

Synthesis, curing of hydroxyl-terminated liquid fluoroelastomer: thermal, chemical resistant and mechanical properties

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Abstract. A novel hydroxyl-terminated liquid fluoroelastomer (HTLF) was synthesized; FT-IR, GPC and ¹H-NMR result show that HTLF was synthesized successfully. Then HTLF was cured with HDI trimer, the structure of cured product was characterized by FT-IR. Compared with traditional solid fluorine elastomer, Cured HTLF has higher char yield and faster thermal decomposition rate. It ascribed to the introduction of ring structure the cross-link structure formed in the curing process. The study of chemical resistant properties and tensile strength of cured fluoroelastomer film suggested that Cured HTLF was provided with similar mechanical properties, chemical resistant property than solid fluorine elastomer.

1. Introduction

Liquid fluoroelastomers (LFs) are a class of polymer material with some special functions, such as curable, chemical resistance, low surface energy, thermostability, easy processing and molding, good mobility and so on; they are widely used in the field of special coating, adhesive, sealant, and medicine industry. Since the early 1960s, Dupont and 3M Company successfully developed the LFs on a large scale [1-4], greatly improve its application in industry. According to the present research, fluoroelastomer synthesis via fluorinated monomers including glycol[5] polyether glycol [6-9] side group [10] and end-capper [11]. Nowadays, liquid fluoroelastomer has not only been used as a processing aid, but also be used as raw materials of coating, sealant, and adhesive. However, compared with traditional solid fluorine elastomer, mechanical properties and thermal resistance of LFs are poor. So far, there are none of LFs and their cured products are provided with similar mechanical properties and thermal resistance with solid fluorine elastomer [12-17].

In this work, a novel hydroxyl-terminated liquid fluoroelastomer (HTLF) which is a liquid fluoropolymer with reactive end group was prepared. What is more, HTLF can be cured with the polyisocyanate. Compared with traditional solid fluorine elastomer, it was provided with similar mechanical properties, chemical resistant property and more excellent thermal resistance. According to the present research, this kind of LFs has not been reported now.



The structure of HTLF was characterized and the cure reaction and properties of HTLF with HDI trimer were studied. The study of chemical resistant property, tensile strength and TGA of cured fluoroelastomer film(Cured HTLF) indicate that above properties of the product is still excellent compared with traditional solid fluorine elastomer. What is more, Cured HTLF has better machinability than traditional solid fluorine elastomer. This novel liquid fluoroelastomer is suitable for sealing the fuel tanks of aircraft and coating the external surfaces of building owing to overcoming the practical limitations in size and shape of high molecular weight fluoroelastomer which is mostly formed by compression molding.

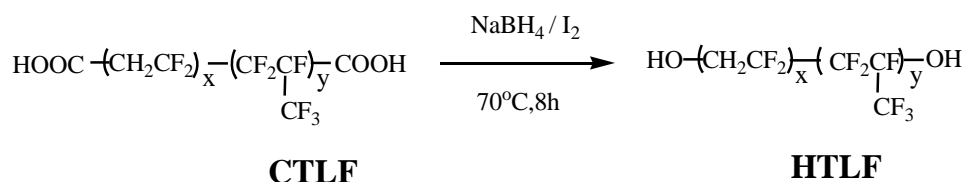
2. Experimental

2.1. Materials and chemical agents

Carboxyl-terminated liquid fluoroelastomer(CTLF) were synthesised by our laboratory[18]. Iodium borohydride (NaBH_4), iodine(I_2), dibutyltin dilaurate, anhydrous sodium sulfite (Na_2SO_3), hydrochloric acid (HCl), sulfuric acid (H_2SO_4), tetrahydrofuran(THF), acetone were commercially obtained. HDI (HT-100, the mass percent of isocyanate= 21.8 ± 0.3) was purchased from YANTAI WANHUA POLYURETHANE CO., LTD.

