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Accelerated Aging Behaviors and Mechanism of Fluoroelastomer in Lubricating Oil Medium

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Electronic Supplementary Information

Abstract The aging behaviors and mechanism of fluoroelastomer (FKM) under lubricating oil (FKM-O) and air (FKM-A, as a comparison) at elevated temperatures were studied from both physical and chemical viewpoints. The obvious changes of mechanical and swelling performances indicate that the coupling effect of lubricating oil and temperature causes more serious deterioration of FKM-O compared to that of FKM-A. Meanwhile, much stronger temperature dependence of both bulk properties and micro-structures for FKM-O is found. Three-stage physical diffusion process is defined in FKM-O due to the competition between oil diffusion and elastic retraction of network. FTIR results reveal that the dehydrofluorination reaction causes the fracture of C—F bonds and produces a large number of C=C bonds in the backbone. The coupling effect of oil medium and high temperature could accelerate the scission of C=C bonds and generate a series of fragments with different molecular sizes. The TGA results, crosslinking density V_e, and glass transition temperature T_g derived from different measurements coherently demonstrate the network destruction in the initial stage and the simultaneous reconstruction occurring at the final stage. The newly formed local network induced by reconstruction cannot compensate the break of the original rubber network and thus only provides lower tensile strength and thermal stability.

Keywords Fluoroelastomer; Aging behaviors; Mechanism; Lubricating oil; Network reconstruction

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INTRODUCTION

Fluoroelastomer (FKM) has been widely used in aircraft and aerospace systems as the most susceptible sealing parts, such as O-rings, gaskets, and other types of static and dynamic seal.[1] Due to the unique chemical structure and higher bond energy of C—F (485 kJ/mol) that is very stable and provides shielding effect to C—C bonds on the backbone, FKM shows superior thermal and chemical resistance.[2,3] However, during their long period of services, the sealing materials are usually exposed to complex and harsh environmental conditions including high stress, high temperature, and special medium, which independently or coupled together could cause the aging problems.[4,5] Generally, the aging behavior of a polymer involves two processes: chemical aging (chain scission, crosslinking, *etc.*) and physical aging (chain relaxation, swelling, *etc.*).[6] Both of them could bring performance deterioration or even failure of polymer materials. Particularly for FKM used in aerospace, its aging behavior could not only cause the failure of the sealing assembly but also related to the safety of the whole aerospace system. Because of the complicated service conditions and multi-components of the rubber materials (crosslinking networks, various small molecule additives, *etc.*),[7–9] the aging mechanism of FKM is so sophisticated and remains unknown. Therefore, to figure out the aging mechanism of FKM under the real service conditions, and to improve the long-term stability are of particular importance but facing big challenges.

In recent years, some studies have explored the aging mechanism of FKM in different media coupling with other factors, such as elevated temperature, oxygen concentration, *etc*. Many researchers have reported that the fluorine atoms and hydrogen atoms on the backbone of FKM could react with each other to extract hydrofluoric acid (HF) and generate C=C bonds,[2] which is more vulnerable at severe conditions resulting in polymer degradation. When exposed to the alkaline environment or long-term usage, due to the reaction between HF and alkaline, the degradation of FKM molecular chains is significantly accelerated.[10,11] Similarly in the biodiesel medium, the C=C bonds of FKM could also react with the oxidation products from the unsaturated components of biodiesel, promoting the chain scission.[12] As exposed to other conditions,[13–16] for example geothermal environment (water/oxygen), due to the existence of oxygen, the C—F bond could also be disturbed through a three-stage oxidation mechanism, which has significant influence on the

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thermal stability of FKM. Besides the chemical changes, swelling-induced aging could inevitably occur especially at higher temperatures as the FKM is used in oil medium. Generally, three simultaneous processes are included: rubber swelling, additive extraction, and polymer chain relaxation.[6,17–19] Apparently, the aging behaviors and mechanism of FKM are strongly dependent on the medium properties, such as chemical structure, polarity or solubility parameter, and interactions between the medium and polymer molecules.

The aviation lubricating oil is a complex mixture composed of a base oil and a variety of additives.[20] To the best of our knowledge, extremely little attention has been paid to the degradation and stability of FKM under this medium or combined with temperature gradient even though it is quite close to the actual applications. In addition, previous studies usually discuss the chemical aging and physical changes independently, while the interference between these two processes is ignored due to sophisticated mechanism. Therefore, the aim of the present study is to figure out the aging mechanism of FKM under the coupling effect of higher temperature and aviation lubricating oil, and give an in-depth discussion on the interference between the chemical and physical aging. A selected type of FKM (VDF-*co*-HFP copolymer) was exposed to an aviation lubricating oil (Mobile Jet Oil II) and air (as a comparison) environment at relatively high temperatures (150, 175, and 200 °C). The changes of mechanical properties were evaluated by tensile strength and dynamic storage modulus. Changes in the chemical structure of FKM were characterized by the content of C=C, CF, CF_2, and CF_3 groups detected by attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR). The thermal stability was estimated by thermogravimetry analysis (TGA). The physical aging, diffusion of oil, and extraction of additives were characterized by mass changes and glass transition temperature (T_g). The fracture and surface morphologies of rubber specimens before and after aging were assessed by scanning electron microscopy (SEM). Finally, the crosslinking density was calculated based on the equilibrium swelling and DMA results, and correlated with other properties. The coupling of oil medium and temperature has significant impacts on the aging behaviors of FKM compared to air.

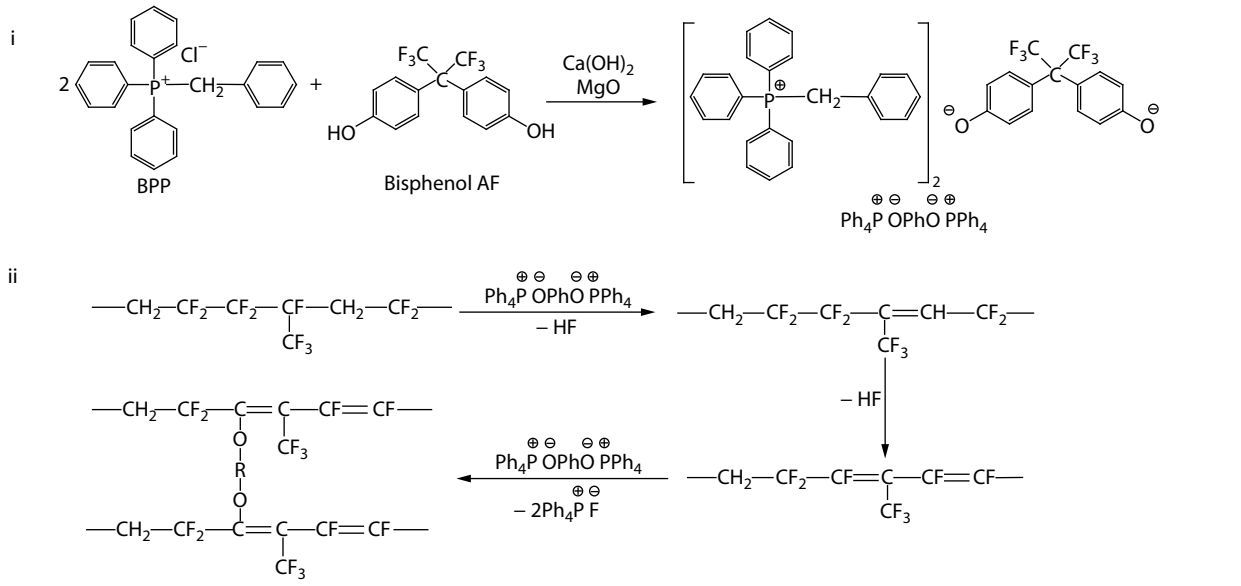
EXPERIMENTAL

Materials and Sample Preparation

The FKM copolymer (containing 60 wt% vinylidene fluoride and 40 wt% hexafluoropropylene) with additives was supplied by Zhonghao Chenguang Research Institute of Chemical Industry Co. Ltd., China. The additives required for FKM sample preparation are listed in Table 1, in which benzyltriphenylphosphonium chloride (BPP) is vulcanizing aid, bisphenol AF is the vulcanizing agent, calcium hydroxide ($Ca(OH)_2$) and magnesium oxide (MgO) are used as acid absorptions, and the carbon black (blank N990) is the filler. The "phr" means parts per hundreds of rubber, which is used to represent the filler or additive content in FKM matrix. Samples were firstly cured and hot-pressed into sheets (100 mm × 30 mm × 2 mm) at 175 °C for 10 min at a pressure of 10 MPa, and sequentially post-cured at 150, 180, 200, and 230 °C for 2, 2, 2, and 18 h in an oven, respectively. The specific curing reactions[21] are shown in the Scheme 1, which involves the formation of curing precursor, the generation of C=C bonds through dehydrofluorination reaction, and the formation of crosslinking network. The cured rubber has a T_g of –18.39 °C (measured by DSC (differential scanning calorimetry)) and a tensile strength of 14.73 MPa.

