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A novel vulcanization of fluoroelastomer by fluorination is studied, simultaneously accompanied fluorine content increase, and tribological property is improved.
A novel vulcanization method for crude fluoroelastomer by direct fluorination with fluorine/nitrogen gas has been investigated. The results show that the vulcanization reaction of fluoroelastomer is closely related with fluorination temperature, fluorination time and fluorine gas partial pressure. The maximum crosslink degree can be up to 97%, and the fluorine content of fluoroelastomer increased from 48.2% to 60% during the fluorination. The static friction coefficient of fluoroelastomer is decreased from 0.91 to 0.55, about 39.6% reduction after fluorination. The ATR-FTIR spectra indicate the crosslink reaction process of fluoroelastomer by direct fluorination arises three reaction stages and successively goes through four elementary reactions: substitution reaction; elimination reaction; addition reaction; crosslink reaction. The increase of fluorine content mainly takes place in the first stage, and the crosslink reaction mainly takes place in the second stage and third stage.

1. Introduction

Fluoroelastomers gain increasing concern in view of their excellent thermo stability, oil resistance, mechanical property, anti-radiation performance and abrasive resistance. Most of these properties are linked to the low polarizability and the strong electronegativity of the fluorine atom, to its small van der Waals radius (0.64 Å), and to the strong C-F bond (485 kJ·mol⁻¹). Therefore, fluoroelastomers have extensive application in industry, including engine oil seals, fuel system components like hoses and O-rings, and drive train seals.

Fluoroelastomers, like all other thermosetting elastomers, need useful and practical chemical crosslink system. The traditional vulcanization methods of fluoroelastomer mainly include ionic vulcanization and free radical vulcanization. During ionic vulcanization process, HF is eliminated from -CH=CF₂ structure to form -CH=CF₂ structure. Sequentially, the nucleophilic addition of a crosslinker to the -CH=CF₂ double bond proceeds, yielding crosslinks. However, the fluorine content of fluoroelastomer may decreases after ionic vulcanization. Free radical vulcanization (peroxide curing, such as a,a′-bis(t-butylperoxy)disopropyl benzene and triallylisocyanurate) is a way to use free radicals to attack polymer chains to form polymeric free radicals. The polymeric radicals form crosslink networks directly or via the intermediary of radical traps. In addition, the fluorine content of fluoroelastomer still remains unchanged after free radical vulcanization.

Direct fluorination with fluorine gas has been rapidly developed in recent years. Direct fluorination reaction is usually heterogeneous, exothermic and spontaneous, owing to the high reactivity of fluorine and the formation of fluorine free radical (F·) in the process. The F· can react with methylene (-CH₂-) of polymer chain to form alkyl free radical (-CH–). The –CH– is reportedly able to form crosslink networks, according to previous study of polyethylene fluorination.

Therefore, it is expected that the F· can also be used as a new vulcanizing agent to vulcanize fluoroelastomer, and the fluorine content of fluoroelastomer increases simultaneously because the hydrogen atoms of -CH₂- can be substituted by fluorine atom during the direct fluorination. Sequentially, the properties of fluoroelastomer, such as abrasive-resistance and solvent-resistance, can be improved effectively. Due to the strong penetration ability of fluorine gas in rubber, not only the surface of fluoroelastomer is vulcanized but also the bulk of fluoroelastomer with sufficient thickness can be vulcanized. The analysis above inspired us to explore the possibility of fluoroelastomer vulcanized by fluorination with fluorine/nitrogen gas and simultaneously preparation fluoroelastomer with ultrahigh fluorine content.

In this study, the investigation on fluoroelastomer vulcanized by direct fluorination with fluorine/nitrogen gas was first reported. The fluorinated fluoroelastomer films have formed chemical crosslink networks. The fluoroelastomer shows different solubility and mechanical properties before and after fluorination. Meanwhile, the direct fluorination can also increase the fluorine content and decrease the static friction coefficient with no damage to the elastic property of fluoroelastomer film. The reaction kinetics and mechanism of crosslink reaction by direct fluorination have been studied systematically.

2. Experimental

2.1 Film fabrication

The crude fluoroelastomer (F26, terpolymer of vinylidene fluoride and hexafluoropropylene copolymer) is supplied by...
Zhonghao Chenguang Research of Chemical Industry. 5 g crude fluoroelastomer was dissolved in 25 mL acetone, and the solution was cast on glass. Then the films were dried at 140 °C for 6 h to remove acetone completely. The thickness of film was controlled at about 40-50 μm.

