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Preparation and properties of acrylate tackifying agent modified by ionic liquid for Fluororubber

Yin Zhigang, Zou Wei, Luo Jiamin, Chen Yinpeng, Huang Lin
[1] *College of Chemical Engineering, Sichuan University of Science and Engineering, Zigong City, Sichuan Province, P. R. China, 64300.*
** Correspondence: Dr. Zou Wei*

Abstract: *Fluororubber and polytetrafluoroethylene (PTFE) composite materials have significant application value in aerospace, automotive sealing and other fields due to their excellent chemical corrosion resistance, high-temperature performance and low surface energy characteristics. However, the poor interfacial compatibility between the two materials leads to insufficient bonding strength, which has become a key issue restricting their application. Traditional tackifiers often fail to meet the bonding requirements of highly inert surface materials, and there is an urgent need to develop new tackifiers to enhance the interfacial bonding strength. Fluorinated acrylate polymers, due to their strong chemical affinity with fluororubber and PTFE, have been proven to be highly potential candidate materials for tackifiers, but their insufficient molecular polarity still needs to be improved in terms of wetting and adhesion durability.*

In this paper, HFBA was used as the main monomer, and VBImTFSI was introduced to construct a two-component copolymer (PHV). The unique ion-dipole interaction of ionic liquids was utilized to enhance the interfacial wettability and thermal stability of the tackifier. Further, HEMA was introduced as a functional monomer, and the introduction of hydroxyl groups can enhance the hydrogen bonding force between polymer molecules and improve the interfacial adhesion. The chemical structure and molecular weight distribution of the polymer were systematically characterized by Fourier transform infrared spectroscopy (FT-IR), proton nuclear magnetic resonance (1HNMR) and gel permeation chromatography (GPC). The optimal tackifier system was screened out based on the core index of peel strength. Finally, the effects of the tackifier on the oil resistance and durability of the fluororubber/PTFE composite material bonding interface were systematically evaluated under simulated working conditions (lubricating oil immersion, thermal oxidation aging, etc.). The research provides theoretical and technical support for solving the interfacial bonding problems of fluorine-based composite materials.

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I. Introduction:

Fluorine rubber (FKM), as a core material in aviation sealing, has irreplaceable properties in extreme conditions due to its high-temperature resistance (up to 250°C for long-term use), chemical corrosion resistance, and elastic recovery ability [1-4]. However, when it serves at temperatures above 250°C for a long time, the degradation of the cross-linked network leads to a sharp increase in the compression set rate (up to 40%), resulting in a significant decrease in sealing contact stress. Meanwhile, polytetrafluoroethylene (PTFE) has a wide temperature stability range (-180 to 260°C) and a low friction coefficient [5], but its low surface energy (18.5 mN/m) and high crystallinity make it difficult to bond at the interface, and it is prone to creep failure under dynamic loads [6-8]. Therefore, constructing a FKM/PTFE composite material system is an ideal solution that combines medium resistance and creep resistance: the PTFE outer layer can prevent the erosion of thermal and oxygen media on the FKM main chain, while the three-dimensional network of FKM can inhibit the plastic deformation of PTFE [9-10]. However, as a typical difficult-to-bond material, PTFE faces severe challenges in surface activation and interface strengthening [11-16] - traditional sodium naphthalene chemical modification is banned due to toxicity, and although plasma or corona treatment can produce active sites, the surface activation life is only 10-15 minutes, which is difficult to meet the requirements of continuous industrial production [17].

To address these bottlenecks, this study focuses on developing an environmentally friendly interface composite technology with high active site density and long-term stability [18-20]. By introducing ionic liquid (ILs) functionalized acrylate tackifiers and combining with nitrogen ion implantation surface modification, a synergistic strengthening strategy is proposed: high-energy nitrogen ions bombard the PTFE surface to induce micro-region lattice distortion and chemical bond recombination, simultaneously forming stable -CF3 dipoles and increasing surface roughness; at the same time, a functionalized acrylate system containing 1-vinyl-3-butylimidazolium trifluoromethanesulfonate (VBImTFSI) is designed, and the ion-dipole interaction between the ionic liquid components and the active sites on the PTFE surface is utilized to achieve strong chemical adsorption. Through systematic research on the performance evolution of the composite material under 200°C thermal oxygen aging and long-term immersion in aviation lubricating oil (150°C), the long-term stability of the interface bonding is verified, providing a theoretical basis and process paradigm for the reliable service of aviation seals in extreme conditions. This research not only breaks through the environmental and life limitations of traditional modification technologies but also opens up a new path for the design of green and efficient composite materials.

II. Experimental and methods

2.1 materials

Polytetrafluoroethylene (PTFE) sheets with a thickness of 0.2 mm (NITOFLOON® no. 900UL, Nitto Denko, Japan) were cut into dimensions of 70 mm × 45 mm × 0.2 mm. The PTFE sheets were washed with acetone (99.5%, Kishida Chemical, Japan), and then rinsed with pure water in an ultrasonic bath (US-4R, AS-ONE, Japan) for 1 minute. The washed PTFE sheets were dried with pressurized nitrogen (99.99%, Iwatani Fine gas, Japan). Fluororubber (246M), hexafluorobutyl acrylate, ionic liquid.

2.2 Ion implantation treatment method

Before conducting the ion implantation treatment, the PTFE sample was ultrasonically cleaned with absolute ethanol and deionized water for 10 minutes each time, then dried and placed on the sample stage of the vacuum treatment chamber. The vacuum degree of the vacuum treatment chamber was reduced to below the set background vacuum degree. The flow rate of nitrogen gas was controlled by a mass flow meter, and the vacuum degree inside the treatment chamber was controlled by a hand-operated gate valve to be raised to approximately 1 Pa. Then, the high-voltage power supply was started to begin the experiment. The PTFE sample after cleaning was implanted with nitrogen ions at an energy of 10 keV, 15 keV, and 20 keV at an incident angle of 90°. After extraction, it was quickly sealed and properly stored.