Table 1 The constituents of the FKM samples.

Constituent	phr
FKM copolymer	100
Bisphenol AF	2
Benzyltriphenylphosphonium chloride (BPP)	0.5
Calcium hydroxide ($Ca(OH)_2$)	6
Magnesium oxide (MgO)	3
Carbon black	30



Scheme 1 The curing reaction of FKM by bisphenol AF/BPP.

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The lubricating oil Mobile Jet Oil II that is commonly used in civil and military aviation gas turbine engines was supplied by ExxonMobil. The density of the lubricating oil is 1.0035 kg/L at 15 °C and the flash temperature is about 270 °C. As a military used lubricating oil, the constituents are quite complicated (Fig. S1 in the electronic supplementary information, ESI) and the specific formulation cannot be defined.

Aging Conditions (Oil and Air)

Under the oil condition, the samples denoted as FKM-O were completely immersed in the lubricating oil. After undergoing different aging histories, they were removed from the oil medium and their surfaces were cleaned with filter paper to eliminate the residue oil. Under the air condition, the samples named FKM-A were directly aged in air-circulating oven. The specified aging conditions in both oil and air are presented in Table 2.

Table 2 The specified aging conditions.

Medium	Temperature (°C)	Aging time (day)
Oil	150	0.5, 4, 7, 10, 14, 16, 19, 21, 23, 25, 28, 30, 32, 35, 42, 49, 63, 77
	175	0.25, 0.5, 1, 3, 5, 7, 9, 11, 14, 16, 18, 20, 22, 24
	200	0.25, 0.5, 1, 2, 3, 5, 7, 9, 11, 13, 14, 15, 16, 18, 20
Air	150	2, 7, 14, 21, 28, 35, 42, 49, 63, 77
	175	2, 7, 14, 21, 28, 35, 42, 49, 63, 77
	200	2, 7, 14, 21, 28, 35, 42, 49, 63, 77

Mechanical Properties

The electro-universal testing machine (Instron 5569) was used to measure the tensile strength of the control and aged FKM samples (dumb bell: 50 mm × 4 mm × 2 mm) according to GB/T 528-2009, and the crosshead speed was set as 200 mm/min controlled by a 500 N load cell. The average tensile strength was obtained by at least three specimens of each sample.

Mass Tests

The uptake of lubricating oil in the aged FKM samples was determined by using a Mettler-Toledo balance (precision = 0.01 mg). For each sample, three circular parts with the same size were cut from different positions for repeating experiments. The mass change was calculated according to:

$$\Delta m(\%) = \frac{m_1 - m_0}{m_0} \times 100\% \quad (1)$$

where m_0 and m_1 are mass of the sample before and after exposure to the lubricating oil, respectively.

SEM Observation

Fracture and surface morphologies of the control and aged samples were observed by scanning electron microscopy (SEM, JSM-5900LV). The samples were cryo-fractured in liquid nitrogen (fracture morphologies) or cut to small piece (surface morphologies), and then the surface was purged with clean nitrogen. The micrographs were taken at an acceleration voltage of 10 kV and a current of 10 mA. Before observation, all samples were coated with gold powder.

ATR-FTIR Characterization

The attenuated total reflection-Fourier transform infrared (ATR-FTIR Germanium Crystal, Thermo Nicolet 10, USA) spectroscopy was applied to evaluate the chemical changes of the specimens aged under different conditions. The range of spectra was 4000–650 cm^{-1} with the resolution of 4 cm^{-1}. At least two different positions on the sample surface were selected for scanning to guarantee the repeatability. The spectra of FKM-A were normalized referring to the absorbance at 886 cm^{-1} (C—F stretching mode of non-reactive CF_3 groups of hexafluoropropylene). For FKM-O, due to the obvious changes of the CF_3 absorbency after aging, an internal reference, the lubricating oil with a distinguishable and independent characteristic band at 1740 cm^{-1} (C=O), was reintroduced for quantitative analysis. As demonstrated in Fig. S1 (in ESI), the lubricating oil itself is quite stable (without unsaturated component) and cannot react with FKM during aging. The sample treatment is as follows. Firstly, the readily existing medium oil diffused in FKM-O during aging was completely extracted by ultrasonication and Soxhlet extractor in methyl-ethyl-ketone (MEK) solvent for 1 and 48 h, respectively. Secondly, the completely extracted and dried samples were exposed to the oil medium at 150 °C for 6 h to reintroduce the oil with a same amount. Finally, the spectra of these samples were normalized referring to the absorbance of referenced oil at 1740 cm^{-1}. Two processes of smoothing and manual baseline correction provided by OMNIC software were applied to the FTIR spectra for all samples. The band decomposing and fitting processes were performed in the region of 1800–1500 cm^{-1} by Origin software, through which the independent band of C=C bonds could be distinguished. To get better fitting results over the experimental data, two-peak mode was chosen and several parameters, *e.g.*, peak height, half-peak width, were adjusted.

TGA Measurements

The thermal stability of control and aged FKM samples was determined by thermogravimetry (TGA550, TA instruments). Each sample (mass = 7.0–9.0 mg) was placed in a 70 mL aluminium oxide crucible, and then heated to 800 °C at a rate of 10 °C/min under dry nitrogen. All the tested samples were cut along the cross section with 2 mm thickness.

DMA Measurements

The dynamic storage modulus and T_g of the control and aged FKM samples were recorded by a Q800 dynamic thermomechanical analysis (DMA) analyzer (TA Instruments) in the tensile mode. Long strips of specimens (30 mm × 3.5 mm × 2 mm) were fixed between the clamps with a gauge length of 15 mm. Isothermal strain sweeps ranging from 0.01% to 10% were performed at 50 °C under a static force of 0.01 N at a constant frequency of 1.0 Hz. T_g of the sample was determined by temperature ramp from –60 °C to 60 °C with a constant frequency of 1.0 Hz at a heating rate of 3 °C/min.

Swelling Experiments

The swelling experiments were performed to analyze the changes of crosslinking density of FKM-O. To avoid the influence of diffused oil in the swelling process, the oil-extracted samples like those in FTIR experiments were used. Samples with nearly equal weights were swelled in MEK at 25 °C for 48 h (the equilibrium swelling time). After swelling, the samples were then weighed immediately and dried to a constant weight in a vacuum oven at 50 °C for 48 h. The crosslinking density (V_e) was calculated according to the Flory-Rehner equation:[22]

$$V_e = -\frac{\ln(1 - V_r) + V_r + \chi V_r^2}{V(V_r^{1/3} - V_r/2)} \quad (2)$$

where V_r is the volume fraction of the FKM samples after immersion in MEK, V the molecular volume of MEK, and χ the Flory-Huggins interaction parameter between polymer and solvent. For FKM-MEK system, the value of χ is –1.[10]

DSC Measurements

Differential scanning calorimetry (DSC) experiments were carried out on a TA Q20 (USA) instrument with the sample weight of 7.0–9.0 mg under nitrogen purge. The FKM samples were firstly heated to 80 ℃ and held for 5 min to eliminate the thermal history, and then cooled to –60 ℃ with a rate of 10 ℃/min and kept isothermal for 5 min. After that, the samples were subsequently heated to 60 ℃ with a rate of 3 ℃/min to measure the T_g. The tested samples were all cut along the cross section of the aged sheet to eliminate the heterogeneity of oil diffusion and avoid the error.

