

The reaction kinetics and mechanism of crude fluoroelastomer vulcanized by direct fluorination with fluorine/nitrogen gas

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Supporting Information

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Fig.2S ATR-FTIR spectra of short-fluorinated fluoroelastomer films in different temperature: 30°C fluorination (left); 60°C fluorination (right). Page S2.

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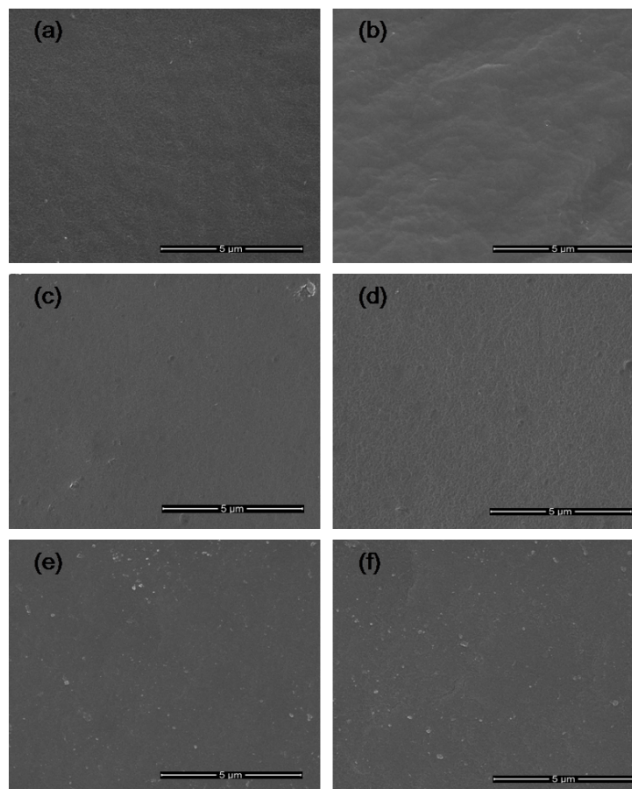


Fig. 1S Surface morphology of the crude fluoroelastomer film(a) and fluorinated fluoroelastomer film:(b)15°C fluorinated film,(c)30°C fluorinated film,(d)40°C fluorinated film,(e)60°C fluorinated film,(f)90°C fluorinated film.

It has been known excessive fluorination can cause an irreversible deformation or crack of polymer surfaces. However, no irreversible crack on the fluoroelastomer film surfaces occurred under different temperature fluorination in this research. The SEM images show no obvious changes on fluorinated fluoroelastomer films surface compared to crude fluoroelastomer film surface shown in Fig.1S. It can be concluded that direct fluorination can generate the crosslink networks in fluoroelastomer films without any damage on film surface.

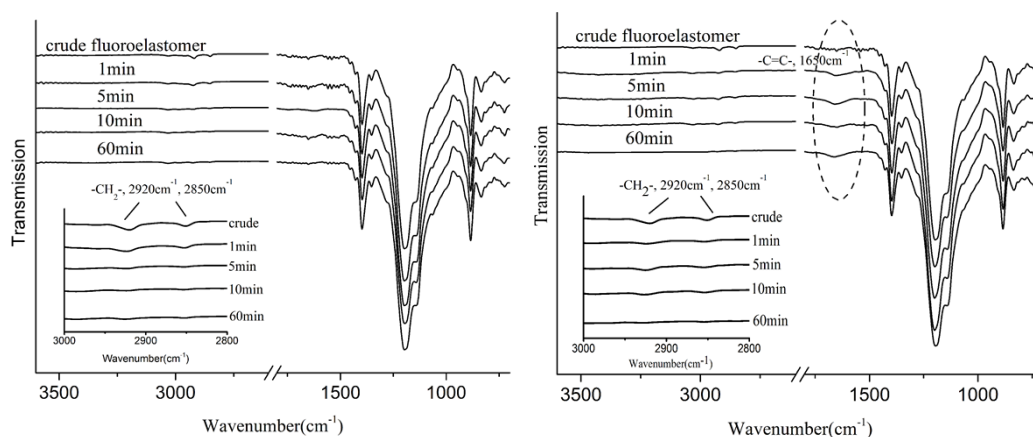


Fig.2S ATR-FTIR spectra of short-fluorinated fluoroelastomer films in different temperature: 30°C fluorination (left); 60°C fluorination (right)

The short time fluorinations (fluorinated for 1min, 5min, 10min) were processed, in order to observe the elementary reaction. The ATR-FTIR spectra of short time fluorinated films are presented in Fig.2S 30°C fluorination (left); 60°C fluorination (right). In stage I (30°C fluorination), the $\text{-CH}_2\text{-}$ (2920cm^{-1} , 2850cm^{-1}) structure was substituted by fluorine atom completely after only five minute fluorination. In whole stage I fluorination, the -C=C- (1650cm^{-1}) structure was not generated. In stage I, elementary reaction I (substitution reaction) occurs only and preferentially before the other reactions. Furthermore, the fluorine substitution reaction can improve the fluorine content of fluorinated film. Therefore, the fluorine content is considered to increase in this stage. In stage II (60°C fluorination), the $\text{-CH}_2\text{-}$ structure was substituted by fluorine atom entirely and -C=C- structure was generated after only one minute reaction. Because 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 in stage II. However, the rate of each elementary reaction might be different in stage II and stage III.