Material, School of Materials Science and Engineering, Yancheng Institute of Technology, Yancheng, China

ABSTRACT

The preparation of liquid fluoroelastomers that are liquid with excellent mechanical properties remains a challenge. Here, we show a very straightforward method to produce liquid fluoroelastomers by introducing carborane. Carborane-terminated liquid fluoropolymer was synthesized by Steglich reaction of carboxyl-terminated liquid fluoropolymer and 1,7-bis (hydroxy)-carborane. The product is brown, viscous at room temperature and in the semi-solid state. On this basis, HDI Trimer was used as a curing agent to cure liquid fluoroelastomer. Thermogravimetric analysis of the cured products was carried out. The carbon residue rate of the cured product increased from 35% to 58% of the cured product. The results show that the addition of carborane structure can effectively improve the carbon residue rate of liquid fluoroelastomer. The tensile strength, elongation and shore hardness of the cured product were also examined, and the results show that the tensile strength of carborane modified liquid fluorine increased by 463% compared with that before modification, but the elongation at break was reduced by 42%, which was mainly due to the introduction of rigid structure of carborane. At the same time, the solvent resistance test results show that the introduction of carborane structure has little effect on the aviation kerosene resistance and organic solvent resistance of fluororubber, but it can improve its alkali resistance.

ARTICLE HISTORY

Received 6 May 2021
Accepted 21 May 2021

KEYWORDS

Fluoroelastomer; carborane; tensile strength; alkali resistance

1 Introduction

Owing to their excellent properties such as thermal stability, chemical resistance, low surface energy, and electric property, fluoropolymers have been widely utilized as fluoroplastics, fluoroelastomers, and fluorocarbon coatings in the field of mechanical engineering, chemical industry, traffic vehicles, construction industry, etc. [1,2]. More specifically, curable liquid fluoropolymers with lower molecular weight (MW) are paid exclusive attention by solvent-free sealant and adhesive formulators for they are indispensable starting materials with anticipated chemical and thermal resistance [3,4]. However, compared with traditional fluoroelastomer, liquid fluoroelastomer has lower molecular weight and better processability. Moreover, its chemical properties, especially heat resistance and chemical resistance, are the same as those of solid fluoroelastomers, but their mechanical properties are lower than those of traditional fluoroelastomers [5–8].

On the other hand, dicarba-closo-dodecaborane ($C_2B_{10}H_{12}$), referred to as carborane, is composed of two carbon atoms and ten boron atoms. The two carbon atoms and ten boron atoms are six coordinated. The molecule has a highly symmetrical skeleton and an

icosahedral structure. This icosahedral structure gives this molecule and its derivatives many unique properties [9]. Its ‘super aromatic’ cage structure can play the role of ‘energy trough’ to stabilize the whole molecule. At the same time, the cage structure is bulky and has shielding effect on adjacent groups, so it has high thermal stability. Moreover, the B-C bond has a good water resistance and chemical stability [10]. Icosahedral carborane has a ‘super aromatic’ cage structure, which is characterized by thermal stability, chemical resistance, unique geometry, and the high-energy capture cross section of boron nuclei [11–16]. Due to its remarkable stability, icosahedral carborane has been regarded as an ideal material to improve the heat resistance and mechanical properties of polymers.

Our group has already conducted research work on the oxidative degradation of higher MW fluoroelastomer and obtained liquid fluoropolymers with COOH, activated pentafluorophenyl ester and silane [17,18]. In this paper, we report our studies on the formation of carborane groups in liquid fluoropolymers and the cure properties of the obtained fluoropolymers were also studied. Carborane liquid fluoroelastomer, on the basis of liquid fluoroelastomer, introduces carborane [19,20] with high

CONTACT Juan Li  julialijuan@163.com  Department of Polymer and Composite Material, School of Materials Science and Engineering, Yancheng Institute of Technology, Yancheng, China

© 2021 The Author(s). Published by Informa UK Limited, trading as Taylor & Francis Group.
This is an Open Access article distributed under the terms of the Creative Commons Attribution-NonCommercial License (<http://creativecommons.org/licenses/by-nc/4.0/>), which permits unrestricted non-commercial use, distribution, and reproduction in any medium, provided the original work is properly cited.

thermal stability, hydrolysis stability and oxidation stability to further improve its stability, so that it can be used in more severe working environment.

2 Experimental

2.1 Materials

Carboxyl-terminated telechelic fluoropolymers ($M_n = 2900$, $M_w/M_n = 1.86$, self preparation); $m\text{-C}_2\text{B}_{10}\text{H}_{12}$ was purchased from Russia (1, 7-carborane); oxetane (99.10%), polyoxymethylene (POM), *N*-butyl lithium (n-BuLi), *p*-Toluenesulfonic acid monohydrate (TsOH), *N,N*-dicyclohexylcarbodiimide (DCC), and 4-(dimethylamino)pyridine (DMAP) were purchased from Acros. HDI Trimer (NCO% = 21.99) was purchased from Bayer. Dibutyltin dilaurate (DBTDL), tetrahydrofuran (THF), acetone, ethyl acetate, petroleum ether were commercially obtained.