2.3 Preparation method of tackifier

Under the protection of N2, in a 100 mL dry three-necked flask, acrylate hexafluorobutyl ester, ionic liquid (VBImTFSI) and 1%wt azobisisobutyronitrile were added successively and stirred for 0.5 h. After AIBN was completely dissolved, the temperature was raised to 80 ℃ and the reaction was carried out for 6 h. After the reaction was completed, the mixture was dissolved in ethyl acetate, then precipitated with methanol and washed three times. The polymer was obtained after vacuum drying at 65 ℃ for 10 h, which was colorless and transparent.

2.4 The preparation method of fluorine rubber

The compounded rubber is obtained through mechanical blending method. It mainly consists of three simple steps. In the first step, fluororubber (FKM) and 30 parts of carbon black filler (N990), 5 parts of zinc oxide, and 4 parts of TAIC are mixed and added to the plasticizing machine for blending for 5 minutes. Then, the fluororubber compounded rubber is transferred to the open-molding machine to adjust the roller distance to 1 mm, and mixed with 3 parts of adhesive (HFBA-VBImTFSI) in the vulcanizing machine for 10 times of flipping materials. After the blending is uniform, it is thin-wound 5 times, and triangular-shaped packaging is performed 6 times or more. The rubber sheet is placed for 4 hours for standby. In the second step, the rubber sheet after standby is thin-wound 5 times on the open-molding machine, and 3 parts of adhesive (HFBA-VBImTFSI) are slowly added on the open-molding machine. It is flipped 10 times, and then the blending is uniform. It is thin-wound 5 times again, and triangular-shaped packaging is performed 6 times or more. The roller distance is adjusted to 2 mm, and the rubber sheet is placed for 4 hours for standby. Next, the rubber compound is vulcanized for a period of time in a flat vulcanizing machine. The first vulcanization condition is 180 ℃ × 6 min. Then, it is vulcanized for a period of time in a forced drying oven. The second vulcanization condition is 230 ℃ × 4 h. After cooling, the rubber compound composite material is obtained.

2.5 The preparation method of fluororubber/PTFE composite materials

Place the modified PTFE onto the prepared rubberized sheet, and together with it, place it in the flat plate vulcanizing machine for one-stage vulcanization. Then complete the two-stage vulcanization in the oven. Here, the one-stage vulcanization is carried out at 180 ℃ and 14 MPa for 6 minutes; the two-stage vulcanization is conducted at 230 ℃ and atmospheric pressure for 4 hours. Thus, the PTFE/fluorine rubber composite material is obtained.

2.6 Adhesion measurement

According to the measurement in GB2792-2014, the above-mentioned PTFE/fluorine rubber composite material was cut into (25 mm × 200 mm) pieces. The specimens were measured on a universal testing machine at a speed of 300 mm/min. At least three samples were prepared and repeated for the specimens. The average value was taken.

2.7 X-ray photoelectron spectroscopy (XPS)

The elemental composition and chemical state of the material surface were characterized by using the ESCALAB Xi+ type X-ray photoelectron spectroscopy system. During the experiment, an extremely high vacuum environment of 8×10-10 Pa was maintained in the analysis chamber, and A1ka rays were used as the excitation source. In the data processing stage, the C1s characteristic peak at 284.6 eV was adopted for energy spectrum calibration to ensure the accuracy of the test results.

2.8 SEM

The surface morphology of the samples was analyzed by using Thermo Scientific Apreo 2C scanning electron microscope. Before the experiment, the pre-dried samples were fixed with conductive glue and the conductive performance of the samples was optimized through gold spraying process. During the test, the electron beam scanning technology under high vacuum environment was utilized to precisely characterize the microstructure of the material surface.

2.9 IR

The characteristic functional groups of acrylate polymer were characterized by Fourier Transform Infrared Spectroscopy (FTIR) using Thermo Scientific Nicolet iS5 instrument in attenuated total reflection (ATR) mode. Before the experiment, the polymer gel was dried to obtain a solid sample. The dried polymer dry gel was placed in the sample chamber, and the spectral resolution was set at 4 cm^{-1}. A total of 32 scans were performed, and the spectral acquisition range covered the mid-infrared region of 4000-400 cm^{-1}. This testing method directly acquires the vibrational information of chemical bonds on the material surface through the total reflection mode, and can complete the non-destructive analysis of the polymer molecular structure without complex sample preparation.

2.10 ^{1}HNMR

The nuclear magnetic resonance (NMR) structural analysis of polymers was accomplished by using the Bruker Avance NEO 600 NMR spectrometer. During the experiment, the polymer dry gel samples were dissolved in a deuterated chloroform solvent system, and the characterization was carried out by solution NMR technology. The test working frequency was set at 500 MHz.

2.11 Rubber vulcanization performance test

The vulcanization behavior of the compounded rubber was characterized by using the high-speed U-R-2030SD type vulcanization instrument. The experiment was set up with a constant temperature vulcanization condition at 180 ℃, with a test cycle of 6 minutes. The torque changes during the vulcanization process of the rubber compound were monitored in real time. Through quantitative analysis of key parameters such as the maximum torque increment (MH-ML), positive vulcanization time (t90), scorching time (TS2), and vulcanization rate index CRI, the vulcanization kinetics characteristics of the compounded rubber were systematically evaluated.