2.2 Direct fluorination

Direct fluorination was carried out in closed stainless steel vessel. The air in the closed vessel was removed and replaced by nitrogen gas (N\textsubscript{2} > 99.99%) for three cycles to remove residual oxygen and moisture in the chamber and on the polymer films. Then the crude fluoroelastomer films were preheated in the closed vessel for 10 min at specific temperature (e.g. 15 °C, 30 °C, 40 °C). After preheating, the vessel was replenished with a specific pressure of the F\textsubscript{2}/N\textsubscript{2} (10 vol% for F\textsubscript{2}) mixed gas (e.g. 6 kPa, 10 kPa, 20 kPa) to fluorinating. The direct fluorination of fluoroelastomer films was performed at different fluorination temperatures, fluorination times and fluorine gas partial pressures to investigate the influence of these factors on the crosslink reaction of fluoroelastomer.

2.3 Crosslink degree test

The crosslink degree of fluoroelastomer film (mass M\textsubscript{1}) was dissolved in acetone for 10 min. The insoluble part was separated from acetone, dried at 100 °C for 10 min and weighted (mass M\textsubscript{2}). Crosslink degree was calculated according to the following equation:

\[ \text{Crosslink degree} = \frac{M_2}{M_1} \times 100\% \]  

(1)

2.4 Fluorine content tests

The bulk fluorine content of the crude and fluorinated fluoroelastomer films were tested by oxygen flask combustion (OFC) method, which is referred to the previous literatures.\textsuperscript{12-13} Additionally, the fluorine content of crude and fluorinated fluoroelastomer film’s surface were measured by energy dispersive X-Ray spectroscopy (EDX, FEI company, USA).

2.5 Characterization

The surface morphology of the crude and fluorinated fluoroelastomer film was measured by scanning electron microscope (SEM). SEM was operated with FEI Inspect F (FEI company, EU/USA) at 20 kV and the magnification was set at 10,000×.

The tensile mechanical properties of the fluoroelastomer were measured by an Instron Model 5567 twin column table mounted testing system at ambient conditions with a gauge length of 40 mm and a crosshead speed of 50 mm/min. Glass transition temperature (Tg) was characterized by differential scanning calorimetry (DSC), performed on Netzsch 204 DSC with a heating rate of 5 °C/min in flowing nitrogen. The static friction coefficient of crude and fluorinated fluoroelastomer was obtained through the ratio of the maximum static friction force to the vertical gravity force.

The chemical composition and structure of fluorinated fluoroelastomer film were characterized by attenuated total reflectance Fourier transform infrared (ATR-FTIR). ATR-FTIR spectra of fluoroelastomer films were recorded on a Nicolet Magna 650 spectroscope in the range from 4000 to 400 cm\textsuperscript{-1}.

3. Results and discussion

3.1 Crosslink degree of fluorinated fluoroelastomer film

![Fig.1 The crosslink degree as a function of fluorination temperature (°C), the fluorine gas (F\textsubscript{2}/N\textsubscript{2} mixed gas, 10 vol% for F\textsubscript{2}) partial pressure was 30 kPa and the fluorination time was 60 min.](image)

It is known that fluorination is a free radical reaction. During the polyethylene fluorination process, -CH\textsubscript{2}- structure can react with fluorine atom to develop the -CHF- structure or generate -CH= and -F. The polymeric radicals of different polymer chains can be coupled to develop chemical crosslink networks.\textsuperscript{10} The crude F26 fluoroelastomer contains -CH\textsubscript{2}- structure in its macromolecular backbone that provides the possibility of crosslink reaction. The crude fluoroelastomer can be well dissolved in acetone solvent. However, the solubility of fluoroelastomer film becomes poor in acetone after fluorination, indicating that fluorinated film has developed crosslink networks during the process of direct fluorination. The crosslink degree was characterized by the solubility of fluoroelastomer in acetone after fluorination. The influences of three significant fluorination factors (fluorination temperature, fluorination time, fluorine gas partial pressure) on the crosslink degree of fluoroelastomer film were investigated.