RESULTS AND DISCUSSION

Mechanical Properties and Mass Changes

Mechanical properties of the FKM exposed to both lubricating oil (FKM-O) and air (FKM-A) were investigated at different aging conditions. In the entire aging process, the tensile strength of FKM-O shows decreasing trend at all temperatures as shown in Fig. 1(a). At elevated temperatures, the tensile strength decreases more seriously, especially after long-term exposure. For clarity, three aging stages can be specified. In the early stage, all samples exhibit an abrupt decrease within three days as amplified in the insert, which might be due to the absorption of oil medium. With the prolonged aging, there appears a transient plateau as guided by the dotted line, which becomes shorter at higher temperature. In the later stage, a significant decline of the tensile strength is observed and has strong temperature dependence. This serious deterioration of the mechanical properties could be induced by the disruption of cross-linked rubber network and even the formation of micro-cracks on the surface, especially at higher temperature. Generally, in life prediction and engineering application, when the tensile strength decreases to 50% of the original value, the material will fail. Considering such a common recognition and the fast deterioration of the tensile strength for FKM-O samples at higher temperature, the present study only focuses on their aging behavior within shorter time. For reference, Fig. 1(b) shows the changes of tensile strength for FKM-A at the same temperatures. One can see that after long-term exposure, only slight decrease of the tensile strength for FKM-A can be observed. The large contrast between Figs. 1(a) and 1(b) suggests that the oil medium could significantly accelerate the aging process of FKM. Many reports have indicated that the tensile strength of the rubber is closely associated with crosslinking density and additive content.[23,24] Herein, the decrease in tensile strength for FKM-O may be attributed to the co-effect of oil diffusion, decreased crosslinking density, and filler migration and aggregation.

To quantify the diffusion of oil medium, the mass changes of FKM-O and FKM-A at different aging temperatures were measured as shown in Fig. 2. In contrast to the slight decrease in mass for FKM-A, obvious mass increase is observed for FKM-O. Consistent with the changes of tensile strength, higher aging temperature results in more pronounced increasing mass of FKM-O, indicating faster diffusion of oil medium. For example, at lower temperature of 150 ℃, 10% mass increase needs 77 days of aging, but only 2 days are required at higher temperature of 200 ℃. Also similar to the trend of tensile strength, three stages can be divided for the mass changes of FKM-O. As expected, the remarkable increase in mass at initial stage is attributed to the rapid diffusion of lubricating oil. And then an equilibrium plateau stage is reached, indicating a balance between the swelling of rubber and retraction of the network. At the later stage, a significant mass increase can be noticed, which is ascribed to more oil diffusion because of the breaking of rubber network, especially at higher temperature. The oil medium as a plasticizer could reduce the molecular interaction in the rubber, including polymer-polymer, polymer-filler, and filler-filler interaction, which as a key factor causes the remarkable decline of tensile strength at the early and later stages. Note that the slight decrease in mass of FKM-A might be attributed to the possible dehydrofluorination reaction, where the generated HF could react with MgO or $Ca(OH)_2$ to form H_2O, which would be gradually evaporated. The dehydrofluorination reaction becomes more serious at higher temperature and leads to larger decrease in mass.[2]

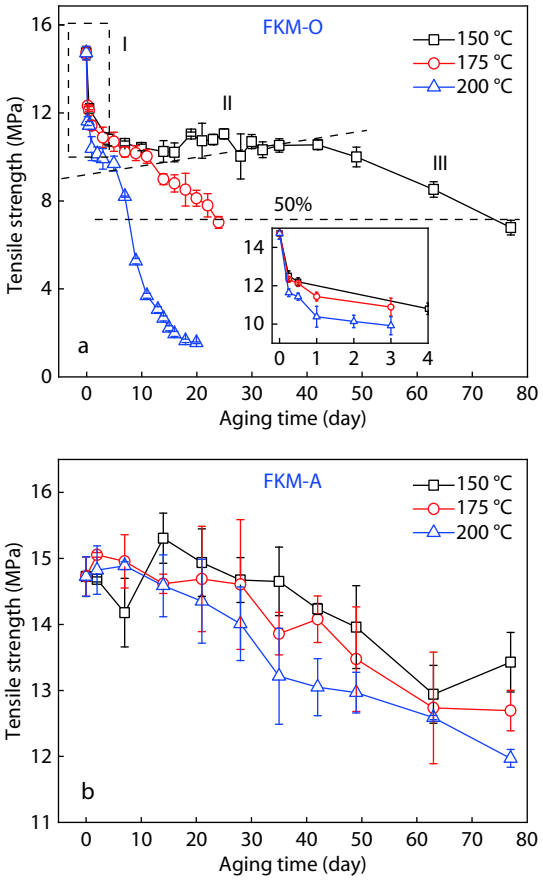


Fig. 1 Evolution of the tensile strength with aging time at different temperatures of 150, 175, and 200 °C for FKM-O (a) and FKM-A (b).

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Changes of Chemical and Network Structures

Morphological evolution

In order to investigate the influence of aging process on the microstructure changes of FKM-O and FKM-A under different conditions, SEM experiments are performed. Fig. 3 shows the effect of aging time on the fracture morphologies of FKM-O and FKM-A. For the control sample without aging, relatively smooth fracture is observed and the filler particles are uniformly distributed in the rubber matrix. In contrast, for specimens exposed to lubricating oil at 175 °C, some voids and particle agglomerates gradually form, which could be induced by the migration of fillers and volatilization of small molecules

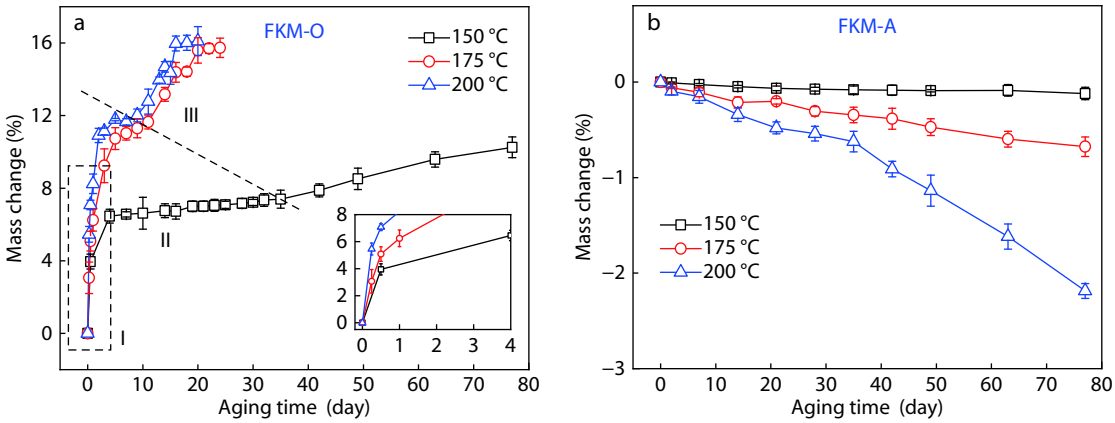


Fig. 2 Mass changes with aging time at different temperatures of 150, 175, and 200 °C for FKM-O (a) and FKM-A (b).

