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Modification of NBR Surface by Low Energy and High Current Ion Implantation

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Abstract: Acrylonitrile-Butadiene Rubber (NBR) is one of the widely used synthetic rubbers currently used for a variety of non-tire rubber products. Ion implantation is foreseen to be an efficient way to improve the NBR surface characteristic such as lower coefficient, higher resistance. Ion implantation with N^+ and H^+ ions was carried out to treat NBR surface to understand the irradiation influence on functional properties of the vulcanizates, like friction and hardness on Peking University (PKU) ion source test bench recently. Analysis on friction coefficient, hardness, thermal aging resistance, tribology and wear resistance were done after ion implantation.

Key words: Acrylonitrile-Butadiene rubber; ion implantation; surface modification

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1 Introduction

Acrylonitrile-Butadiene Rubber (NBR) is one of the widely used synthetic rubbers currently which is mainly used for a variety of non-tire rubber products, such as hoses, seals, tape and other oil resistance products[1]. With the development of the oil and automobile industries, the surface of NBR is expected to have much more excellent properties such as higher wear resistance and anti-aging ability, and so on. Traditional chemical surface modification methods are unable to meet the requirements of industrial application. Ion implantation has been proven to be greatly potential in modifying the mechanical and tribological properties of polymers.

Right now, ion implantation has been widely used in the area of semiconductor, and there are also numerous researches on ion implantation modifying surface properties of metal. However, knowledge on effects possible to obtain for amorphous elastomers remains unexplored[2]. It is truly unclear why so important materials as rubbers are forgotten by ion-beam scientists, especially if one takes into account very interesting possibilities offered by ion irradiation in these materials *e.g.* a tremendous decrease in friction coefficient[3]. Among all radiation techniques which include γ rays, electron and ion beams, ion beams are particularly efficient because they offer the highest attainable densities of energy losses[4]. Roche *et al.*[5] implanted nitrogen ions into HNBR and got an apparent smoother surface although slightly wrinkled. Katzenberg researched strain-induced self-organization of elastomer surfaces irradiated by ions and electrons. From the viewpoint of chemical bonds, he proposed a dynamic equilibrium of "cross-linking" and "chain-scission" which results in a compressive strain in the irradiated surfaces, leading to the undulation of elastomer surfaces[6].

In this work, N^+ and H^+ ions with different energy and doses were implanted into the surface of NBR. The micromorphology, friction coefficient, wear resistance, element contents of surface and hardness in different injected energy and doses were tested before and after ion implantation.

2 Experiment setup

The NBR used for ion implantation was provided

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by Anhui Zhongding Holding (Group) Co., LTD. For ease of ion implantation, the geometry of NBR was prepared in circle. The implantation of N^+ and H^+ ions was carried out on PKU ion source test bench. Fig. 1 shows the details of PKU ion source test bench, which is composed of 2.45 GHz ECR (electron cyclotron resonance) ion source, an emittance measurement device and a target plate[7]. PKU ion source can produce more than one hundred mA H^+, dozens of mA N^+ and other ion beam with energy from 25 keV up to 55 keV. The emittance meter has ability to give out the total extracted beam current, beam emittance and beam distribution at the same time. The target plate is specific designed for sample treatment. Special bypass vacuum design associated with a valve cuts the sample changing period from 4 h to 10 min. The target plate is isolated from ground, which can not only reduce the beam energy to several hundred electron volts but also increase ion energy up to 80 keV.

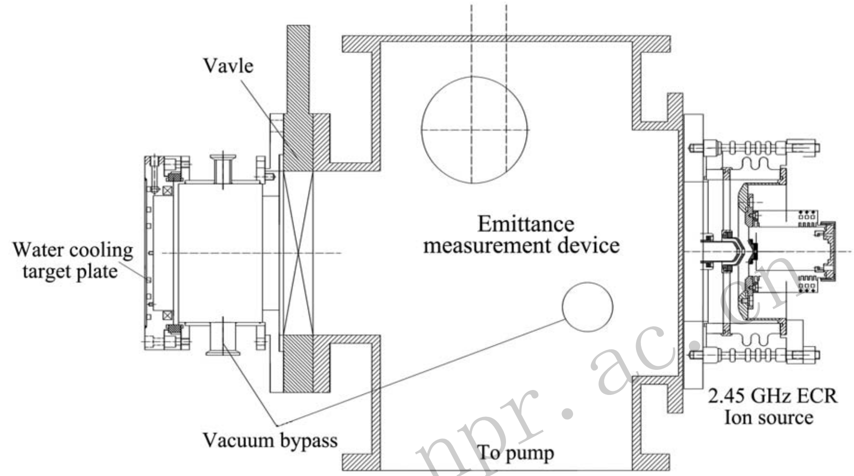

Fig. 1 PKU ion source test bench.