The crosslink degree of fluoroelastomer films fluorinated at different temperature was measured in Fig.1. The fluorine gas (F\textsubscript{2}/N\textsubscript{2} mixed gas, 10 vol% for F\textsubscript{2}) partial pressure in the fluorination ambience was 30 kPa, and the fluorination time was 60 min. Fluoroelastomer films fluorinated at relative low fluorination temperature (15 °C, 30 °C) have a low crosslink degree. The crosslink degree increased along with fluorination temperature increases. When the reaction took place at 30-60 °C, the crosslink degree of fluorinated films increased rapidly. The maximum value of crosslink degree can reach 97%, when the fluoroelastomer film is fluorinated at 90 °C. At 100-140 °C fluorination, the crosslink degree declines gradually due to the degradation of fluorinated fluoroelastomer film possibly. Chain degradation reaction caused by fluorine radicals rather than crosslink reaction is possibly the dominant reaction at 100-140 °C fluorination.

The influence of fluorination time and fluorine gas partial pressure on the crosslink degree of fluorinated films were investigated as well. As shown in Fig.2 (a), at low fluorination
temperature (15 °C), the fluoroelastomer film had the relatively low crosslink degree. At high fluorination temperature (50 °C, 100 °C), there is a linear relationship between crosslink degree and fluorination time after 10 min fluorination. When the fluoroelastomer film was fluorinated at 100 °C for 10 min with different fluorine gas partial pressure, there is also a linear relationship between crosslink degree and fluorine gas partial pressure as shown in the Fig. 2 (b). Fluorinated with 50 kPa F<sub>2</sub>/N<sub>2</sub> mixed gas (10 vol% for F<sub>2</sub>) for only 10 min, the fluoroelastomer film got the highest crosslink degree (96%). However, when fluorinated with 30 kPa F<sub>2</sub>/N<sub>2</sub> mixed gas (10 vol% for F<sub>2</sub>) for a long time (60 min), the fluoroelastomer film can get the same crosslink degree (97%). The increase of F<sub>2</sub> partial pressure can substantially shorten the fluorination time, when the fluorinated films achieve the identical crosslink degree.

It can be concluded that the fluorination temperature is the most important influence factor of the crosslink reaction, which not only affects the crosslink degree but also possibly causes the chain degradation reaction. The fluorine gas partial pressure can be regarded as the second important influence factor which shortens the fluorination time.

![Fig.2 The crosslink degree as a function of (a) fluorination time (min), the fluorine gas (F<sub>2</sub>/N<sub>2</sub> mixed gas, 10 vol% for F<sub>2</sub>) partial pressure was 30kPa and the fluorination temperature was 15 °C, 50 °C, 100 °C; and (b) F<sub>2</sub> partial pressure (kPa), the fluorination temperature was 100 °C and the fluorination time was 10min](image)

### Table.1 the fluorine content tested by EDX and OFC method

<table>
<thead>
<tr>
<th>Method and Samples</th>
<th>F (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDX Crude film</td>
<td>58.7</td>
</tr>
<tr>
<td>Fluorinated film</td>
<td>70.5</td>
</tr>
<tr>
<td>OFC Crude film</td>
<td>57.9</td>
</tr>
<tr>
<td>Fluorinated film</td>
<td>67.7</td>
</tr>
</tbody>
</table>

The fluorine content of the fluorineelastomer was tested before and after direction fluorination by energy dispersive X-Ray spectroscopy (EDX) and oxygen flask combustion (OFC) method. The fluorine contents of crude film and fluorinated film are listed in Table.1 as weight percent (wt%). It is known that the fluorine content of rubber film’s surface is tested by EDX and that of the bulk film is tested by OFC method. As shown in Table.1, after the fluorination, the fluorine contents of the film surface and the bulk film increase to 70.5 wt% and 67.7 wt%, respectively, which have no significant difference between each other. Therefore, it can be concluded that the bulk of fluoroelastomer film was fluorinated rather than the surface, when it was reacted at 90 °C with 30 kPa F<sub>2</sub>/N<sub>2</sub> mixed gas (10 vol% for F<sub>2</sub>) for 60 min. Therefore, fluorination with fluorine gas has strong penetration ability in rubber, unlike in plastic (PE, PP) and fiber (aramid fiber). The whole fluoroelastomer film (40-50μm) can be fluorinated with fluorine gas, and fluorinated layer in rubber is much thicker than it is in PE (0.5μm). In this respect, the fluorination with fluorine gas is an effective vulcanization method for fluoroelastomer with significant increase in its fluorine content.