2.2 Instrumentation

Fourier transform infrared (FTIR) spectra measurements were performed using a Nicolet Nexus 670 (FTIR) instrument (USA). The spectra were obtained at resolution 4 cm^{-1} in the range $3200 \sim 500\text{ cm}^{-1}$. Solid samples were prepared as pellets using spectroscopic grade KBr. $[1]\text{H-NMR}$ spectra were measured on a Bruker ARX 400 NMR spectrometer using acetone- d_6 (TMS; $\delta = 0\text{ ppm}$) as internal standard. Molecular weights (M_w and M_n) and polydispersity indexes ($\text{PDI}, M_w/M_n$) of the polymers were estimated in THF by a Waters gel permeation chromatography (GPC) system (Waters, 515 HPLC Pump). Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGS-2 under nitrogen ambience with a heating rate of $10^\circ\text{C}/\text{min}$ in the temperature range of $25 \sim 800^\circ\text{C}$. The mass fraction of carboxyl was characterized by automatic potentiometric titration. Glass electrode and calomel electrode were used as the electrode. Tensile test of dumbbell specimens was carried out on a testing machine (CMT4104, ShenzhenSANS Testing Machine, Shenzhen, Guangdong Province, China) at a velocity of $500\text{ mm}/\text{min}$, according to ASTM D882.

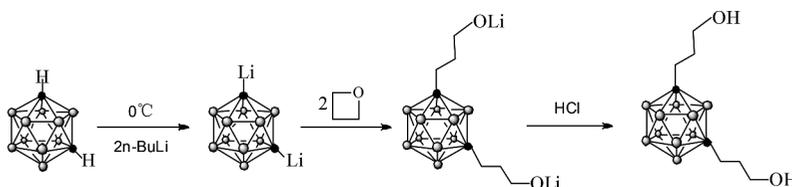
2.3 Preparation for *C,C'*-bis-hydroxypropyl-1,7-carborane

The H on the carbon in carborane is a weak acid and relatively active. It is easy to deproton with strong basic organic lithium reagents, such as n-BuLi, to obtain nucleophiles. The nucleophiles can further react with electrophilic agents (such as cyclic ethers and aldehydes) and finally acidify with hydrochloric acid to form carborane alcohols. The tetrahydrofuran solution of carborane was deprotonized by n-butyl lithium, and then dilithiation was carried out. Oxy heterocyclobutane was added, and the carbon borane double lithium compound attacked the C on the edge of oxygen atom in oxobutane to open the ring. Finally, dilute hydrochloric acid was added to acidify to obtain bis (hydroxypropyl) carborane. The synthetic route is shown in Scheme 1.

The typical synthesis process is as follows: 1, 7-carborane (1.59 g, 11.0 mmol) was dissolved in 20 ml of inert solvent tetrahydrofuran. N-butyl lithium (9.5 ml, 22.8 mmol) was added in anhydrous and oxygen-free environment. The reaction was carried out in an ice water bath and magnetic stirring for 0.5 h. Double molar amount of oxobutane (1.5 ml, 22.8 mmol) was added, and then 1 mL hydrochloric acid was added. After stirring for 0.5 h, a quenching reaction was carried out. After the reaction, the solvent tetrahydrofuran was evaporated, extracted with ether for three times, then washed with deionized water and brine for three times. The organic layer was collected, dried with anhydrous magnesium sulfate, filtered, and filtrated. Most of the solvent was evaporated, dried in a vacuum oven, washed with petroleum ether, and dried to obtain white solid. The yield of 7-Bis (hydroxypropyl) carborane was 90.1%, and the melting point was 87.6°C . FTIR, ν (cm^{-1} , KBr): 3290 (-OH), 2931, 2839 (C-H), 2593 (B-H), 1452 (C-H), 1374 (OH), 1181 (C-O), 1065 (B-H), 1028 (B-B); $[1]\text{H-NMR}$ (CDCl_3): δ : 1.70 ~ 3.10 ppm (br m, 10 H, B-H), 3.62 ppm (t, 4 H, C-H), 2.04 ppm (t, 4 H, C-H), 1.62 ppm (qui, 4 H, C-H), 1.32 ppm (s, 2 H, O-H)

2.4 Preparation for *C,C'*-bis-hydroxymethyl-1,7-carborane

The synthesis mechanism is the same as that of scheme1. The tetrahydrofuran solution of 1,7-carborane



Scheme 1 Synthesis Route of bis(hydroxypropyl)-carborane.

was dilithicized under the initiation of *n*-butyl lithium, and polyformaldehyde was added. The C-O bond in paraformaldehyde was attacked by a carborane double lithium compound. Finally, 1,7-bis (hydroxymethyl) carborane was obtained by acidification with dilute hydrochloric acid. The synthetic route is shown in Scheme 2.

The typical synthesis process is as follows: 1,7-carborane (1.03 g, 7.1 mmol) was dissolved in 20 ml of inert solvent tetrahydrofuran. *N*-butyl lithium (6.4 ml, 15.4 mmol) was added in anhydrous and oxygen-free environment. The reaction was carried out in an ice water bath and magnetic stirring for 0.5 h. Double molar amount of paraformaldehyde (0.46 g, 15.4 mmol) was added, and then 1 m/L hydrochloric acid was added. After stirring for 0.5 h, a quenching reaction was carried out. After the reaction, the solvent tetrahydrofuran was evaporated, extracted with ether for three times, then washed with deionized water and brine for three times. The organic layer was collected, dried with anhydrous magnesium sulfate, filtered, and filtrated. Most of the solvent was evaporated, dried in a vacuum oven, washed with petroleum ether, and dried to obtain white solid. The yield of 7-Bis (hydroxymethyl) carborane was 81.0%, and the melting point was 133.7°C. FTIR, ν (cm^{-1} , KBr): 3285 (-OH), 2944, 2888 (C-H), 2596 (B-H), 1463 (C-H), 1375 (OH), 1179 (C-O), 1065 (B-H), 1028 (B-B); [1]H-NMR (CDCl_3): δ 1.70 ~ 3.10ppm (br m, 10 H, B-H), 5.83 ppm (s, 2 H, O-H), 3.62 ppm (t, 4 H, C-H) .