2.2. The synthesis of hydroxyl-terminated liquid fluoroelastomer(HTLF)

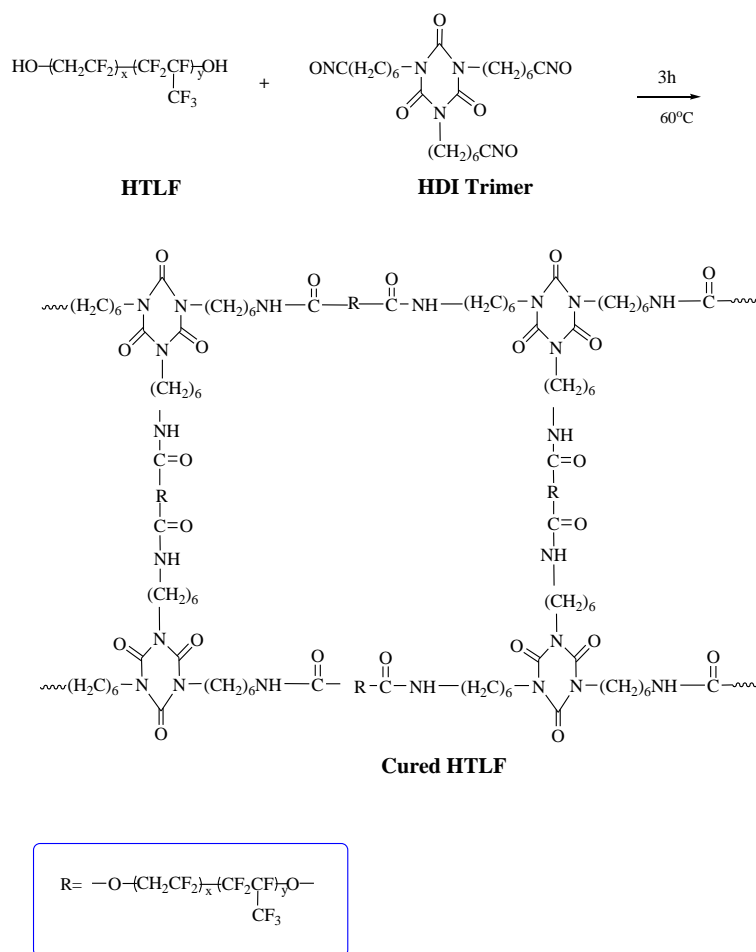
HTLF was prepared *via* reduction reaction of CTLF. A typical preparation method is as follow. To a stirred solution of NaBH_4 (10 mmol) in dry THF(20 mL) a solution of iodine (5 mmol) in dry THF(10 mL) was added dropwise under argon at 0°C over 45 min. Next, carboxyl-terminated liquid fluoroelastomer s (10g, 3.85mmol carboxyl group) in dry THF (100mL) was added and then the temperature was raised to 70°C , the reduction reaction was allowed to proceed for 8h. The mixture was then cooled to 0°C and the excess hydride was carefully destroyed by dropwise addition of 2mol/L hydrochloric acid (10 mL). Filtered the mixture, separating, Then the product was added deionized water. The resultant product was concentrated by a rotary evaporator. A viscous yellow liquid was obtained. (Yield is 91%)



Scheme 1. The synthesis route of hydroxyl terminated liquid fluorine elastomer (b).

2.3. Curing of hydroxyl-terminated liquid fluoroelastomers

HTLF (5 g) was mixed thoroughly with 0.5 g HDI trimer. The mixture was shaped in mold and cured at 60°C for 3h .



Scheme 2. Cure mechanism of hydroxyl-terminated liquid fluoroelastomer (**b**) with HDI Trimer.

3. Results and discussion

3.1. Characterization of hydroxyl-terminated liquid fluoroelastomers(**HTLF**)

3.1.1. FT-IT. FT-IR spectra of HTLF and CTLF are shown in Figure1. These two compounds exhibit 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 they have the same backbone structure. The new peak at 3500 cm^{-1} in the spectrum of HTLF is ascribed to the stretching vibration of hydroxyl groups, indicating the formation of $-\text{CH}_2\text{OH}$. While, IR spectra at 1730 cm^{-1} which characteristic of the carbonyl group disappeared, showing that the reduction of the carboxylic end groups was complete. However, after this quantitative reduction evidenced by means of IR spectroscopy, it appears that the amount of $\text{CH}=\text{CF}$ was higher.