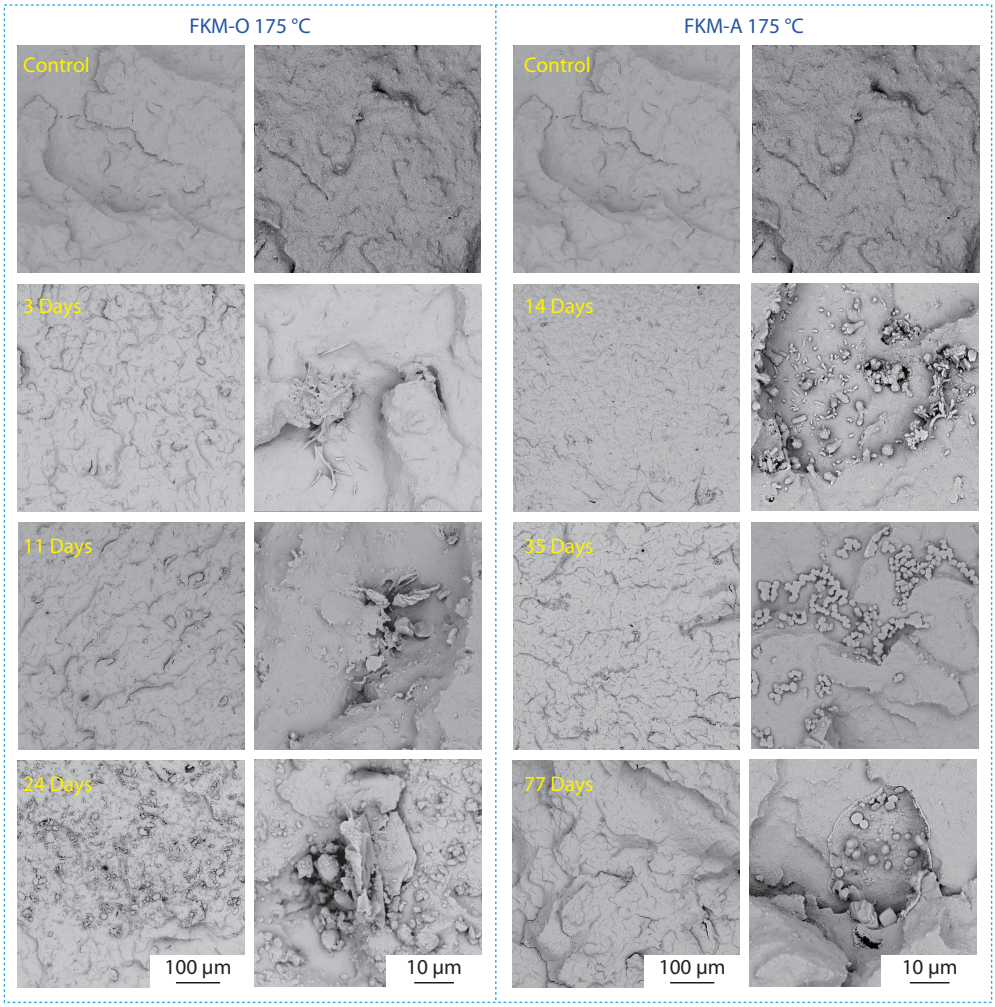


Fig. 3 Morphological changes of the fracture surface with aging time at 175 °C for FKM-O (left) and FKM-A (right).

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produced by the reaction between HF and acid absorption $Ca(OH)_2$ or MgO. As the time prolongs, obvious cavities can be found for FKM-O due to the diffusion of oil medium which causes the swelling of rubber network and facilitates the migration of fillers. Note that the position where the voids or cavities generated in the sample could be located at the original aggregation of the fillers or additives. After further absorption of medium oil, the voids gradually expand and eventually cause the break and fragmentation of the rubber network due to the coupling effect of swelling and degradation. Unlike FKM-O showing apparent morphological transition, only subtle changes of the filler accumulation are observed in FKM-A. This further confirms the accelerating effect of oil medium.

Fig. 4 shows the influence of aging temperature on the micro-structure changes of FKM-O and FKM-A. With the increasing temperature, serious fragmentation is observed in FKM-O, but there are no obvious changes of polymer matrix in the FKM-A even aged for 77 days at 200 °C. This indicates that

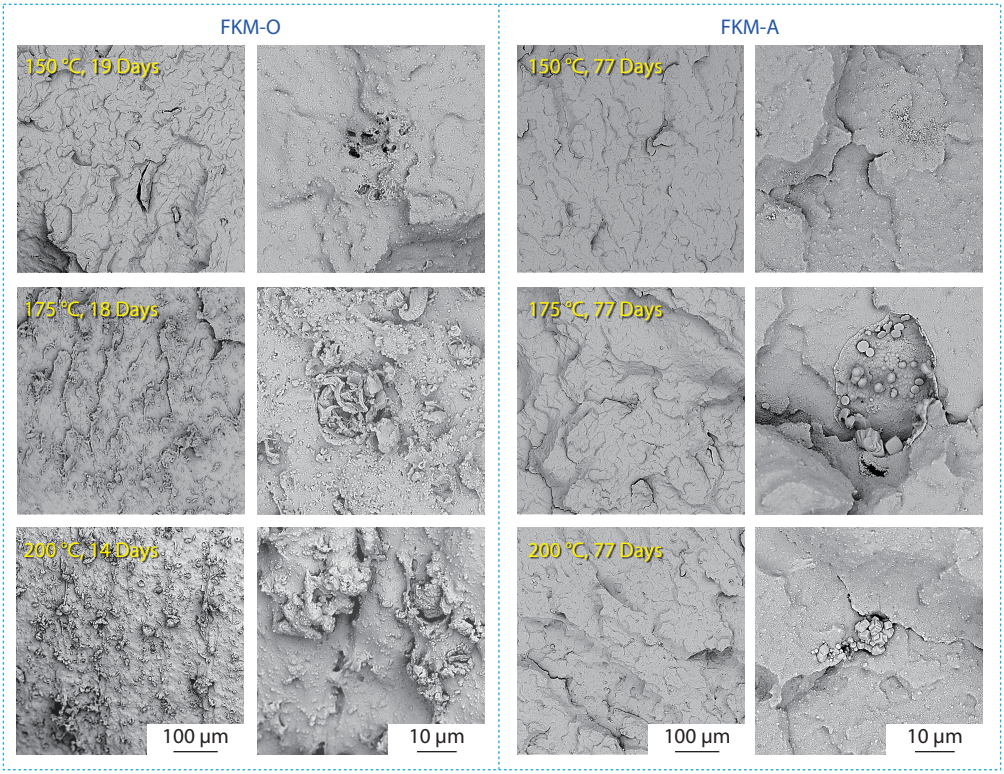


Fig. 4 Morphological changes of the fracture surface at different temperatures of 150, 175, and 200 °C for FKM-O (left) and FKM-A (right).

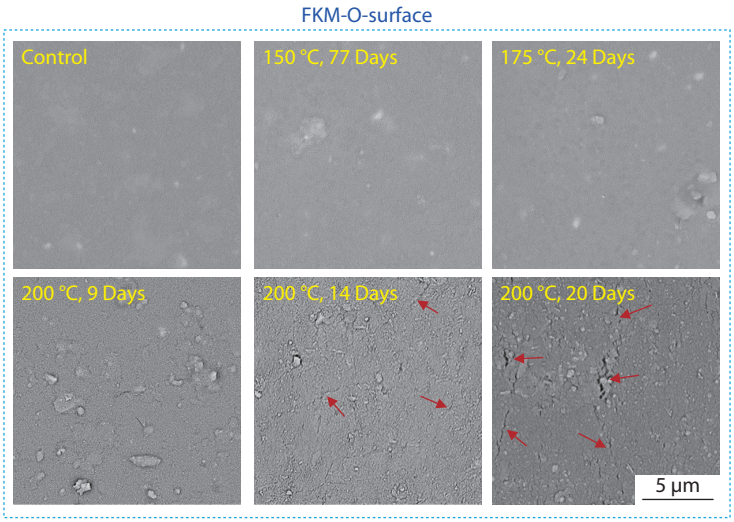


Fig. 5 Micro-cracks formation and evolution on the sample surface at different temperatures of 150, 175, and 200 °C for FKM-O.

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high temperature could facilitate the diffusion of oil medium and accelerate the degradation of FKM matrix accompanied by the migration of fillers, which finally leads to the disruption of the rubber network. Besides the evident morphological changes of the fracture surface inside the sample, the noticeable changes on the outside surface can also be observed at higher temperature of 200 °C for FKM-O. As shown in Fig. 5, one can see that some micro-cracks on the sample surface begin to form after 14 days of aging at 200 °C and become denser after 20 days of aging (as guided by the red arrows). Note that at lower temperatures of 150 and 175 °C, no obvious changes on the surface can be observed even at the longest aging time. These micro-structure changes are consistent with the variation of mechanical properties under different conditions.

Changes of chemical structure

To examine the chemical changes of FKM in the aging process, ATR-FTIR measurements were carried out and the results for FKM-O and FKM-A are shown in Figs. 6 and 7, respectively. In the spectra, the absorption band at 1386 cm^{-1} is assigned to the