2.5 Synthesis of carborane-terminated telechelic fluoropolymers (P2)

Carborane-terminated liquid fluoropolymers were prepared by steglich reaction of carboxyl-terminated fluoropolymer and C,C'-bis-hydroxymethyl-1,7-carborane shown in Scheme 3. Typical experimental procedures for the steglich reaction is given below as an example.

Carboxyl-terminated fluoropolymers (6.27 g, 2.03 mmol of carboxyl), 1,7-Bis-(hydroxypropyl)-carborane (0.2754 g, 2.11 mmol), DCC (0.5559 g, 3.01 mmol), DMAP (0.0229 g, 0.21 mmol), TsOH (0.0203 g, 0.12 mmol) were added to 50 mL dry THF in a 250 mL flask. The mixture was stirred at room temperature for 8 h, and a white precipitate was formed. Then, the solid was discarded by filtration and the oligomer was purified by precipitation from petroleum ether. After

evaporation of the solvents, yellow viscous liquid was collected with a yield of 73%. FTIR, ν (cm^{-1} , KBr): 2996, 3034 (-CH₂-), 2600 (BH), 1766, 1720 (C = O), 1600–1680 (C = C), 1396 (-FCH₂), 1204 (-CF₂-), 886 (-CF₃), 720 (C-C). [1]H NMR (400 MHz) δ 4.71 (s, -C (CF₃) = CH-), 4.15–2.74 (m, -CH₂CF₂-), 3.64, 1.81, 2.07 (CH₂CH₂CH₂), 1.32 (OH), 2.13–0.81 (B-H)

2.6 Curing of fluoropolymers P1 and P2

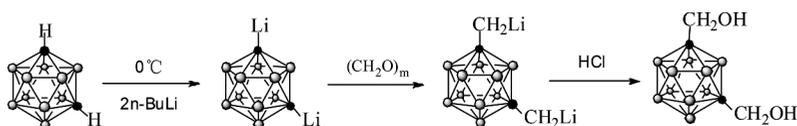
According to Scheme 1, the Fluoropolymer 2 was cured with HDI trimer in the presence of catalyst. The procedures are given as follows: 1 g HDI trimer and 0.01 g DBTDL catalyst solution were added to 20 mL THF solution of fluoropolymer 2 (9.95 g). After 10 min mixing, the solution was transferred to PTFE mould (diameter = 100 mm). The mould system was placed at 60°C for removing the solvent and cured at 80°C for 24 hours. A crosslinked film with 0.3 mm thickness was obtained. FTIR, ν (cm^{-1} , in KBr pellet): 3200 (-NH-), 3034, 2996 (-CH₂-), 2600 (B-H) 1766–1670 (C = O), 1396 (-FCH₂), 1204 (-CF₂-), 886 (-CF₃), 720 (C-C).

For comparison, fluoropolymer 1 was also cured with HDI trimer (NCO = 21.99%) according to the procedures below. 1 g HDI trimer and 0.01 g DBTDL catalyst solution were added to 20 mL THF solution of fluoropolymer 1 (9.21 g). After 10 min mixing, the solution was transferred to PTFE mould (diameter = 100 mm). The mould system was placed at 60°C for removing the solvent and cured at 80°C for 24 hours. A crosslinked film with 0.3 mm thickness was obtained. FTIR, ν (cm^{-1} , KBr): 3200 (-NH-), 3034, 2996 (-CH₂-), 1766–1670 (C = O), 1396 (-FCH₂), 1204 (-CF₂-), 886 (-CF₃), 720 (C-C)