2.12 Oil resistance performance test

According to the experimental procedures stipulated in the national standard GB/T1690-2010, the oil resistance test was conducted on the standard vulcanized rubber specimens with a specification of 25×25 mm. The experimental process included immersing the specimens in 150 ℃ aviation lubricating oil for constant temperature soaking treatment for two periods of 7 days and 30 days respectively. Through the comparative analysis of performance parameters before and after the immersion, key indicators such as quality change rate, density fluctuation and volume expansion rate were systematically recorded. Subsequently, according to the standard mechanical testing methods, the tensile properties of the aged specimens were characterized, with a focus on the variation patterns of mechanical parameters such as tensile strength retention rate and elongation at break.

2.13 Thermal aging performance test

Under high-temperature conditions, rubber products are prone to performance deterioration due to thermal oxidation. Their high-temperature stability can be evaluated by thermal aging performance. In this experiment, the rubber compound samples were placed in a 250 ℃ hot air aging chamber and subjected to accelerated aging treatments for 3 days and 7 days respectively. Subsequently, according to the standard test procedures, the tensile properties of the aged samples were characterized using an electronic universal testing machine, and the key mechanical parameters such as tensile strength and elongation at break were systematically determined.

2.14 Mechanical property test

The mechanical property tests were conducted by using the UT-2080 electronic universal testing machine from GOTECH Company. According to the standard of GB/T528-1998, standard dumbbell-shaped specimens were prepared. During the testing process, a constant loading rate of 500 mm/min was maintained. This equipment is equipped with a gapless ball screw system and has functions of automatic zeroing, adaptive switching of stress-strain range, and multi-mode testing, which can meet the precise determination requirements of the tensile properties of polymer materials.

III. Results and Discussion

3.1 XPS of PTFE

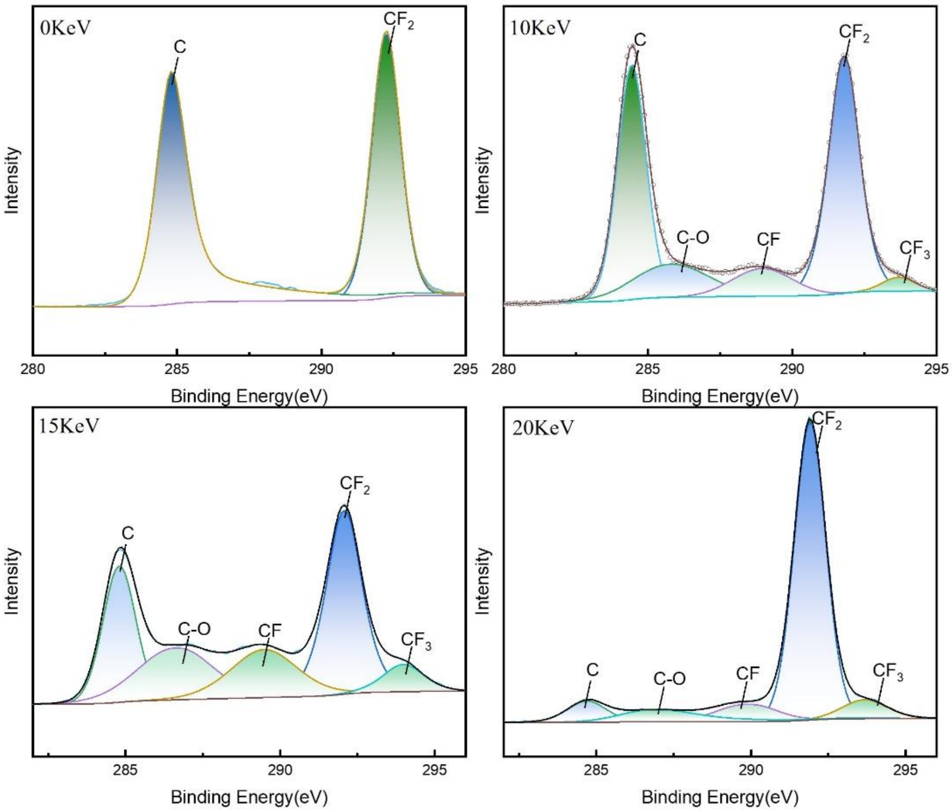

Figure 1 XPS spectra of PTFE samples with different ion implantation energies

(Table 1 Relative intensities of each C1s peak for PTFE samples with different ion implantation energies)

	Relative intensity(%) 0KeV	Relative intensity(%) 10KeV	Relative intensity(%) 15KeV	Relative intensity(%) 20KeV
CF_3 bond	0	2.35	7.14	6.57
CF_2 bond	55.05	40.16	34.25	71.17
CF bond	0	8.61	17.67	8.40
C-O bond	0	13.10	18.11	7.80
C bond	44.95	35.48	22.83	6.05