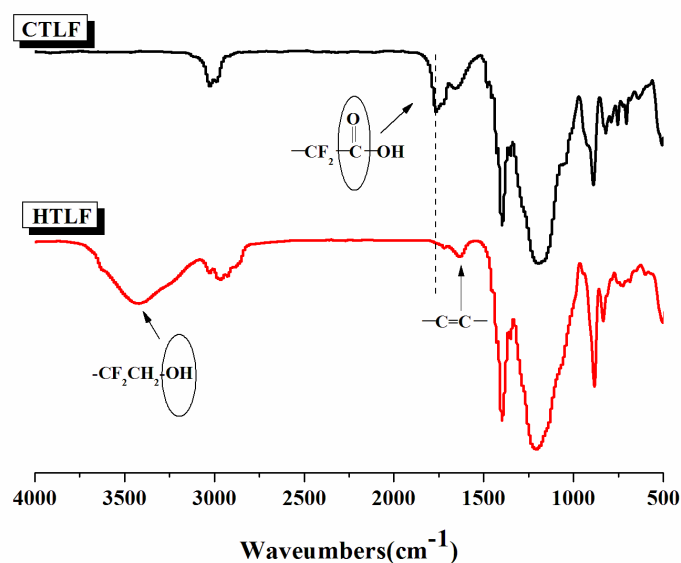


Figure 1. FT-IR spectra of hydroxyl terminated liquid fluoroelastomer (**HTLF**) and its precursor carboxyl terminated fluoroelastomer (**CTLF**).

3.2. $^1\text{H-NMR}$

To further characterize the liquid fluoroelastomers, NMR spectroscopy was utilized. $^1\text{H-NMR}$ spectra of hydroxyl terminated liquid fluoroelastomer (**HTLF**) and its precursor carboxyl terminated liquid fluoroelastomer (**CTLF**) are shown in Figure 2. Compared with the precursor, the fluoroelastomer exhibits two new peaks, chemical shift of 1.6 ppm ascribed to the hydroxyl groups and 1.6 ppm ascribed to the $-\text{CH}_2$ group, they confirm the formation of hydroxyl-terminated liquid fluoroelastomer.

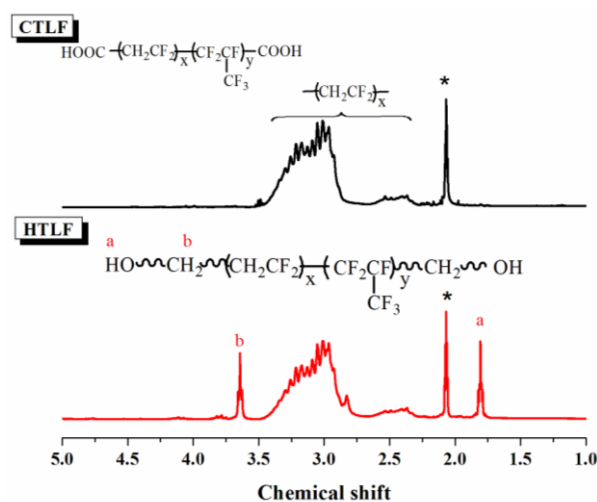


Figure 2 $^1\text{H-NMR}$ spectra of hydroxyl terminated liquid fluoroelastomer (**HTLF**) and its precursor carboxyl terminated liquid fluoroelastomer (**CTLF**) in acetone- d_6 . The solvent peaks are marked with asterisks.

3.3. Characterization of Cured HTLF

3.3.1. FT-IR. FTIR spectra of the cured fluoroelastomer are given in Figure 3. The spectra of their precursor, HDI trimer is also given in the figure for comparison. Compared with the spectra of b, the cured fluoroelastomer exhibits absorption peaks at 1396, 1204, and 886 cm^{-1} ascribed to stretching vibration of $-\text{FCH}-$, $-\text{CF}_2-$, and $-\text{CF}_3$, respectively. Like its precursor, the cured fluoroelastomer exhibits new peaks at 765 cm^{-1} , 1433 cm^{-1} , 1466 cm^{-1} , 1532 cm^{-1} , assigned to benzene ring of HDI trimer. The peak at 1689 cm^{-1} in the spectrum of the cured fluoroelastomer is ascribed to the stretching vibration of carbonyl. Furthermore, the cured fluoroelastomer exhibits a new peak at 3372 cm^{-1} , which confirms the formation of $-\text{NH}-$. The result of FTIR spectra also shows that the liquid fluoroelastomer s can be cured by HDI trimer.