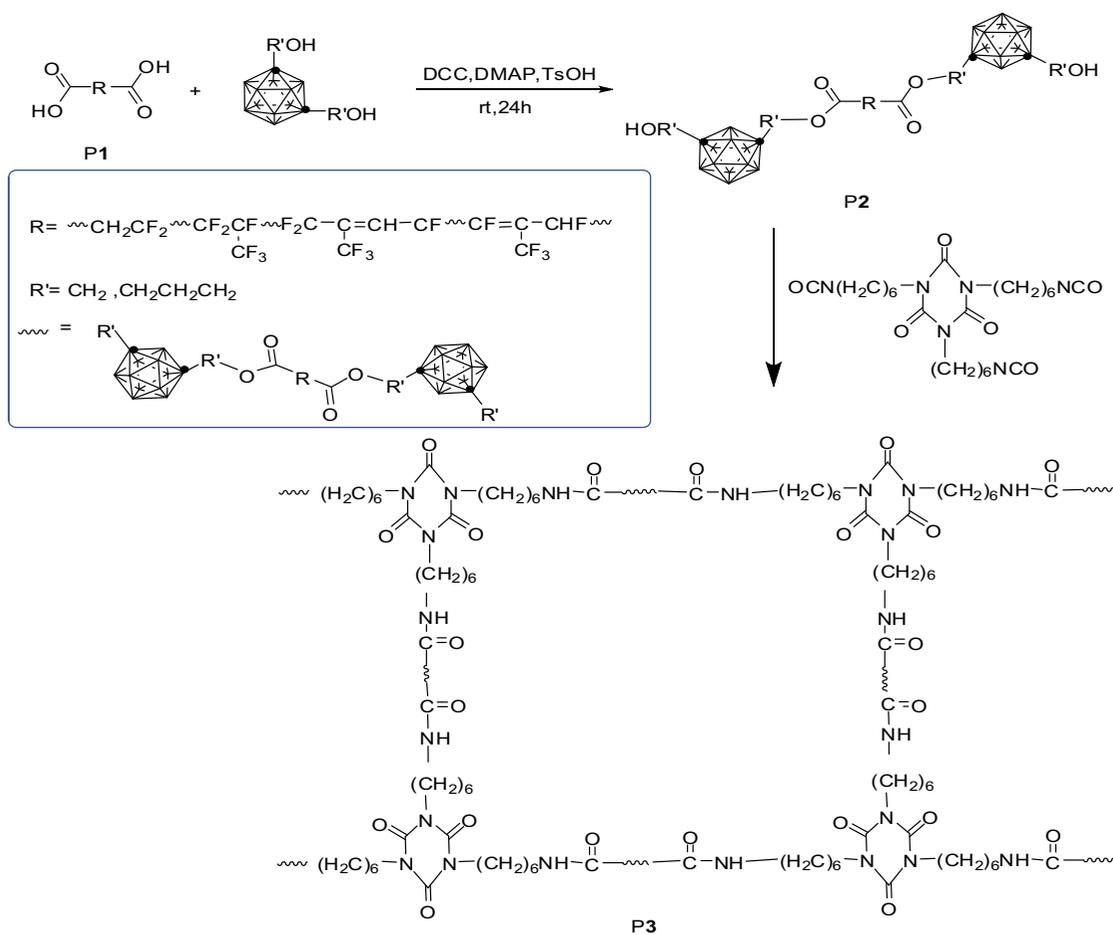
3 Results and discussion

3.1 Characterization of carborane-terminated telechelic fluoropolymers

By Steglich reaction of carboxyl-terminated fluoropolymer and C,C'-bis-hydroxymethyl-1,7-carborane, we obtained liquid fluoropolymers with carborane end groups. These polymers were synthesized through Steglich reactions according to the synthetic route shown in Scheme 3. All the reactions proceeded smoothly, and the desired reactive polymers were isolated with satisfactory yields.



Scheme 2 Synthesis Route of 1,7-bis(hydroxymethyl)-carborane.



Scheme 3 Synthesis and Cure of Carborane-terminated liquid fluoropolymers.

All the liquid fluoropolymers were characterized by standard spectroscopic methods, from which satisfactory analysis data were obtained according to their expected molecular structures (see Experimental section for details). The IR spectra of liquid fluoropolymers **1** and **2** are given in Figure 1; the spectra of their precursors, P1 and C,C'-bis-hydroxypropyl-1,7-carborane, are also given in the figure for comparison. Like its precursor, fluoropolymer **1** exhibits absorption peaks at 1396, 1204, and 886 cm^{-1} ascribed to stretching vibration of $-\text{FCH}_2-$, $-\text{CF}_2-$, and $-\text{CF}_3$, respectively, which clearly shows that fluoropolymer **2** has the same backbone structure as its precursor. The new peak at $\sim 2600 \text{ cm}^{-1}$ in the spectrum of fluoropolymer **2** is ascribed to the stretching vibration of B-H.

NMR is a very effective way to further characterize the structure of the products. Figure 2 shows the $[1]\text{H}$ -NMR spectra of liquid fluoroelastomer and carborane liquid fluoroelastomer before and after reaction. Acetone is used as solvent in the test. It can be seen from Figure 2 that compared with the carboxyl terminated liquid fluoroelastomer, the characteristic peaks of CH_2 in 1,7-di(hydroxypropyl) – carborane and oh at 1.32 ppm appear at 3.64

ppm, 2.07 ppm and 1.81 ppm, respectively. A wide B-H characteristic peak appeared at 0.81–2.13 ppm. Similarly, the products from 1,7-bis(hydroxymethyl) – carborane showed characteristic peaks of hydrogen in hydroxymethyl at 3.64 ppm and 1.32 ppm, and B-H peaks at 0.81–2.13 ppm. The characteristic peak of hydrogen in COOH disappeared at 7.64 ppm. These results indicate that there are VDF-HFP copolymer structure and carborane structure in the target product carborane liquid fluoroelastomer, and the polymer chain is terminated with hydroxyl group. This is consistent with the result of infrared analysis.

3.2 Characterization of curing properties of fluoropolymer P1 and P2

By using Steglich reaction of carboxyl-terminated fluoropolymer and C,C'-bis-hydroxymethyl-1,7-carborane, carboxyl-terminated fluoropolymer is successfully transformed to curable carborane liquid fluoropolymer (**P2**). On the basis of detailed reference research, we selected HDI trimer as the curing agent to cure carborane liquid fluoroelastomer. The molar ratio of **P2** to HDI trimer is designed to be 1:1.