<table>
<thead>
<tr>
<th>C (wt%)</th>
<th>untreated</th>
<th>30°C</th>
<th>40°C</th>
<th>60°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>F (wt%)</td>
<td>58.7</td>
<td>70.7</td>
<td>72.1</td>
<td>70.1</td>
</tr>
</tbody>
</table>

Meanwhile, the fluorine content of the fluorinated film’s surface at different temperature fluorination was tested by EDX shown in Table.2 as weight percent (wt%). The fluorine content of the fluorinated film’s surface increased from 58.7 wt% to 70.7 wt% after 30 °C fluorination. And the fluorine contents kept about 70wt% with the fluorination temperature increased from 40 °C to 90 °C. However, the crosslink degree was elevated obviously with increase of the fluorination temperature as shown in Fig.1. In general, the crosslink degree and the fluorine content are both increased in 30 °C fluorination. The crosslink degree increased, but the fluorine content remained unchanged in 40 °C-90 °C fluorination. Therefore, further research is required to investigate the mechanism of the observed phenomenon.

### 3.3 The kinetics and mechanism of crosslink reaction by direct fluorination

As we know, direct fluorination with fluorine gas is a solid-gas reaction actually, which is described as a multi-stage, multi-reaction untreated shrinking core model. The untreated shrinking core model is accepted as the best simple model for the majority of reacting solid-gas systems presented by Ishida at 1971. The model successfully represents the fluorination of...
uranium dioxide where uranium hexafluoride gas is produced through uranyl fluoride as a solid intermediate.\textsuperscript{17} The solid-gas reaction is controlled by two main parameters: the non-dimensional diffusion rates of reactant gas and the reaction rates. When reacting for 60 min, the bulk of fluorinated film was fluorinated completely, which were testified by the results of EDX and OFC method shown in 3.2. Therefore, we can ignore the influence of the reactant gas diffusion in fluorostomer film. Only considering the reaction rates, we calculated the kinetics parameters of the fluorination with fluorine gas through the curve of crosslink degree and fluorination temperature.

So the equation of fluorination reaction rate can be displayed by the Arrhenius equation\textsuperscript{16}:\textsuperscript{17}

\[ F(\alpha) = A e^{-\frac{E_a}{R_\text{T}}} t = k t \]  

Where \( \alpha \) is solid conversion percent (we can regard crosslink degree as \( \alpha \)), \( t \) is fluorination time, \( A \) is pre-exponential factor, \( E_a \) is apparent activation energy, \( R \) is gas constant, \( k \) is reaction speed constant, \( F(\alpha) \) is integral equation of solid conversion percent. When solid-gas reaction is controlled by chemical reaction as far as flaky material, \( F(\alpha) \) is equal to \( a \) in the untreated shrinking core model.\textsuperscript{19,20} Then the Arrhenius equation can be written as:

\[ \ln F(\alpha) = \ln a = \ln A t - \frac{E_a}{R} \cdot \frac{1}{T} \]  

Thus, there is a linear relationship with \( \ln \alpha \) and \( 1/T \). The slope indicates apparent activation energy \( (E_a) \) and the intercept represents pre-exponential factor \( (A) \). The \( \alpha \), \( \ln \alpha \) and \( 1/T \) of different fluorination temperatures were listed in Table.3 and Fig.3.

![Fig.3 The relationship between \( \ln \alpha \) and \( 1/T \)](image)

There are three linear relationships with \( \ln \alpha \) and \( 1/T \) in Fig.3. Thus, the whole fluorination crosslink reaction can be divided into three stages. The apparent activation energy \( (E_a) \) and pre-exponential factor \( (A) \) of three stages are shown in Table.4.

### Table 4: \( E_a \) and \( A \) of different fluorination reaction stage

<table>
<thead>
<tr>
<th>Reaction stage</th>
<th>( E_a ) (kJ/mol)</th>
<th>( A ) (min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>stage I</td>
<td>7.4±1.5</td>
<td>0.05±0.003</td>
</tr>
<tr>
<td>stage II</td>
<td>70.1±3.4</td>
<td>2.5±0.06×10(^{3})</td>
</tr>
<tr>
<td>stage III</td>
<td>6.4±0.9</td>
<td>0.13±0.02</td>
</tr>
</tbody>
</table>

The fluorination crosslink reaction can be divided into three stages through the study of reaction kinetics. The structure changes in these three reaction stages were studied by ATR-FTIR spectroscopy. Referring to Fig.3, 30 °C fluorination was regarded as the end of stage I; 40 °C fluorination was regarded as the center of stage II; 60 °C fluorination was regarded as the start of Stage III; 90 °C fluorination was regarded as the end of stage III. Then ATR-FTIR spectroscopy of fluoroelastomer film fluorinated at 30 °C, 40 °C, 60 °C, 90 °C for 60 min is shown in Fig.4.