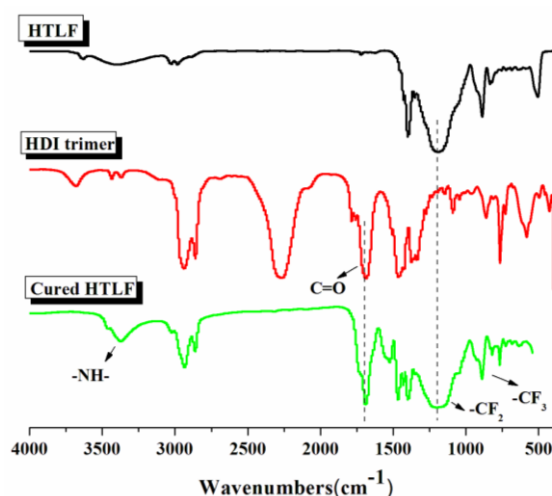


Figure 3. FT-IR spectra of hydroxyl terminated liquid fluoroelastomer (**HTLF**), HDI trimer and the **Cured HTLF**.

3.4. Thermal property of the cured fluoroelastomer(**Cured HTLF**)

TGA analysis of hydroxyl terminated liquid fluoroelastomer (**HTLF**) and **Cured HTLF** were shown in Figure 4, solid fluoroelastomer (Poly(VDF-HFP)) is given for comparison. In order to evaluate the thermal decomposition rate, T_5 is defined as the temperature at which the polymers lose 5% of their original weight. It is shown that T_5 of **Cured HTLF**, **HTLF** and Poly(VDF-HFP) is 335°C, 240°C and 223°C respectively. Obviously, after cured, the thermal decomposition rate of hydroxyl terminated liquid fluoroelastomer is slower than solid fluoroelastomer. Besides, the char yield of (Poly(VDF-HFP)) at 750°C is 11%, while the char yield of **Cured HTLF** remains at 29%. Based on the study of the thermal degradation rate and the char yield of these two kinds of fluorine elastomers, it is found that the cured product based on hydroxyl terminated liquid fluoroelastomer has better thermal resistance than the solid fluorine elastomer. The result is ascribed to the introduction of ring structure (HDI Trimer) improve the thermal resistance of the cured product, what is more, cross-link structure formed in the curing process, it make the thermal decomposition rate of liquid fluoroelastomer further reduced.

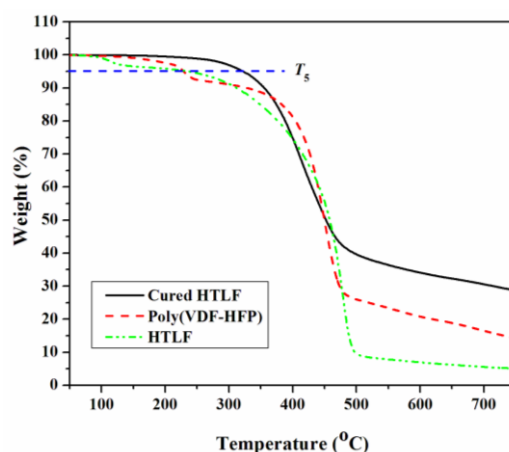


Figure 4. TGA curve of hydroxyl terminated liquid fluoroelastomer (HTLF, green dashed line), Cured HTLF (black solid line) and solid fluoroelastomer (Poly(VDF-HFP), red dashed line) under N_2 ($10^\circ C/min$).