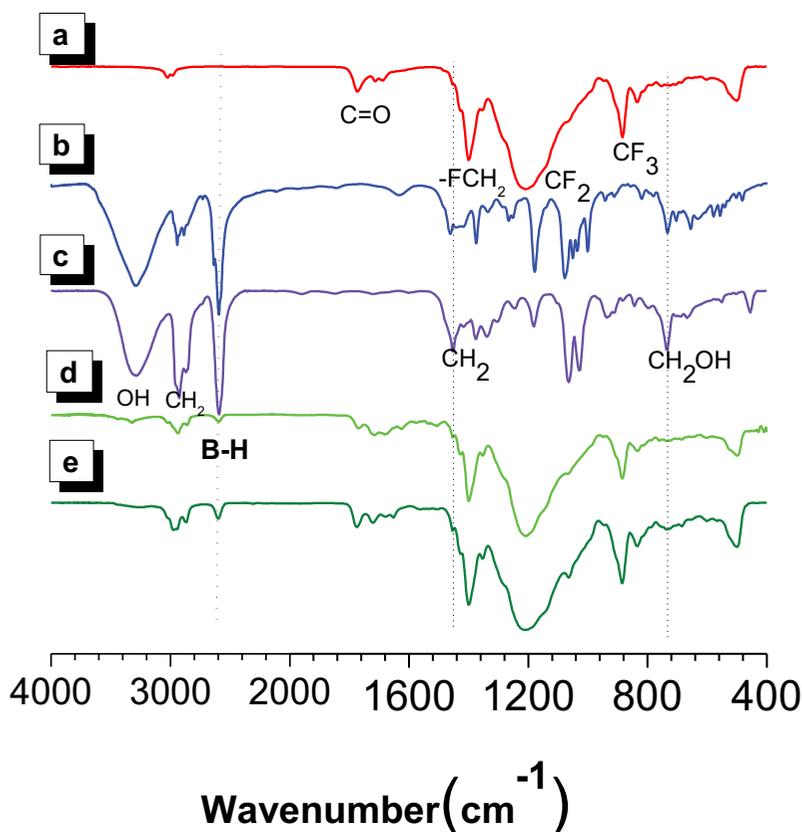


Figure 1. FTIR of (A) carboxyl-terminated fluoropolymer, (B) 1,7-Bis-(hydroxymethyl)-carborane, (C) 1,7-Bis-(hydroxypropyl)-carborane, (D) carborane-terminated fluoropolymer **2** (sample from Table 1, No.1), and (E) carborane-terminated fluoropolymer **2** (sample from Table 1, No.2).

FTIR spectra of the cured fluoropolymer are given in Figure 3. The new peak at $\sim 2600\text{ cm}^{-1}$ in the spectrum of cured carborane fluoropolymer **P3** is ascribed to the stretching vibration of B-H, which is different from cured **P1**. Compared with the spectra of fluoropolymers (shown in Figure 1), the cured fluoropolymer exhibits absorption peaks at 1396 , 1204 , and 886 cm^{-1} ascribed to stretching vibration of $-\text{FCH}_2-$, $-\text{CF}_2-$, and $-\text{CF}_3$, respectively. Furthermore, the cured fluoropolymer exhibits new peak at $\sim 1686\text{ cm}^{-1}$, which confirms the formation of carbonyl of ester. The peak at $\sim 3325\text{ cm}^{-1}$ and 1546 cm^{-1} in the spectrum of the cured fluoropolymer is ascribed to the formation of NHCO structure. And there is no characteristic peak of NCO at 2280 cm^{-1} , which due to HDI reacts with carboxyl terminated liquid fluoroelastomer completely. The result of FTIR spectra also shows that the liquid fluoropolymers can be cured by HDI Trimer.

Thermal properties of the cured fluoropolymers

Carborane structure has excellent high-temperature resistance, so the samples were analyzed by thermogravimetry. TGA thermograms of liquid fluoropolymer and

cured fluoropolymer are shown in Figure 4. It can be seen from **P1** and **P2** in the figure that the thermal decomposition of the carboxyl terminated liquid fluoroelastomer of the raw material continues from 102°C to 480°C , and 13.80% of the total mass is decomposed in the range of $102\text{--}433^\circ\text{C}$, which may be related to the small molecules and structural defects in the material. In the temperature range of $433\text{--}480^\circ\text{C}$, 85.06% of the total mass was decomposed, and the final carbon residue rate was 8.139% at 600°C . The results show that the carborane liquid fluoroelastomer decomposes slowly at 158°C and decomposes 10.41% of the total mass in the range of $158\text{--}389^\circ\text{C}$, rapidly decomposes in the range of $389\text{--}442^\circ\text{C}$, tends to moderate after 442°C , and the carbon residue rate of **P2** is 20.87% at 600°C . It shows that the introduction of carborane structure can improve the carbon residue rate of fluoroelastomer.

TGA analysis of the cured product can further prove this point. The carbon residue rate of the cured product increased from 8% to 35% at 800°C , which was mainly due to the formation of crosslinking structure. The carbon residue rate of the cured product increases from 12% to 58% at 800°C , which is mainly due to the formation of crosslinking structure. The change of carbon