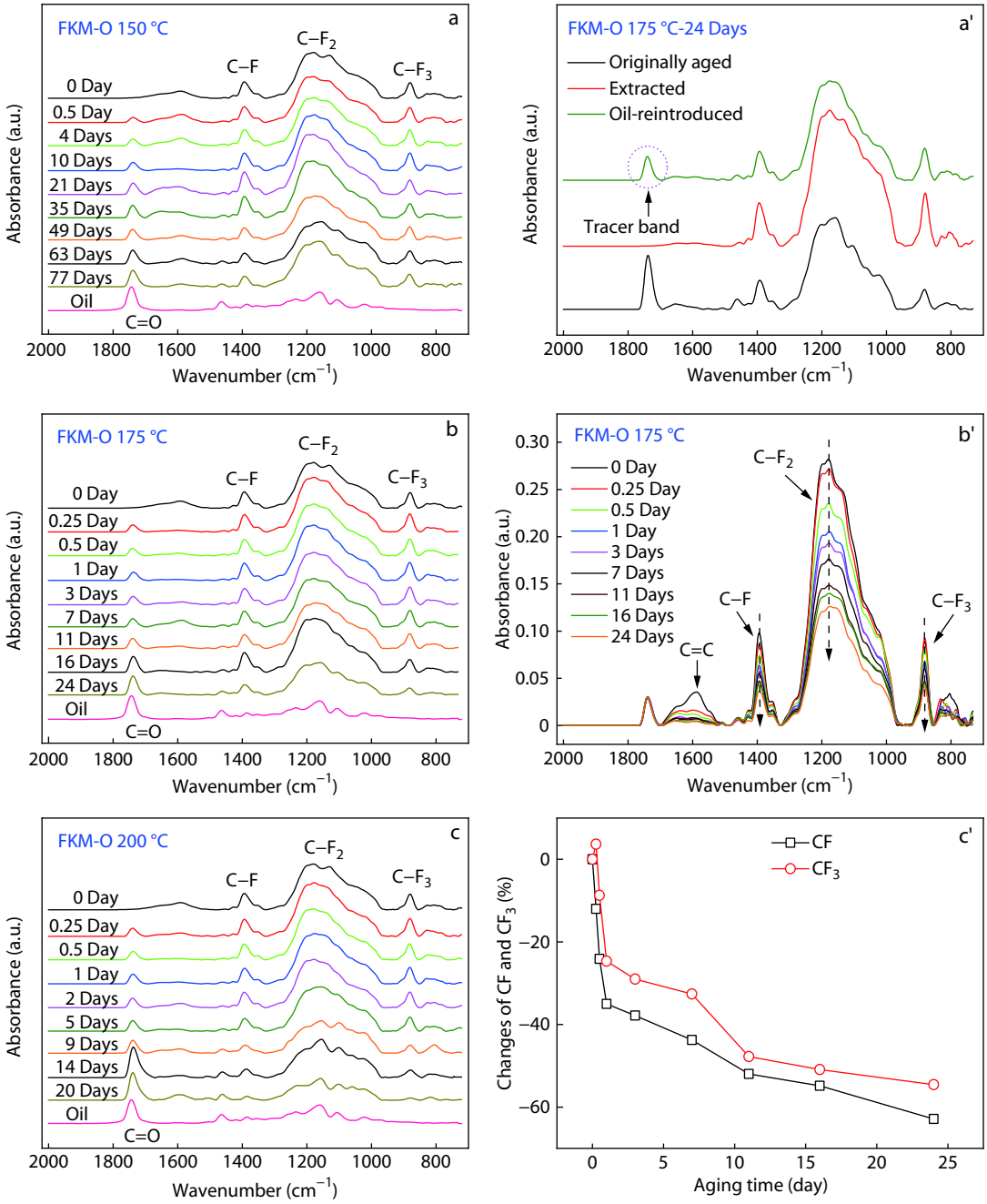


Fig. 6 ATR-FTIR spectra of FKM-O after aging at 150, 175, and 200 °C (a–c); comparison among the aged (24 days at 175 °C), extracted and oil-reintroduced FKM samples (a'); normalized spectra of FKM-O aged at 175 °C for different time (b') and the corresponding changes of peak intensity of CF and CF_3 (c').

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stretching vibration of CF group. The bands at 1060, 1130, and 1178 cm^{-1} correspond to CF_2 group, and that at 880 cm^{-1} is ascribed to the CF_3 group on hexafluoropropylene.[12,16] Figs. 6(a)–6(c) show the evolution of characteristic absorbencies with aging time for FKM-O samples aged at different temperatures of 150, 175, and 200 °C. Note that these curves have not been normalized. Compared to the original FKM, a new band at 1740 cm^{-1} that belongs to lubricating oil is apparently observed after aging for sufficient time. Consistent with the mass change, this indicates that the oil has been diffused into the FKM matrix. Particularly at higher temperature of 200 °C, the spectra of aged FKM (> 9 days) are even closer to that of the oil, suggesting larger amount of oil absorption, which might be induced by surface micro-cracks as evidenced by SEM. Of course, the characteristic bands of FKM (CF, CF_2, and CF_3) also show a significant change after aging due to the serious degradation. To quantify the data, we need to introduce a tracer band for normalization. As described in the experimental section, we first completely extracted the absorbed oil in the aged FKM and then reintroduced it as the tracer (treated at 150 °C for 6 h). As shown in Fig. 6(a'), after extraction, the medium oil absorbed during aging has been completely eliminated. The reintroduction process of oil has almost no influence on the structure changes of FKM except introducing a referenced oil band at 1740 cm^{-1}. Based on this procedure, the normalized spectra of all aged (at 175 °C as an example) and oil-reintroduced FKM samples are obtained in Fig. 6(b'). Obviously, an evident decrease of C=C intensity in FKM-O can be observed with aging time and it almost disappears at the later stage. The changes of C=C intensity might be due to the completion between the dehydrofluorination reaction and the degradation corresponding to the generation and consumption of C=C bonds, respectively. It is considered that the reduction of fluorine content could significantly weaken the protection of C–F bonds to C=C/C–C bonds on the backbone, leading to easier breaking or degradation. Besides, the decrease trends of band intensity for CF and CF_3 are summarized in Fig. 6(c'), where the abrupt decline at shorter time and gradual decrease at later stage are consistent with other report.[12] The decrease of CF or CF_2 is also ascribed to the dehydrofluorination process. It is worth noting that the break of C=C bonds randomly in the network could produce a series of fragments with different molecular sizes.[25] Some of the low molecular degradation products may volatilize at high temperature, which could explain the decrease of CF_3 groups.

Unlike the data treatment of FKM-O, the spectra of FKM-A aged at 175 °C presented in Fig. S2 (in ESI) are directly normalized by the non-reactive band of CF_3 and the results are shown Fig. 7(a). In contrast to the robust decrease of characterized bands for FKM-O, only slight changes in the band intensity of CF and CF_2 are found for FKM-A, which demonstrates that the elimination reaction also exists. To obtain the changes of C=C group, as characterized by the band at about 1590 cm^{-1}, band fitting in the region of 1800–1500 cm^{-1} is shown in Fig. 7(b). Through fitting, the variation of bond intensity of C=C bonds is obtained and shown in Fig. 7(c). One can see that the band intensity of C=C bonds in FKM-A shows a slight but step change in the whole aging

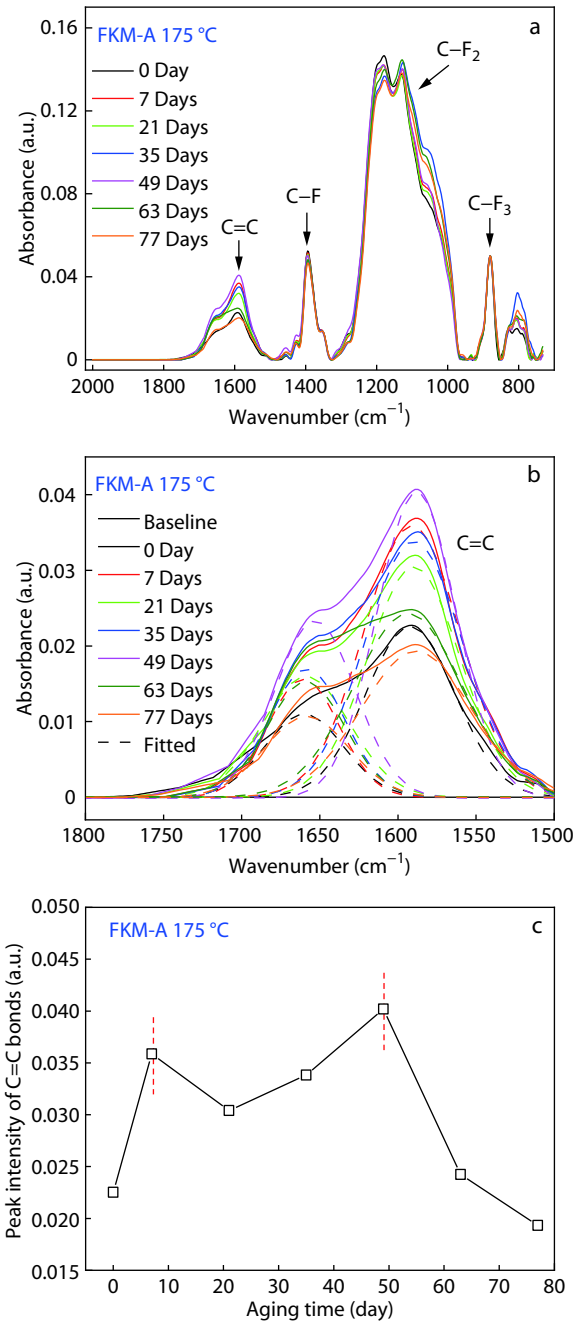


Fig. 7 Normalized ATR-FTIR spectra (a) and peak fitting results (b) of FKM-A aged at 175 °C; variation of peak intensity of C=C bonds (c).

process. The initial stage increase might be due to the post-curing of FKM, and the invariant intermediate stage or late stage decrease could also be dominated by the competition between generation of C=C bonds induced by dehydrofluorination reaction and their consumption caused by degradation. Note that the aging mechanisms of FKM-A at 150 and 200 °C are the same as that at 175 °C. In both cases of FKM-O and FKM-A, the dehydrofluorination reactions are dominant during aging. However, different from FKM-A, the coupling of lubricating oil and high temperature in FKM-O could significantly accelerate the break of C=C bonds, which

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causes more serious destruction of the network. In addition, the *α* carbon near the C=C bonds is more active to generate the free radicals,[26] which could react with each other and form the reconstructed network structure.