In order to verify the entire preparation and ion implantation process, X-ray photoelectron spectroscopy (XPS) was used to characterize the PTFE membrane materials in the preparation and implantation steps. The surface chemical element composition and chemical bonding of the implanted PTFE membranes were analyzed through XPS. Figure 1 shows the full spectra of XPS for four samples prepared by controlling different ion implantation energies. Table 1 represents the relative intensities of various C1s peaks. The observed C1s peaks are located at 293.5-294.0 eV for CF3 bonds, 292.2-292.5 eV for CF2 bonds, 289.8-290.4 eV for CF bonds, 286.7-288.1 eV for C-O bonds, and 284.3-284.7 eV for carbon bonds. The five chemical bonds are CF3, CF2, CF, C-O, and elemental C-C bonds. Nitrogen ion implantation destroys the CF2 and C-C bonds in PTFE. The formation of CF3 and CF bonds is due to chain breakage, de-fluorination, and reactions. The intensities of CF3, CF2, and CF bonds also change with the increase in ion energy. The intensity of CF3 bond increases first and then decreases with the increase in nitrogen ion implantation energy, while the CF2 bond decreases first and then increases with the increase in ion energy, and the intensity of CF bond increases first and then decreases with the increase in ion energy. As shown in Figure 2, with the increase in ion energy, chain breakage becomes more severe and the surface becomes rougher. As a typical long-chain polymer, the C-C bonds in the main chain of PTFE break preferentially under the action of the nucleus stop, releasing carbon atoms and generating free radicals. The formation of C-O bonds is attributed to the formation of alkyl radicals generated in a vacuum environment combining with oxygen in the air. Meanwhile, the surface roughening caused by the increase in ion energy will cause displacement of binding energy due to structural defects. With the increase in ion energy, the content of C-C bonds in the main chain changes significantly. In Figure 1, 0 KeV is 44.95%, then decreases to 22.83% at 15 KeV and 6.05% at 20 KeV in Figure 2. The results show that with the increase in ion energy, the C-C bonds in the main chain are gradually decreasing, indicating the generation of a large number of main chain breakages; with the increase in ion energy, the -CF3 bond shows a state of increasing first and then stabilizing.

3.2 SEM of PTFE

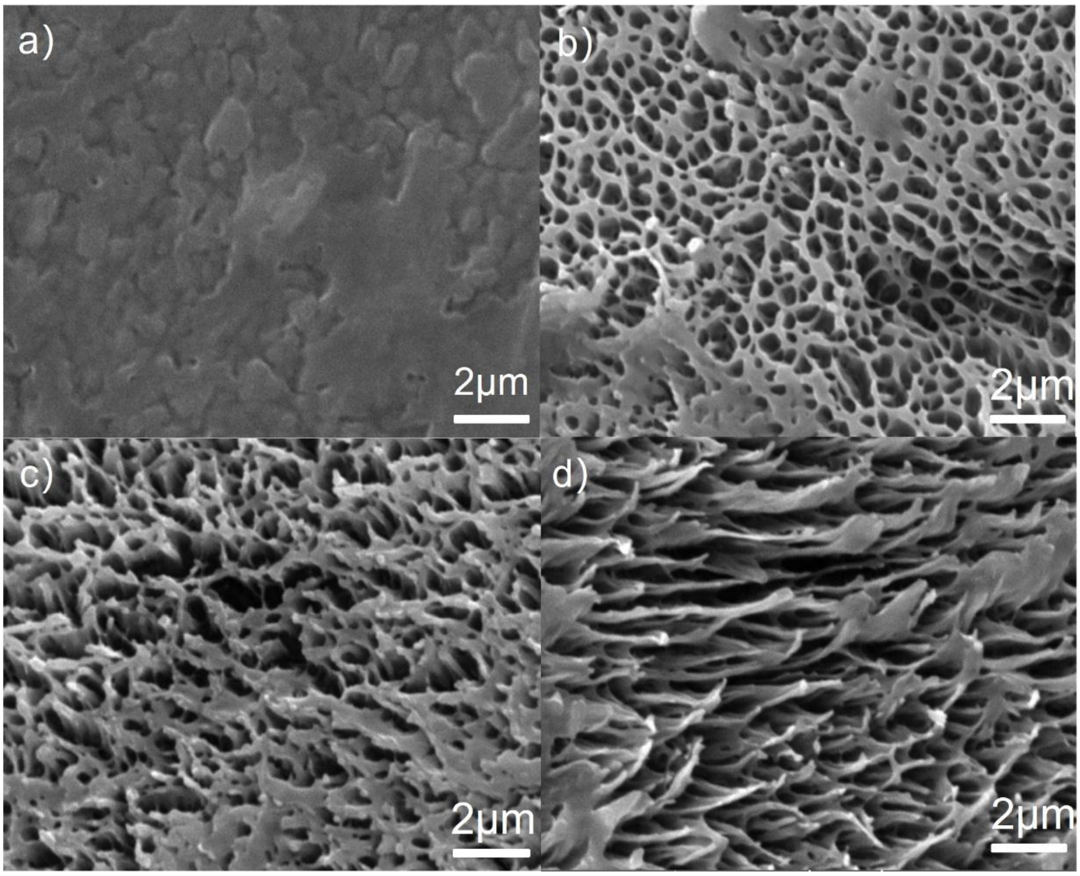

Figure 2 SEM images of ion injection energy of a) 0 keV, b) 10 keV, c) 15 keV, d) 20 keV

The morphology of PTFE after ion implantation was observed by scanning electron microscopy (SEM). The magnification of all SEM microscopic photos was 10,000. Figure 2 a) shows that the control sample with 0 keV displayed a very smooth surface. The morphology of the samples after implantation changed with the variation of ion energy. Figures 2 b)-d) show the morphology of PTFE samples implanted with 10-20 keV ions. From Figure 2 b), it can be seen that the surface of PTFE samples implanted with 10 keV nitrogen ions has a large number of large microfibers and large pores. It is pointed out that more main chains have been damaged by the incident nitrogen ions, and the surface has undergone heavy ion erosion. Figure 2 c) shows a similar morphology. The surface of the sample implanted with 15 keV nitrogen ions forms a large number of larger microfibers and larger pores. There is a significant heavy ion erosion effect on the surface, and more main chains have been damaged by the N ions. Figure 2 d) shows the maximum microfibers and pores formed on the surface of the PTFE sample implanted with 20 keV nitrogen ions. From Figure 2 d), it can be seen that during the N ion implantation process, the main chain breaks most severely, and the surface undergoes the most severe ion erosion in an instant. The void ratio on the surface is the largest. Figure 2 c) shows that the microfibers are very similar, although their sizes are different, due to ion erosion, they contract in the same direction. With the increase of ion energy, the size of ultrafine fibers increases, the number of main chain breaks increases, and the ion erosion effect intensifies. The scanning electron microscopy results indicate that the structural damage caused by lower ion energy implantation is relatively mild, mainly including slight main chain breaks and ion erosion; the structural damage caused by higher ion energy implantation is relatively deep, mainly including severe main chain breaks and ion erosion.