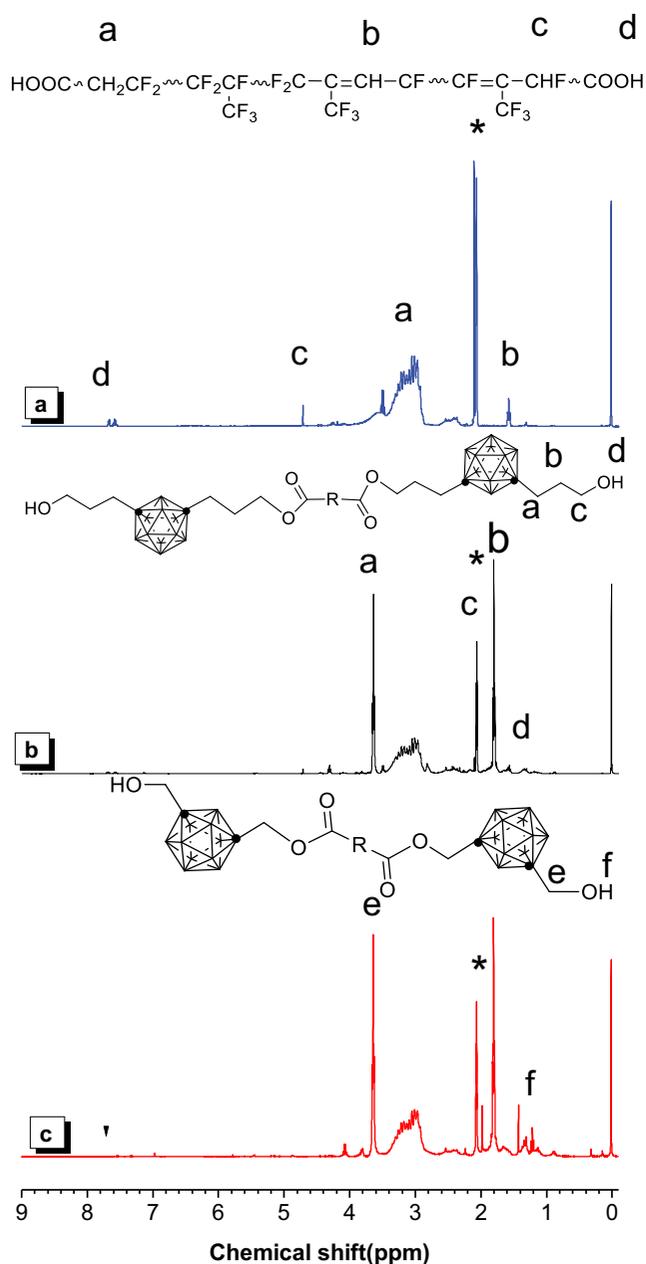


Figure 2. ^1H NMR spectra of (A) carboxyl-terminated fluoropolymer 1, (B) carborane-terminated fluoropolymer 2 (sample from Table 1, No.2), (C) carborane-terminated fluoropolymer 2 (sample from Table 1, No.1), in actone- d_6 . The solvent peaks are marked with asterisks.

residue rate of the product before and after curing further indicates that liquid fluororubber can be cured by HDI Trimer [20–23].

Compared to the cured products of carboxyl-terminated liquid fluoroelastomer and carborane liquid fluoroelastomer, it can be seen that the carbon residue rate of the products increases from 35% to 58% due to the introduction of carborane. It shows that the introduction of carborane can effectively improve the carbon residue rate of the product.

Mechanical and Chemical Resistant Properties of Cured Fluoropolymer Films

Mechanical properties of cured fluoropolymer are shown in Table 2. The tensile strength, elongation and shore A hardness of the cured product were 10.59 MPa, 80% and 55, respectively. Compared with the mechanical properties of the cured products of carborane liquid fluororubber, the tensile strength, elongation and hardness of the cured products increased significantly. The tensile strength of carborane modified liquid fluorine increased by 463% compared with that before modification, but the elongation at break was reduced by 42%, which was mainly due to the introduction of rigid structure of carborane. It shows that the introduction of carborane structure can effectively improve the tensile strength of liquid fluororubber, and improve the problem of tensile strength reduction caused by the decrease in molecular weight.

It is well known that fluoropolymers have good chemical resistances, such as acid resistance, oil resistance and organic solvent resistance, but their alkali resistance is not ideal^[2]. The carborane structure has excellent chemical stability, so whether the introduction of carborane structure can improve its alkali resistance is discussed here. In this paper, the chemical resistance of the cured product is characterized by measuring the quality change of the cured product after soaking in the solvent for a period of time. Here, we choose jet aircraft oil, cyclohexane, 37% HCl and 45% NaOH as the immersion media. Percentage change in mass of the cured film is shown in Table 3. The mass change rates of cured products in aviation kerosene, cyclohexane for 24 h, 72 h and 168 h were 1%, and the difference was not significant, which indicated that the cured products had good aviation kerosene resistance and solvent resistance, and the introduction of carborane structure had little effect on the aviation kerosene resistance and solvent resistance of fluororubber. The mass change rate of carborane liquid fluororubber curing product in 37% hydrochloric acid is higher than that of carboxyl terminated liquid fluororubber, but the long-term mass change rate of carborane liquid fluororubber is small. After soaking in 45% NaOH for 24 h, the cured products of carborane liquid fluororubber and common carboxyl terminated liquid fluororubber became black and the change rate of product quality was not significant. However, after 3–7 days, the mass change rate of carborane liquid fluororubber curing product was significantly lower than that of carboxyl terminated liquid fluororubber. The introduction of carborane structure has an effect on the acid resistance and