3.5. Chemical resistant properties of cured fluoroelastomer film(Cured HTLF)

In order to verify the chemical stability of cured fluoroelastomer in different media, we made the cured fluoroelastomer film immerse in 37% HCl, 45% NaOH, jet aircraft oil and cyclohexane for 7 days respectively. The common solid fluoroelastomer poly(VDF-HFP) is for comparison. To evaluate the chemical stability behavior of polymers, “change in mass” was be used. Change in mass was calculated as follows:

$$\text{Change in mass (\%)} = [(M_2 - M_1) / M_1] \times 100\%$$

The result is shown in Figure 5, and Table1 is detail. It clear that the cured liquid fluoroelastomer exhibits almost the same chemical resistance as poly(VDF-HFP). No matter in the organic solvent or in the acid-base reagent, the change in mass of Cured HTLF has no more than 5%, it suggested that the chemical resistance of the product cured by liquid fluorine elastomer is still excellent. This attributes to low surface energy of “C-F” group in main chain and side chain. Property of “surface enrichment” make the fluorine content in the surface of the material is enriched, so little fluorine could make fluoropolymer has good hydrophobicity and lipophobicity. It unrelated to product structure.

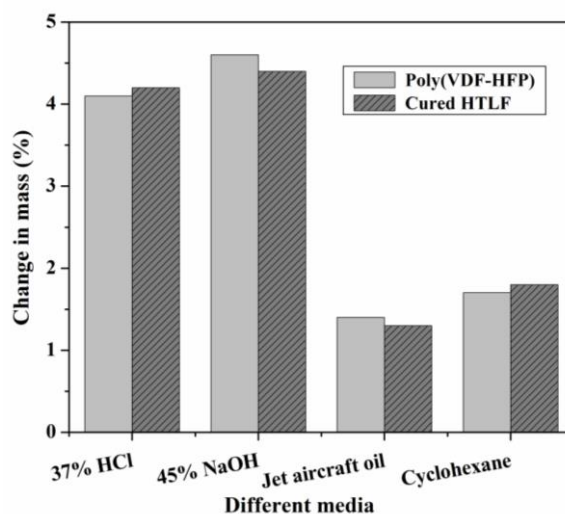


Figure 5. Change in mass(%)of solid fluoroelastomer (Poly(VDF-HFP) and Cured liquid fluoroelastomer (Cured HTLF).

Table 1. Change in mass(%) of Poly(VDF-HFP) and Cured HTLF.

Media solvent	Weight change (%)	
	Poly(VDF-HFP)	Cured HTLF
37% HCl	4.1	4.2
45% NaOH	4.6	4.4
Jet aircraft oil	1.4	1.3
Cyclohexane	1.7	1.8

3.6. Mechanical properties of cured fluoroelastomer film(Cured HTLF)

In order to verify the mechanical properties of cured fluoroelastomer, we research the tensile strength and elongation at break of Cured HTLF, traditional solid fluorine elastomer it was shown in shown in Table2. While, the date of common solid fluorine elastomer (poly(VDF-HFP)) for compare. Five measurements were made and the data were averaged. It is shown that Cured HTLF has the similar tensile strength and elongation at break with Poly(VDF-HFP), attribute to bond energy of “C=O” is 733kJ/mol and “C=N” is 533kJ/mol, although the precursor of Cured HTLF is liquid, the high bond energy of cross-linked structure make Cured HTLF have excellent mechanical property compared with solid fluorine elastomer.

Table 2. Change in mass(%) of Poly(VDF-HFP) and Cured HTLF.

	Poly(VDF-HFP)	Cured HTLF
Tensile strength (MPa) ^a	20	21
Elongation at break (%) ^a	352	349

^a Five measurements were made and the data were averaged.

4. Conclusion

In summary, a novel hydroxyl-terminated liquid fluoroelastomer (HTLF) was synthesized and cured with HDI trimer. The structure of product was characterized by FT-IR and ¹H-NMR. Through the study of the product, Cured HTLF show similar chemical resistant and mechanical property with traditional solid fluorine elastomer. It is attributing to “surface enrichment” and high bond energy of cross-linked structure. Amazingly, Cured HTLF shows more excellent thermal resistant than traditional solid fluorine elastomer. It is ascribed to the introduction of ring structure (HDI Trimer) improve the thermal resistance of the cured product, what is more, cross-link structure formed in the curing process, it make the thermal decomposition rate of liquid fluoroelastomer further reduced. This kind of LFs has not been reported now. This novel liquid fluoroelastomer is suitable for sealing the fuel tanks of aircraft and coating the external surfaces of building owing to overcoming the practical limitations in size and shape of high molecular weight fluoroelastomer which is mostly formed by compression molding.

Acknowledgments

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