3.3 IR of PHV

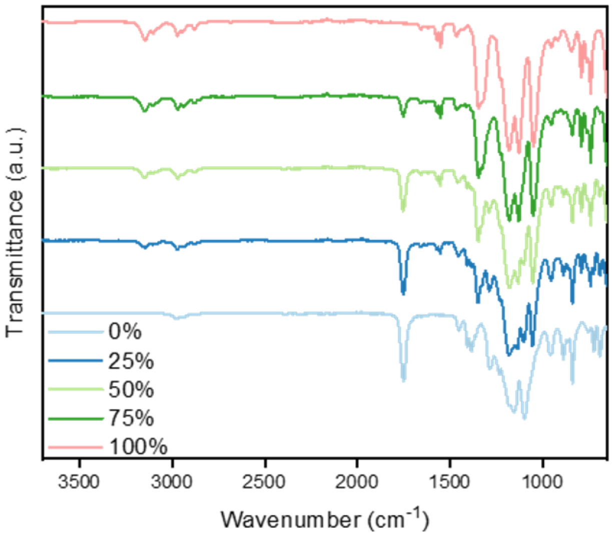

Figure 3 Infrared spectra of HFBA-VBImTFSI

The binary copolymer (HFBA-VBImTFS) obtained according to the above synthesis route was characterized by FT-IR. The results are shown in Figure 3. At 2976 cm-1, there are absorption peaks of methyl and methylene vibrations, with a small peak area, mainly originating from the hexafluorobutyl group in hexafluorobutyl acrylate; at 1742 cm-1, there is a C=O stretching vibration peak, and with the increase of ionic liquid content, the content of C=O is constantly decreasing, and the C=O stretching vibration peak is also gradually decreasing; at 3151 cm-1, there is a C-H vibration of the imidazole ring; with the increase of ionic liquid content, the content of imidazole increases, and the C-H vibration of the imidazole ring also gradually increases; at 1552 cm-1, there is a skeleton vibration of the imidazole ring, and with the increase of ionic liquid content, the skeleton vibration peak gradually increases; and no 1638 cm-1 peak corresponding to the C=C vibration absorption of hexafluorobutyl acrylate ester was observed, indicating that the polymerization was relatively complete.

3.4 ^{1}HNMR of PHV

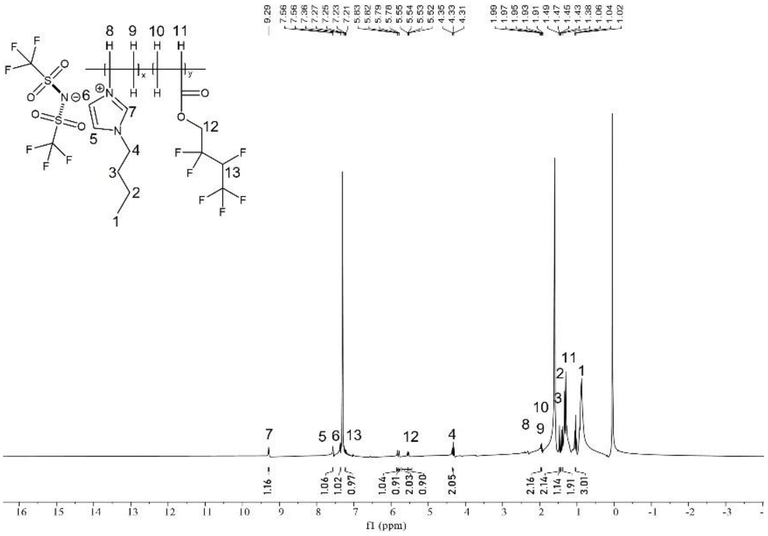

Figure 4 ^{1}HNMR spectra of HFBA-VBImTFSI

The FT-IR analysis of the binary copolymer (HFBA-VBImTFS) was not sufficiently effective. To further verify whether the ionic liquid monomers have copolymerized successfully, 1H-NMR was adopted for further structural analysis. The 1H-NMR hydrogen spectrum of the binary copolymer (HFBA-VBImTFS) is shown in Figure 4, which represents the 1H-NMR spectrum of the binary copolymer (HFBA-VBImTFS). The chemical shifts of the methylene and methylene hydrogen atoms on the main chain of the tackifier correspond to 1.45 ppm and 1.95 ppm, respectively. The hydrogen atoms on the side chain containing fluoromethylene and connected to the ester group correspond to 6.73 ppm and 5.82 ppm, respectively. The chemical shifts of the hydrogen atoms on the imidazole ring at 7.56 ppm and 7.36 ppm correspond to the chemical shifts of the 5,6 hydrogen atoms on the imidazole ring. The chemical shift of hydrogen atom 7 at 9.29 ppm corresponds to the chemical shift caused by the solvent CDCl3. The results further verified the successful copolymerization of the binary copolymer (HFBA-VBImTFS).