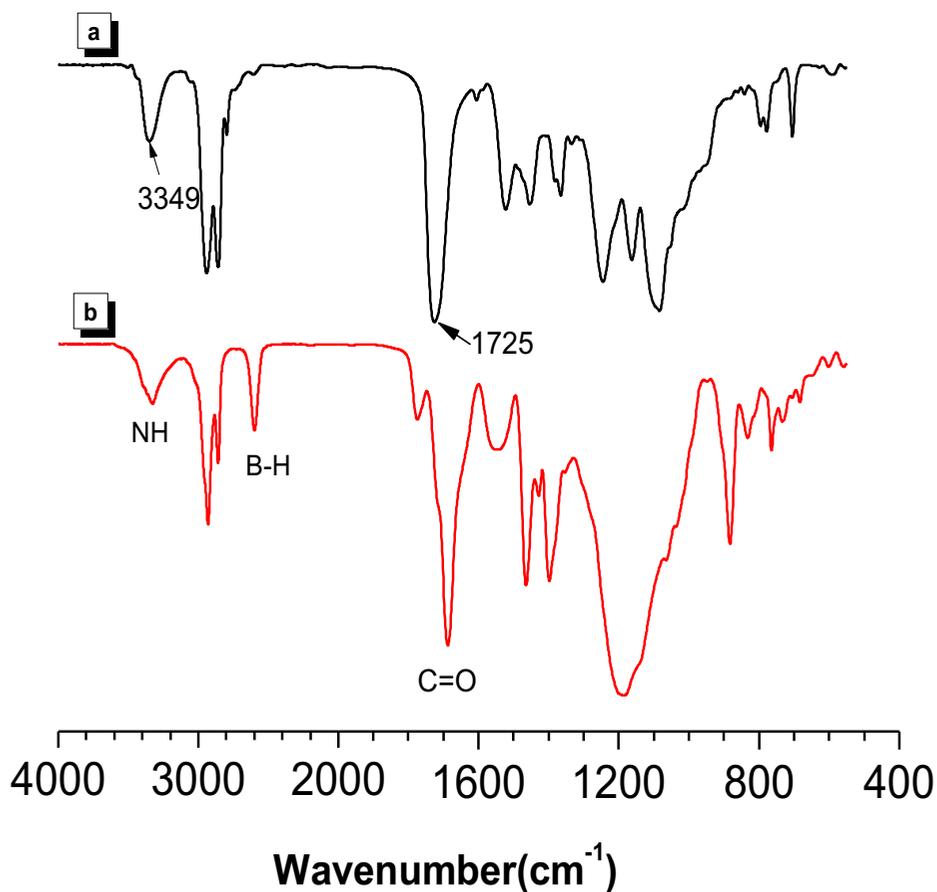


Figure 3. FTIR of (A) cured P1 and (B) cured carborane fluoropolymer P3.

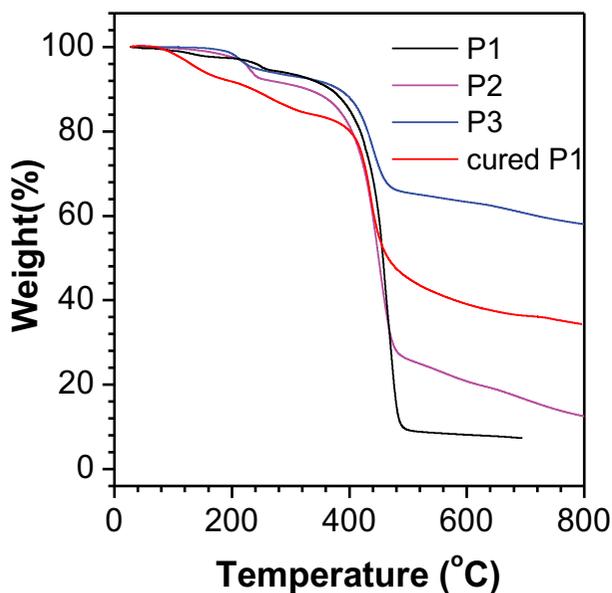


Figure 4. TGA of carboxyl-terminated fluoroelastomer P1, 1,7-Bis-(hydroxypropyl)carborane-terminated fluoroelastomer P2, P3 and cured P1.

alkali resistance of the product. This is mainly due to the stable structure of carborane.

4 Conclusions

Carborane-terminated liquid fluoroelastomer was synthesized by stepwise reaction of carboxyl terminated liquid fluoroelastomer and 1,7-bis (hydroxy)-carborane. The product is brown, viscous at room temperature and in the semi-solid state. The structure of the synthesized carborane liquid fluoroelastomer was characterized by NMR, FTIR and TGA, and its molecular weight was determined by GPC. The results showed that the VDF-HFP copolymer structure and carborane alcohol terminated structure were contained in the carborane liquid fluoroelastomer, and the weight average molecular weight was 8700. HDI Trimer was used as a curing agent to cure liquid fluoroelastomer. Thermogravimetric analysis of the cured products was carried out. The carbon residue rate of the cured product increased from 35% to 58% of the cured product. The results show that the addition of

Table 1. Synthesis of fluoropolymers P2^a.

No.	carborane	yield (%)	M_n^b	M_w/M_n^b
1	C,C'-bis-hydroxymethyl-1,7-carborane	73	4600	1.90
2	C,C'-bis-hydroxypropyl-1,7-carborane	92	4200	2.09

^aSynthesized according to the synthetic route shown in Scheme 1; Abbreviations: M_w = weight-average molecular weight, M_n = number-average molecular weight, [COOH] = carboxyl mass fraction, C = carboxyl conversion of condensation. ^b Estimated by gel permeation chromatograph (GPC) in THF on the basis of a PS calibration. ^c Tested by acid-alkali titration conducted on automatic potentiometric titrator.

Table 2. Mechanical property of cured carboxyl-terminated fluoropolymers and cured carborane fluoropolymer.

Properties	cured P1		P3	
	Mean ^a	Standard deviation ^b	Mean ^a	Standard deviation ^b
Tensile strength (MPa)	1.88	0.24	10.59	0.23
Elongation at break (%)	140	3	80	2.7
Shore A hardness	50	2.07	55	2.28

^a According to ASTM D882, each sample has five parallel specimens. The mechanical properties were taken from the average of five parallel specimens. ^b Standard deviation was calculated by origin software.

Table 3. Change in mass of cured carboxyl-terminated fluoropolymer and cured carborane fluoropolymer.