![Fig.4 ATR-FTIR spectra of the crude and fluorinated fluoroelastomer at different temperature](image)

As shown in Fig.4, in the crude fluoroelastomer film’s ATR-FTIR spectroscopy, 2920 cm\(^{-1}\), 2850 cm\(^{-1}\) peaks are attributed to -CH\(_2\) moieties.\textsuperscript{14,21} The -CH\(_2\) structure vanished completely in 30 °C fluorination. Additionally, the fluorine content increased substantially in 30 °C fluorination as shown in Table.2, which reveals that the hydrogen atom of -CH\(_2\) structure was substituted by fluorine atom. In the direct fluorination of polyethylene, the fluorine atom of -CH\(_2\) is substituted by fluorine atom at about 28 °C initially\textsuperscript{18} and the substitution reaction of fluorine atom occurs.

In 30 °C-60 °C fluorination, -C=C-(1650 cm\(^{-1}\))\textsuperscript{22} structure is present as shown in Fig.4. There is no 1650cm\(^{-1}\) peak in the spectroscopy of 30 °C fluorination. However, the -C=C-(1650cm\(^{-1}\)) structure is formed at 40 °C, 60 °C fluorination. The HF is eliminated from -CHF-CF\(_2\) structure to form -CF=CF- structure. 1283 cm\(^{-1}\), 1197 cm\(^{-1}\), 1137 cm\(^{-1}\), 1063 cm\(^{-1}\) peaks are attributed to C-F moieties.\textsuperscript{10,15,18} The area of 1063 cm\(^{-1}\) peak obviously decrease in 40 °C fluorination. It also indicates that there is a
reaction eliminating HF.

In 60 °C-90 °C fluorination, the -C=-(1650 cm⁻¹) structure still exists at 60 °C as shown in Fig.7. But at 90 °C fluorination (the crosslink degree peak at 97%), the -C=-(1650 cm⁻¹) structure disappeared completely. The -C= structure reacted with fluorine (F·) to form fluoric alkyl free radical (-CF-CF₂). And the fluoric alkyl free radical (-CF-CF₂) were coupled to develop highly crosslink network.

In Fig.4, the changes of fluoroelastomer structure respect to the fluorination temperature were observed. To explain the mechanism of crosslink reaction by fluorination, four elementary reactions (substitution reaction, elimination reaction, addition reaction, crosslink reaction) are presented in Scheme.1.

Elementary reaction I (substitution reaction):

\[ \text{-CF₂=CF₂} + \text{F·} \rightarrow \text{-CF₂=CFCF₂} \]

Elementary reaction II (elimination reaction):

\[ \text{-CF₂=CF₂} \rightarrow \text{CF·} + \text{CF₂} \]

Elementary reaction III (addition reaction):

\[ \text{CF·} + \text{-CF₂} \rightarrow \text{CFCF₂} \]

Elementary reaction IV (crosslink reaction):

\[ \text{CFCF₂} + \text{CF·} \rightarrow \text{CFCF₂CF·} \]

Scheme 1: the four elementary reactions of crosslink reaction by direct fluorination

The short time fluorinations (fluorinated for 1 min, 5 min, 10 min at 90 °C) were processed, in order to observe the elementary reaction. The ATR-FTIR spectra of short time fluorinated films are presented in Fig.5. At 90 °C fluorination, the -CH₂ structure was substituted by fluorine atom entirely and -C=C- structure was generated after only one minute reaction. In view of the fact that the crosslink degree increased with the fluorination time (Fig.2(a)), elementary reaction II (elimination reaction), elementary reaction III (addition reaction) and elementary reaction IV (crosslink reaction) are regarded as occurring concurrently at 90 °C. Meanwhile, one fluorine atom is eliminated in elementary reaction II and one fluorine atom would be added in elementary reaction III. So the fluorine content of fluorinated film is considered to increase after substitution reaction (elementary reaction I) and to remain unchanged after elimination reaction, addition reaction, crosslink reaction.