3.5 Test of Fluorine Rubber Vulcanization Performance

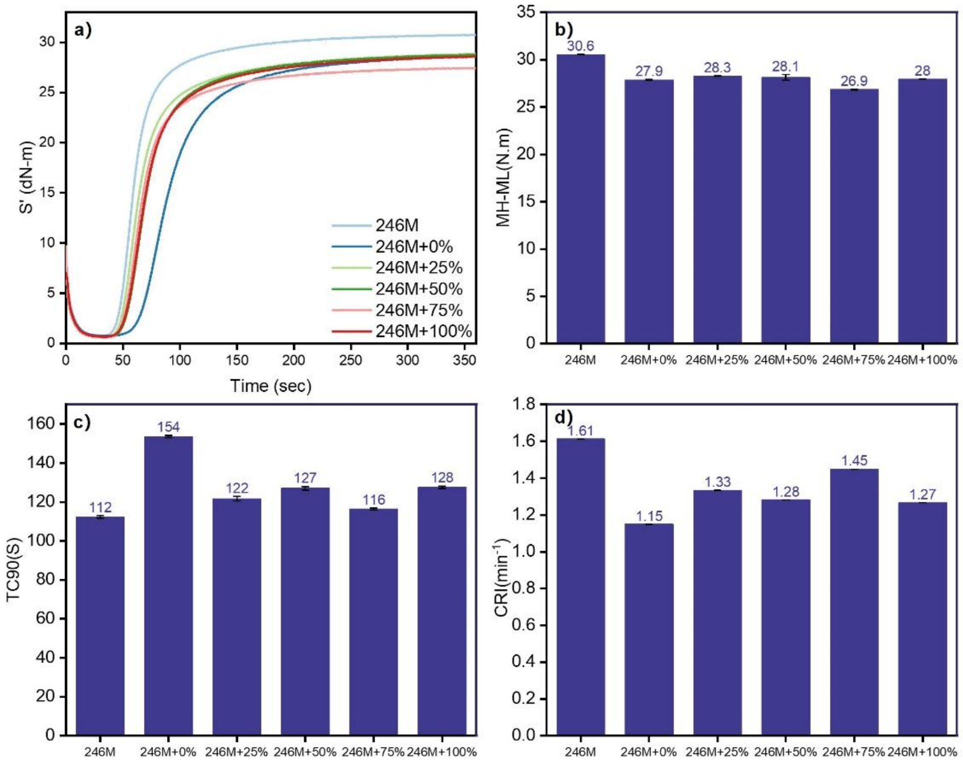

Figure 5 vulcanization characteristic diagram of fluorine rubber compound :a) vulcanization characteristic curve b) incremental torque MH-ML c) normal vulcanization time t90 d) vulcanization speed CRI

The vulcanization performance of fluorine rubber is an important indicator for evaluating its comprehensive performance. Figure 5 shows the influence mechanism of different acrylate tackifiers on the vulcanization behavior of fluorine rubber. From the vulcanization characteristic curve in Figure 5 a), it can be seen that the fluorine rubber without the addition of tackifiers exhibits a faster vulcanization rate. This may be due to the ester groups in the tackifier molecules capturing the peroxide free radicals during vulcanization [21], while the vulcanization mechanism of fluorine rubber relies on the cross-linking reaction initiated by the activation of free radicals by double bonds [22], resulting in a decrease in the concentration of free radicals and delaying the vulcanization process. The incremental torque analysis in Figure 5 b) shows that the unmodified system exhibits a higher final torque value, indicating that the introduction of tackifiers not only delays the kinetics of the vulcanization reaction but also significantly reduces the density of the cross-linked network. The positive vulcanization time data in Figure 5 c) and the vulcanization rate curve in Figure 5 d) further support this phenomenon. The vulcanization rates of all tackifier systems show a varying degree of decline, reflecting the intrinsic correlation between the availability of free radicals in the reaction system and the cross-linking efficiency. It is worth noting that this inhibitory effect is similar to the intervention behavior of reactive groups in reactive polymer systems on the vulcanization process [23], reflecting the competitive influence of oxygen-containing functional groups in the tackifier molecules on the free radical vulcanization mechanism.