Constituent changes

To estimate the constituent changes in FKM, especially after the absorption of oil medium, the TGA thermograms as well as the DTG (differential thermogravimetry) were recorded for FKM-O and FKM-A at different aging conditions as shown in Figs. 8 and 9. It is seen that unlike the control sample with only one decomposition step, apparent two or even three (higher aging temperature) steps appear after aging in lubricating oil. The first weight loss starting at 220 °C belongs to the decomposition of oil medium diffused into the rubber matrix whose TGA curves are provided in Fig. S3 (in ESI) for reference. It grows significantly with the increase of aging time and temperature, indicating the increased content of diffused medium, which is consistent with the mass changes. The second weight loss occurring at 460–500 °C could be mainly attributed to the decomposition of FKM matrix. Besides, a new decomposition peak at around 350–420 °C in the DTG result appears after a certain aging time at both 175 and 200 °C (Figs. 8b' and 8c'). The temperature at which the new peak appears is getting lower and lower with the increased aging time and temperature.

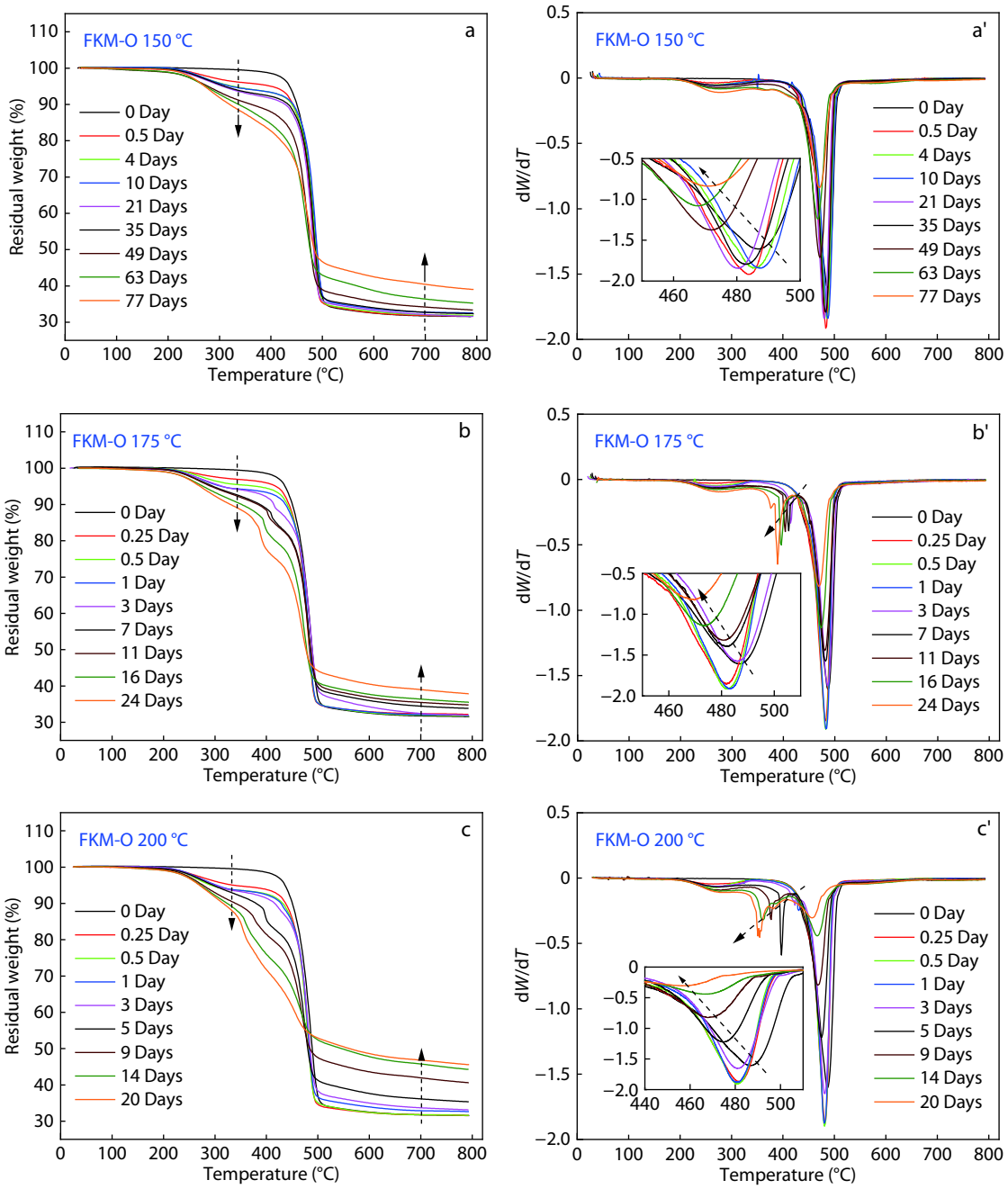


Fig. 8 TGA curves (a–c) and the corresponding DTG curves (a'–c') of FKM-O aged at 150, 175, and 200 °C, respectively.

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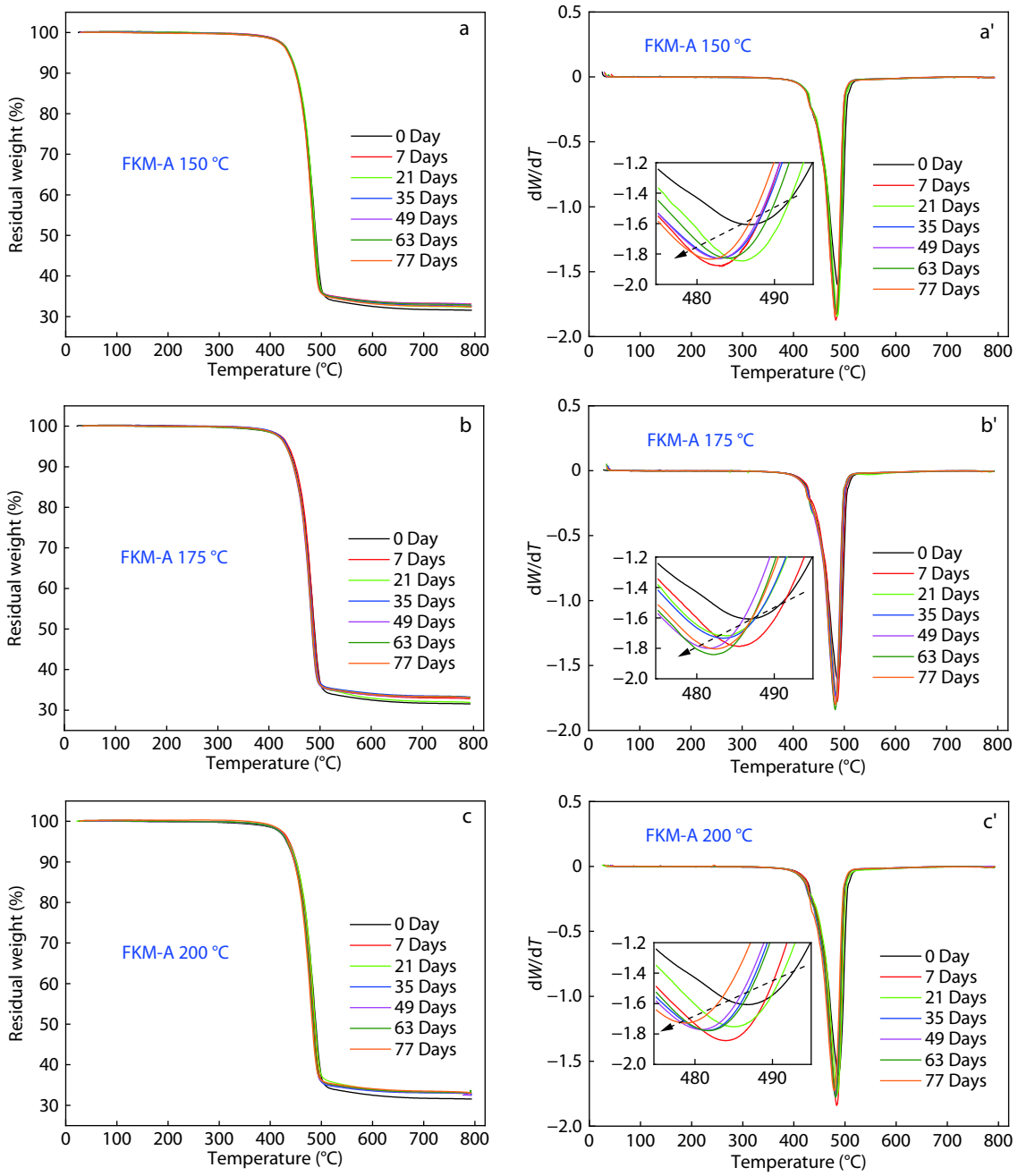