Referring to the above analysis of the elementary reactions, the fluorine content of fluorinated film is predicted to increase in stage I (only substitution reaction occurs) and remain unchanged in stage II and stage III (substitution reaction, elimination reaction, addition reaction, crosslink reaction entirely occur). The prediction is in accordance with the fluorine content result shown in Table.2. The changes of fluorine atom content also can prove the accuracy of elementary reaction theory.

Fig.5 ATR-FTIR spectra of short-fluorinated fluoroelastomer films at 90°C fluorination

3.4 Mechanical properties

Additionally, the increase of fluorine content can alter the solubility of polymers in solvent so that fluorinated film couldn’t be dissolved anymore. Therefore, the solubility changes of fluoroelastomer in acetone may be due to the increase of fluorine content rather than crosslinking. In this regard, the stress-strain curves of fluoroelastomer film before and after fluorination were tested. When the fluoroelastomer film was fluorinated at 90 °C with 30 kPa F₂/N₂ mixed gas (10 vol% for F₂) for 60 min, the crosslink degree can be up to the maximum. The mechanical property of the fluorinated film prepared under the above described condition was tested. The stress-strain curves of crude and fluorinated fluoroelastomer film are shown in Fig.6. The stress-strain curve of crude fluoroelastomer film implies that there...
is no crosslink network. The yield stress of crude fluoroelastomer film is only about 2.58 MPa at 120% strain. However, the stress-strain curve of fluorinated fluoroelastomer film behaves like a thermosetting elastic rubber. After the film was fluorinated at 90 °C for 60 min, the stress at 400% strain is about 4.37 MPa, indicating that there is crosslink network in fluorinated film. 23-24 Furthermore, as shown in Fig.1 and table.2, with the fluorination temperature increased from 40 °C to 90 °C, the crosslink degree increases sharply and the fluorine content keeps unchanged, also indicating that the solubility changes of fluoroelastomer in acetone are caused by the crosslink networks rather than the increase of fluorine content in fluorinated fluoroelastomer film.

3.5 Glass-transition temperature (Tg)

For elastomers, the direct fluorination with fluorine gas can decrease the friction coefficient and improve the wear life of elastomeric, such as ethylene-propylene, acrylonitrile-butadiene elastomers. 25 The static friction coefficient of fluorinated fluoroelastomer film prepared at different temperature were tested, and shown in Table.6. The static friction coefficient of fluorinated film decreases from 0.91 to 0.55 at low temperature fluorination (30 °C). The static friction coefficient of crosslinking fluoroelastomer by fluorination is much lower than that of crosslinking fluoroelastomer by other methods (generally the static friction coefficient >1.0). With the increase of fluorination temperature from 30 °C to 100 °C, the static friction coefficient of fluorinated fluoroelastomer film keeps about 0.55.

Table.6 the static friction coefficients of the crude and fluorinated fluoroelastomer film at different temperature

<table>
<thead>
<tr>
<th>Fluorination temperature</th>
<th>Crude film</th>
<th>30 °C</th>
<th>50 °C</th>
<th>70 °C</th>
<th>100 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Friction coefficient</td>
<td>0.91±0.1</td>
<td>0.55±0.1</td>
<td>0.59±0.1</td>
<td>0.55±0.1</td>
<td>0.52±0.1</td>
</tr>
</tbody>
</table>

4. Conclusions

The present study demonstrates that direct fluorination with F₂/N₂ mixed gas comprises a new and successful way to vulcanize fluoroelastomer. The fluoroelastomer vulcanized by direct fluorination achieves a great increase in the crosslink degree with no damage on its elastic properties while the fluorine content is significantly increased. Moreover, the static friction coefficient of fluorinated fluoroelastomer film was greatly decreased. The crosslink reaction of fluoroelastomer was controlled by fluorination temperature, fluorination time and fluorine gas partial pressure. The mechanism of crosslink reaction by fluorination has been elaborated. The mechanism of crosslink reaction by fluorination mainly successively goes through four elementary reactions. First, a hydrogen atom of -CH₂- is substituted by fluorine atom. Sequentially, HF is eliminated from polymer main chain and develop the -C≡C- structure. In the next step, F⁻ and -C≡C-structure take place addition reaction developing the fluoric alkyl free radicals. Finally, the fluoric alkyl free radicals couple completing crosslink. The increase of fluorine content mainly takes place in first stage, and the crosslink reaction mainly takes place in second stage and third stage.

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Notes and references

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.


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