3.6 Mechanical properties of fluororubber

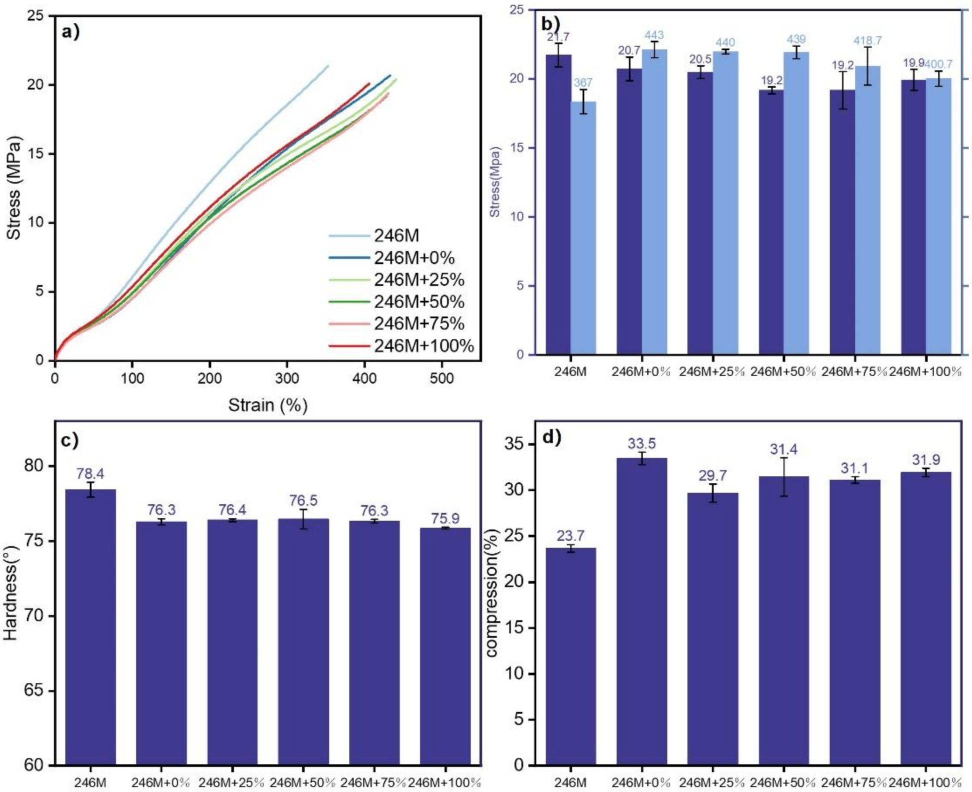

Figure 6: Mechanical properties test chart of fluorine rubber compound

Mechanical properties are the key indicators for evaluating the practical application value of rubber materials. Through systematic analysis and research on the influence of different molecular structure tackifiers on the mechanical behavior of rubber composites, as shown in Figure 6, the tensile properties, hardness, and compressive permanent deformation of vulcanized rubber were measured. From the stress-strain curves as shown in Figure 6 a) and b), it can be seen that after adding different molecular structure tackifiers, the tensile strength of vulcanized rubber shows a slight downward trend (overall maintained at 20 MPa), while the elongation at break significantly increases (from 367% to 430%). This phenomenon may be related to the inherent elastic properties of the tackifiers: although the introduction of the tackifiers does not cause excessive softening of the material, the flexibility of the molecular chains of the tackifiers may weaken the rigid network structure of the rubber matrix [24]. In addition, the polar groups such as ester groups in the tackifiers may interfere with the formation of the rubber crosslinking network through radical action [23], resulting in a decrease in crosslinking density and thus affecting the material strength; the Shore A hardness of vulcanized rubber shows a downward trend with the increase in the content of tackifiers, which is consistent with the trend of tensile strength (Figure 6 b). The decrease in hardness indicates a weakening of the material rigidity, which may be related to the plasticization effect of the tackifier molecular chains and the loosening of the crosslinking network. The compressive permanent deformation significantly increases (from 23.7% to 31.0%) as shown in Figure 6 d), further confirming the decrease in crosslinking density. The reduction of crosslinking sites leads to a weakened elastic recovery ability of rubber under compressive stress, directly affecting the sealing performance.

When the content of ionic liquids in the tackifiers changes, the mechanical properties show a nonlinear response: when the content of ionic liquids is higher than 50%, the cohesive energy of the tackifiers increases, resulting in a decrease in the uniformity of tackifier dispersion, manifested as an increase in the standard deviation of tensile strength. When the content of ionic liquids is 25%, the material shows the best comprehensive performance balance, with stable tensile strength (20.5 MPa), moderate elongation at break (440%), and compressive permanent deformation of 29.7%. Under this condition, the tackifiers are uniformly dispersed and the negative impact on the vulcanization process is minimized.

3.7 Adhesion measurement of fluororubber/PTFE composite materials

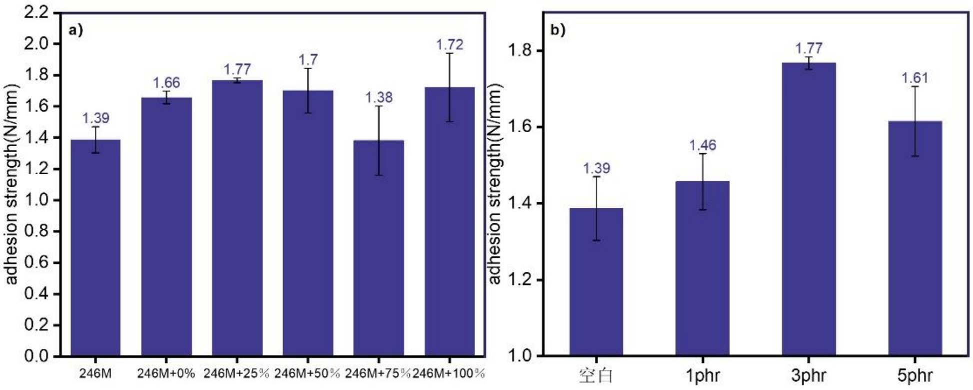

Figure 7 a) peeling strength of different tackifying agents of fluoro rubber /PTFE composites, b) peeling strength of different adding parts of tackifying agents of fluoro rubber /PTFE composites

The adhesive performance is a key property of adhesives. Figure 7a) shows the influence of different types of adhesive functional additives on the bonding strength of fluororubber-PTFE. From the figure, it can be seen that the effect of different contents of ionic liquid-based adhesives on the bonding strength is inconsistent. This is mainly because the influence of different contents of ionic liquid-based adhesives on the interface of fluororubber-PTFE is different. Compared with the control group, the bonding strength of fluororubber-PTFE increased from 1.39 to 1.77 N/mm after adding the adhesive. Among them, the adhesive provides sites for the interface, which is the main factor affecting the bonding strength of fluororubber-PTFE. The adhesive may have several effects at the interface. On the one hand, the HFBA monomer has a strong adsorption energy for PTFE; on the other hand, the addition of ionic liquids, using the ionic dipole effect of VBImTFSI on the increased -CF_3 on the modified PTFE surface, increases the bonding strength to a certain extent. With the increase of ionic liquid content, the bonding strength improves to a certain extent.