Fig. 9 TGA curves (a–c) and the corresponding DTG curves (a'–c') of FKM-A aged at 150, 175, and 200 °C, respectively.

Meanwhile, the decomposition of FKM matrix gradually shrinks accompanied with the increase of this new peak. This means the rubber network gradually breaks down and more small degradation products or locally reconstructed smaller size networks are produced simultaneously, which agrees with the obvious decrease of C=C bonds and non-reactive CF_3 groups in FTIR results. It is reported that such newly formed network only provides relatively low tensile strength of about 1.7 MPa,[3] which well agrees with our results aging at 200 °C in Fig. 1(a). In the range of 600–800 °C, it is more obvious that the portion of the carbon residue becomes larger with prolonging exposure time. Based on the FTIR results, the fragile C=C bonds could form *via* dehydrofluorination process and then broke randomly in the network to produce some volatile fragments with low molecular weight. Meanwhile, the free radicals on the *α*-carbon near the C=C bonds could facilitate the network construction. Therefore, the increase of carbon residue at 600–800 °C might be ascribed to the volatilization of small molecular weight fragments produced by degradation and the increased crosslinking density *via* reconstruction of the free radicals.[27] As comparison, only a slight decrease can be observed even after 77 days of aging at the same temperature. Therefore, the above results indicate that the oil medium could significantly accelerate the aging process of FKM *via* molecular diffusion and swelling,

which further facilitates the chain scission process.

Network structure changes

Generally, suitable crosslinking could improve the tensile strength of rubber, but excessive or less crosslinking might lead to lower tensile strength. To quantify how the temperature and oil medium affect the network structure, DMA and equilibrium swelling experiments were carried out and the crosslinking density was calculated by both methods. Fig. 10 presents the strain sweep curves at selected frequency of 1.0 Hz for FKM-O aging for various time under different temperatures. The decreasing trend of storage modulus is similar to the tensile strength and mass changes with time.

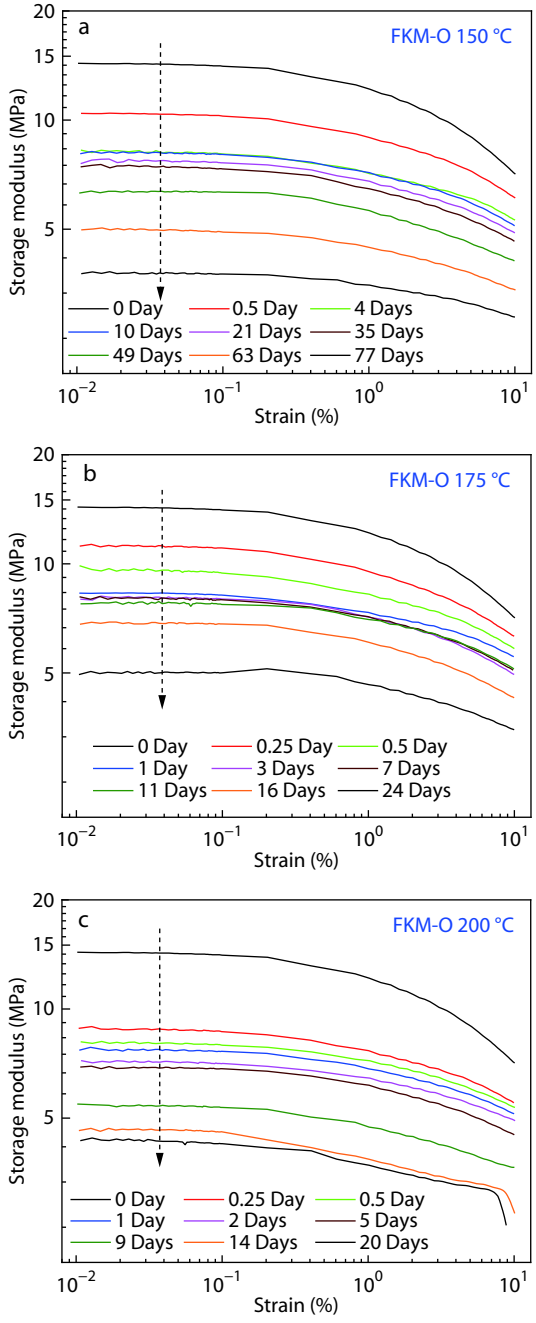


Fig. 10 DMA strain sweep curves of FKM-O aged for various time at different aging temperatures of 150 °C (a), 175 °C (b), and 200 °C (c).

In fact, the filled rubber network includes both the physical and chemical networks. The physical network involves entanglement network of un-crosslinked polymer chains and the filler network (rubber-filler and filler-filler network), whereas the chemical network specifically refers to the crosslinking network of FKM. At higher strain, the storage modulus shows a significant decrease from DMA results, which is called "Payne-effect" relating to the changes of physical network.[28] With the extension of aging time, such "Payne-effect" (decreasing magnitude of the modulus) becomes weaker for FKM-O, suggesting the disruption of physical network is induced by the diffusion of oil medium. According to the basic rubber elasticity theory,[29] the crosslinking density V_e of a rubber network could be tentatively calculated by the storage modulus from DMA data:

$$V_e = \frac{E}{3RT} \tag{3}$$

where V_e is the crosslinking density of rubber network, E is the storage modulus in the rubbery state, R is the constant, and T is the absolute temperature. The time dependence of V_e at different aging temperatures under the circumstance of lubricating oil is summarized in Fig. 11(a). Consistent with the tensile or mass changes, an obvious decline in crosslinking density is also observed and can be divided into three stages. The remarkable decrease of V_e is mainly due to the expansion of

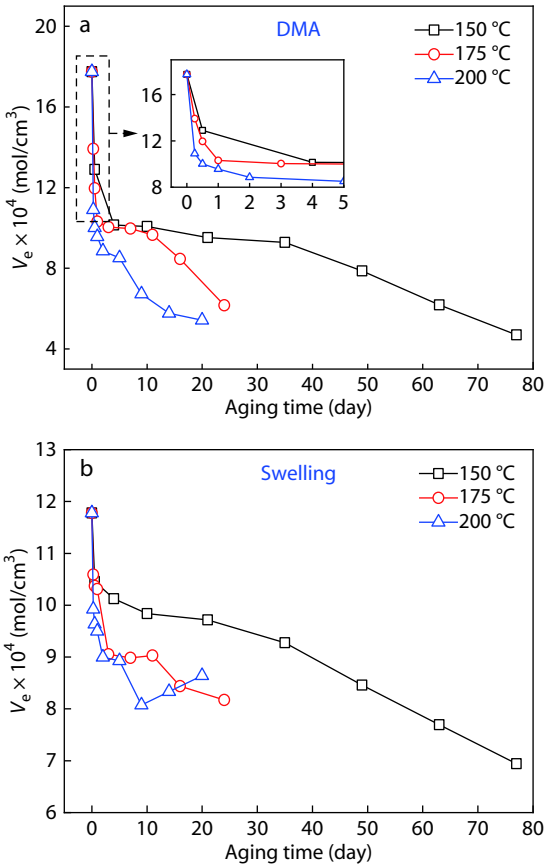


Fig. 11 Time dependences of crosslinking density V_e determined from DMA (a) and equilibrium swelling (b) measurements for FKM-O at various aging temperatures.