Reagent	Time(h)	Weight change (%) ^a			
		cured P1		P3	
		Mean ^b	Standard deviation ^c	Mean ^b	Standard deviation ^c
Jet aircraft oil	24	0.30	0.011	0.40	0.011
	72	0.34	0.011	0.42	0.012
	168	0.42	0.009	0.43	0.010
Cyclohexane	24	0.09	0.005	0.10	0.006
	72	0.14	0.006	0.15	0.007
	168	0.15	0.008	0.15	0.006
37%HCl	24	2.54	0.009	3.60	0.009
	72	3.35	0.010	5.60	0.010
	168	5.06	0.010	5.60	0.010
45%NaOH	24	-0.13	0.008	-0.10	0.009
	72	6.59	0.010	0.99	0.010
	168	8.52	0.010	1.30	0.010

^a a weight change (%) = $100 * (W - W_0) / W_0$, where W is the weight of the swollen sample after immersed and W_0 is the initial weight of sample. ^b Each sample has three parallel specimens. The weight were taken from the average of three parallel specimens. ^c Standard deviation was calculated by origin software.

carborane structure can effectively improve the carbon residue rate of liquid fluoroelastomer. The tensile strength, elongation and shore A hardness of the cured product were 10.59 MPa, 80% and 55%, respectively. The tensile strength of carborane modified liquid fluorine increased by 463% compared with that before modification, but the elongation at break was reduced by 42%, which was mainly due to the introduction of rigid structure of carborane. The results show that the introduction of carborane structure can effectively improve the

mechanical properties of liquid fluororubber. At the same time, the solvent resistance test results show that the introduction of carborane structure has little effect on the aviation kerosene resistance and organic solvent resistance of fluororubber, but it can improve its alkali resistance. All these interesting results will provide the new prospects for the design of new fluoropolymers.

Acknowledgments

The authors thank the Natural Science Foundation of Jiangsu Higher Education Institutions of China (No.18KJB430027), the special fund of Beijing Key Laboratory of Clean Fuels and Efficient Catalytic Emission Reduction Technology.

Disclosure of potential conflicts of interest

No potential conflict of interest was reported by the author(s).

Funding

This work was supported by the Natural Science Foundation of Jiangsu Higher Education Institutions of China [18KJB430027].

ORCID

Juan Li  <http://orcid.org/0000-0002-0146-4566>

References

- [1] Drobny JG. Technology of fluoropolymers. London: CRC Press; 2001. (Chapter 3).
- [2] Ameduri B, Boutevin B. Well-Architected fluoropolymers: synthesis, properties and applications. Amsterdam: Elsevier; 2004. (Chapter 7).
- [3] Ameduri B, Boutevin B, Kostov G. Fluoroelastomers: Synthesis, properties and applications. Prog Polym Sci. 2001;26(1):105–187.
- [4] Klingender RC. Handbook of specialty elastomers. New York: CRC Press; 2008. (Chapter 4).
- [5] Albert LM. Fluoroelastomers handbook - the definitive user's guide and databook. Norwich, NY: William Andrew Publishing; 2006.
- [6] Ameduri B, Boutevin B. Well-Architected fluoropolymers: synthesis, properties and applications. Amsterdam: Elsevier; 2004.
- [7] Hougham G, Davidson T, Cassidy P, et al. Fluoropolymers. New York: Kluwert; 1999.
- [8] Klingender RC. Handbook of specialty elastomers. LLC: Taylor & Francis Group; 2008.
- [9] Dunks GB, Hawthorne MF. Nonicosahedral carboranes. synthesis and reactions. Acc Chem Res. 1973;6(4):124–131.
- [10] Nunez R, Gonzalez-Campo A, Vinas C, et al. Boron-functionalized carbosilanes: insertion of carborane clusters into peripheral silicon atoms of carbosilane compounds. Organometallics. 2005;24(26):6351–6357.

- [11] Hidefumi H, Toshihiko K. Carborane superclusters formed by ion–molecule reactions in an ion trap. *J Mol Struct.* **2005**;735:367–374.
- [12] Bregadze VI. Dicarba-closo-dodecaboranes $C_2B_{10}H_{12}$ and their derivatives. *Chem Rev.* **1992**;92(2):209–223.
- [13] Salinger RM, Frye CL. Facile polyhedral rearrangement of icosahedral silylcarboranes. *Inorg Chem.* **1965**;4(15):1815–1816.
- [14] Schroeder H, Heying TL, Reiner JR. A new series of organoboranes. II. The chlorination of 1,2-dicarbocloso-dodecaborane(12). *Inorg Chem.* **1963**;2(6) 1093–1096.
- [15] Hoffmann R, Lipscomb WN. In tramolecular isomerization and transformations in carboranes and substituted polyhedral molecules. *Inorg Chem.* **1963**;2(1):231–232.
- [16] Grafstein D, Dvorak J. Neocarboranes, a new family of stable organoboranes isomeric with the carboranes. *Inorg Chem.* **1963**;2(6):1128–1133.
- [17] Li J, Lu Y, Liu Y, et al. Synthesis, characterization, curing and properties of carboxyl-terminated liquid fluoropolymers. *Polym-Plast Technol.* **2013**;53(1):46–53.
- [18] Li J, Lu Y, You W, et al. Synthesis, characterization and cure properties of curable liquid fluoroelastomer with siloxy end group. *Acta polym Sin..* **2013**; (11):1430–1437.
- [19] Valliant JF, Guenther KJ, King AS, et al. The medicinal chemistry of carboranes. *Chem Rev.* **2002**;232:173–230.
- [20] Zhao J, Qing N, Jiang SH, et al. Research on the preparation of heat resistant epoxy resin cured by O-carborane-based diamine. *High Perform Polym.* **2017**;30(9):1094–1100.
- [21] Cui M, Zhang L, Lou PP, et al. Study on thermal degradation mechanism of heat-resistant epoxy resin modified with carboranes. *Polym Degrad Stabil..* **2020**;176: 109143.
- [22] Lv T, Fei WC. Bond order analysis based on the Laplacian of electron density in fuzzy overlap space, *J. Phys Chem.* **2013**;117:3100–3108.
- [23] Wu YN, Chen G, Gao LF, Zhang W and Li S. Carborane-containing bismaleimide resins with excellent heat resistance and dimensional stability. *High Perform Polym.* **2021**;33(2):176–183.