Figure 7b) shows the influence of different addition ratios on bonding when the ionic liquid content is 25%. When the addition ratio is 1 phr, the peel strength increases to 1.46 N/mm. The increase in peel strength is limited because the distribution of the adhesive on the fluororubber surface is limited, so the improvement of the bonding performance of the rubber is limited. When the addition ratio is 3 phr, the peel strength increases to 1.77 N/mm; when the addition ratio is 5 phr, the peel strength increases to 1.61 N/mm. When the addition amount reaches 3 phr, increasing the addition amount does not improve the peel strength. When the amount of the adhesive is excessive, the self-polymerization of the adhesive increases its own adsorption, resulting in a decrease in peel strength. Therefore, when the addition amount is 3 phr, it is the most appropriate.

3.8 Oil resistance performance test of fluororubber/PTFE composite materials

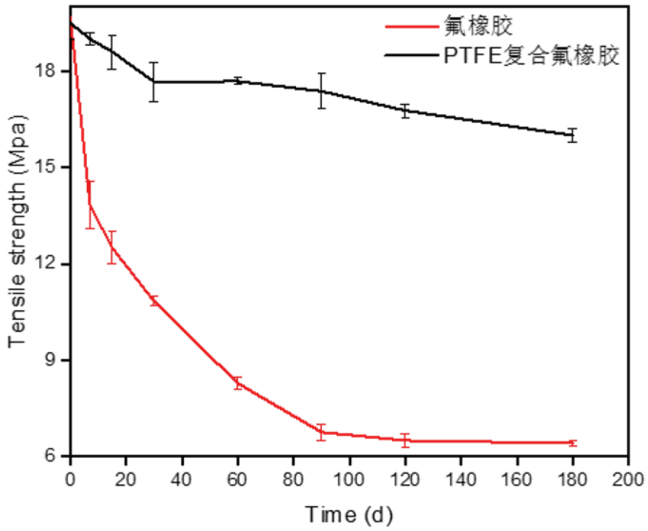

Figure 8 Relationship between strength change of fluorine rubber and PTFE composite fluorine rubber and test time in lubricating oil medium

This study compared the evolution patterns of tensile properties of fluorine rubber composite materials coated with PTFE and unmodified fluorine rubber in high-temperature oil medium, revealing the mechanism of oil aging resistance of the materials. As shown in Figure 8, the initial tensile strengths of PTFE composite fluorine rubber and conventional fluorine rubber were 19.5 MPa and 19.7 MPa respectively, showing similar mechanical properties. After 7 days of high-temperature oil immersion, the strength retention rate of PTFE composite material reached 97.44% (19 MPa), while the strength of conventional fluorine rubber significantly decreased to 10.26 MPa, with a reduction of 47.92%. With the aging time extended to 180 days, the strength retention rate of conventional fluorine rubber dropped to 32.08%, in contrast, the retention rate of PTFE fluorine rubber composite material still reached 77.44%, verifying the protective effect of PTFE/fluorine rubber composite materials on material properties.

This difference stems from the differences in aging mechanisms of the two materials: in the initial aging stage (0-7 days), high temperature enhances the activity of rubber molecular chains, and small molecules in the oil medium penetrate the matrix through diffusion, causing the disentanglement of physical cross-linking points and weakening of the filler-matrix interface. At this time, the strength attenuation of conventional fluorine rubber is mainly dominated by physical aging. The physical barrier formed by PTFE film effectively slows down the penetration rate of the oil medium, and the initial strength decline of the composite material is controlled at 2.56%. With the extension of time to 30-180 days, conventional fluorine rubber enters the chemical aging dominated stage, where the continuous penetration of the oil medium triggers the side chain breakage and main chain degradation of the macromolecular chains, and the dissolution of inorganic fillers exacerbates the formation of internal defects in the material. In contrast, PTFE fluorine rubber composite materials, due to the blocking of the exchange between oil and rubber substances, their strength attenuation mainly results from the thermal decomposition of molecular chains caused by high temperature, and even a strength recovery phenomenon was observed as early as 90 days. It is speculated that this is related to the secondary cross-linking recombination of broken molecular chains. This result is consistent with the multi-stage aging theory proposed in the literature [25], confirming that PTFE/fluorine rubber composite materials can effectively inhibit the cross-link network damage and filler migration caused by oil medium.

IV. Conclusions

This research focuses on the optimization of the interface bonding performance of fluorine rubber and PTFE composite materials. Through a systematic study combining surface modification technology and the development of tackifiers, a breakthrough in the comprehensive performance of the composite materials has been achieved. The research conclusions can be summarized as follows:

(1) The interface regulation mechanism of nitrogen ion injection modified PTFE. By regulating the nitrogen ion energy (10-20 keV) and injection dose, the chemical bond reorganization and morphology optimization of the PTFE surface were realized. The injection of 15 keV energy can increase the rate of C-C bond breakage on the PTFE surface to 49.21%, and form a micron-scale fiber-pore composite structure.

(2) The multi-scale synergistic effect of ionic liquid tackifiers. A 25% ionic liquid (HFBA-VBImTFSI) acrylate tackifier was synthesized. Through the intermolecular ionic dipole interaction and the formation of -CF3 groups on the modified PTFE surface, a strong adsorption interface was formed. This tackifier increased the peel strength of fluorine rubber and PTFE from 1.39 N/mm to 1.7 N/mm, while maintaining the mechanical properties of fluorine rubber (tensile strength 21 MPa, elongation at break 430%).

This research achieved a breakthrough in the interface bonding bottleneck of fluorine rubber/PTFE composite materials through the collaborative strategy of nitrogen ion injection surface engineering and tackifier molecular design, providing theoretical support and technical paths for the high-reliability design of aerospace sealing materials.

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