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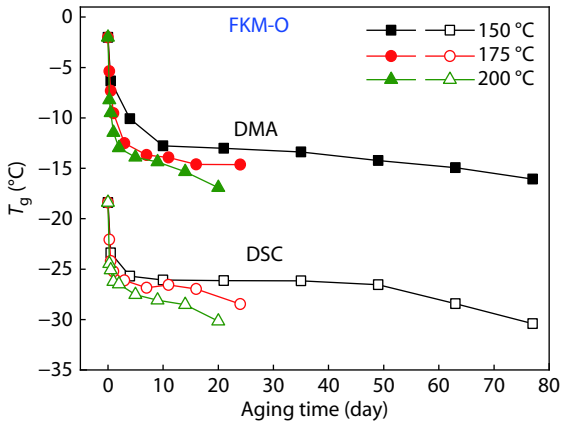


Fig. 12 Changes of T_g from DMA (solid) and DSC (open) measurements at different temperatures of 150, 175, and 200 °C for FKM-O.

crosslinking network caused by the swelling of oil medium and the destruction of network structure *via* the break of C=C bonds. However, the decreasing magnitude of V_e at the later stage is lower, indicating the destruction and reconstruction of network structure occur simultaneously. To further confirm the evolution of chemical network structure, Fig. 11(b) presents the crosslinking density determined by equilibrium swelling method. Almost the same trend can be observed in the whole aging process at 150 and 175 °C, but there seems a little bit difference at 200 °C in the later stage, where V_e even slightly increases with aging time. This might be attributed to the restructuring of polymer network *via* the free radicals reaction as aforementioned in FTIR and TGA results. Such difference between DMA and swelling data at this point could be related to the different measurements. Frankly speaking, V_e estimated from DMA measurements could involve the contribution from fillers and absorbed oil, whereas that determined by swelling method only reflects the changes of chemically crosslinking network. Judged from the similar decreasing trend of V_e determined by both methods, we may tentatively consider that the chemical aging might be dominant in the whole aging process.

Glass transition temperature (T_g) is another important parameter relating to the network of the rubber. Two techniques (DSC and DMA) were used to examine the changes of T_g. The DSC test served to investigate the "static" T_g by the change of heat capacity and the DMA tests were performed to study the viscoelasticity properties by applying a periodically oscillating force ("dynamic" T_g).[30] Both the "static" and "dynamic" T_g of FKM-O are shown in Fig. 12 as extracted from Figs. S4 and S5 (in ESI). At all temperatures, an obvious downward trend of T_gs is seen after exposing to lubricating oil. At elevated aging temperatures, the decreasing trend becomes more evident, which is consistent with the crosslinking density. In the whole aging process, the absorption of oil medium and the destruction/reconstruction of the network structure could all have significant impacts on the variation of T_g in FKM samples. The oil medium diffused in the rubber and acting as a plasticizer could reduce the intermolecular friction. Chain scissions or destruction of crosslinking network will lead to higher segmental mobility. These above two processes combined together contribute to the abrupt decline of T_g in the early stage. However, the rapid decrease like mass change is not found in T_g at the late stage, which is similar to the changes of V_e. This might be ascribed to the competition of the reconstruction of network structure. As evidenced in TGA results and mass change, the oil diffusion still exists in the later stage, so the plasticizing effect is continuously enhanced. Meanwhile, the destruction and reconstruction of the network simultaneously occur. Even though the network reconstruction could enhance T_g, it could not compensate the decreasing magnitude brought by the combined effect of oil diffusion and network destruction. Thus, the net effect of these factors leads to the slight decrease of T_g in the late stage. The situ-

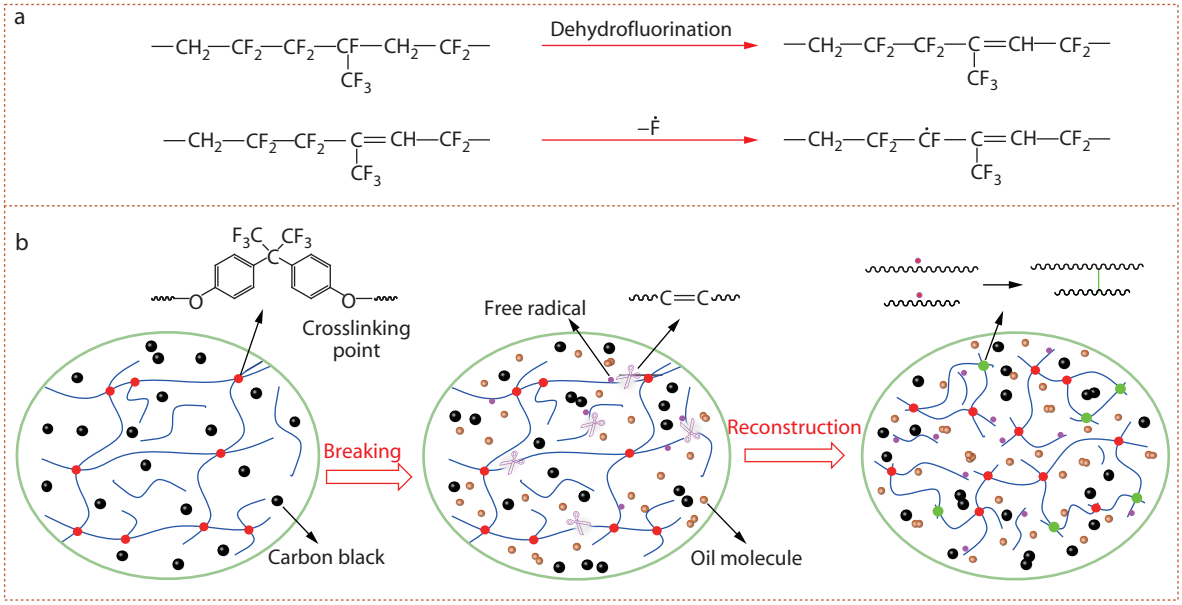


Fig. 13 Changes of chemical (a) and the corresponding network (b) structures of FKM-O.

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ation in FKM-A as comparison is shown in Fig. S4 (in ESI). Only slight changes can be found, which coincides with the other parameters. Note that the gap between static and dynamic T_gs is due to the different measurement instruments and principles.

Aging Mechanism

The degradation mechanisms of FKM containing both hydrogen and fluorine in the repeating units are so extremely complex that at best it is possible to have a meager comprehension,[25] which is illustrated in Fig. 13. As shown in Fig. 13(a), there are two chemical reactions as judged from the FTIR results: one is the aforementioned dehydrofluorination reaction, which could generate C=C bonds, and the other is the break of fragile C=C bonds. Meanwhile, the free radicals on the *α* carbon near the C=C bonds could facilitate the formation of the network construction. Thus, the destruction and reconstruction of the network structure could both exist as shown in Fig. 13(b). The newly formed network structure could further explain the slower decrease of V_e and T_g in Figs. 11 and 12.

CONCLUSIONS

Compared to FKM-A which only shows slight changes caused by the reaction of post-cured and dehydrofluorination, FKM-O exhibits more serious deterioration and much stronger temperature dependence of both the macro-performances and micro-structures due to the coupling effect of oil medium and temperature. The corresponding mechanisms are as follows:

(1) Physical diffusion: there is a competition between medium diffusion and elastic retraction of the network structure in the aging process, which causes a three-step stage. The diffusion oil medium acting as a physical plasticizer could lead to the rapid decrease of tensile strength, storage modulus/crosslinking density and T_g.

(2) Chemical changes: the dehydrofluorination reaction could generate a large number of C=C bonds and cause the reduction of C−F bonds. The C=C bonds are easily broken under the coupling effect of oil medium and high temperature and produce a series of fragments with different molecular size.

(3) Network structure: destruction of the network structure initiated by the break of C=C bonds and reconstruction of small fragmental networks could occur simultaneously in the aging process.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at http://dx.doi.org/10.1007/s10118-020-2410-1.

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