The morphology of NBR before and after ion implantation was scrutinized by scanning electron microscopy (SEM). The friction coefficient was tested by Anhui Zhongding Holding (Group) Co., LTD following the standard of HG/T 2729-2012. EDX (Energy Dispersive X-Ray Spectroscopy) was used to test the element contents of surface before and after ion implantation. The wear properties were tested on abrasion tester which has a wear range of 40 m and the normal load is 10 N. Thermal aging tests (100 ℃/70 h) were carried out in the aging oven. The hardness was tested by hardness tester (Shore M).

3 Surface analysis results

3.1 Surface morphology

Fig. 2 gives a micrograph of the NBR surface before implantation. The surface is undulant and rough, and apparent mineral fillers are visible. Fig. 3 shows the surface of NBR which is implanted using nitrogen ions up to the energy of 30 keV and dose of 3×10^{16} cm^{-2}. The mineral fillers are disappeared and the surface becomes apparent smoother although slightly wrinkled. Apparent patch network can be observed in the micrograph. These phenomena are similar to the results got by Roche *et al.*[5] Random crack network is a typical feature of hard coatings deposited on soft and flexible substrates such as rubber and polymer[8].

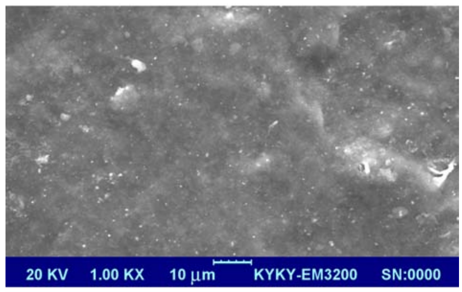

Fig. 2 Surface morphology of unimplanted NBR.

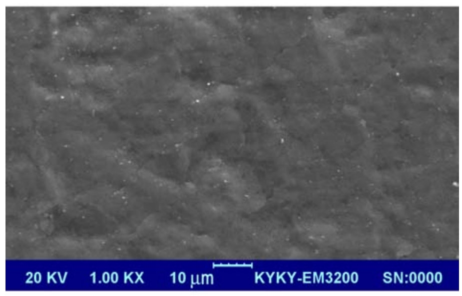

Fig. 3 Surface morphology of NBR treated with implantation of nitrogen ions (30 keV, 0.3×10^{17} cm^{-2}).

Jagielski *et al.*[3] studied the hydrogen loss from elastomers subjected to ion irradiation and found that the inelastic collision of injected ions and electrons can result in hydrogen leaving from the surface of elastomers. Except for the equilibrium of "cross-linking" and "chain-scission" given by Katzenberg[6], the wrinkle and patch network observed in the surface of irradiated NBR may also be explained by the fact that hydrogen leaves from the surface of NBR which produces compression strain during ion implantation. What's more, the substrate is partly heated and dilated, and then shrinks when cooling down while the top layer has a lower coefficient of thermal expansion, leading to the upper layer crackled.

Fig. 4 shows the surface of NBR which is implanted using nitrogen ions up to energy of 40 keV and dose of 1.0×10^{17} cm^{-2}. Compared with the surface shown in Fig. 3, this surface seems to be polished and much flatter with the increase of energy and dose. According to the analyses above, this is probably due to the fact that the "cross-linking" and "chain-scission" become intense and the hydrogen loss gets nearly saturated which makes the surface more compression with the growth of energy and dose.

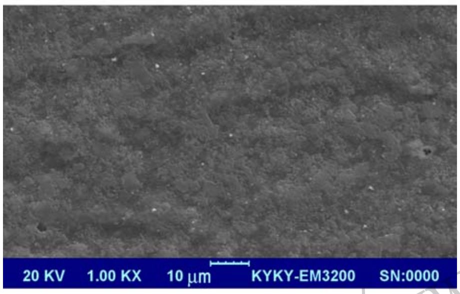

Fig. 4　Surface morphology of NBR treated with implantation of nitrogen ions (40 keV, 1.0×10^{17} cm^{-2}).

3.2　Tribology and wear resistance

The tribological feature of NBR is greatly improved by ion implantation. The friction coefficient of unimplanted NBR is 0.267 while that of the treated samples with N^+ ions is 0.097, which has a great reduction of about 64%. The reason why the friction coefficient is greatly reduced can be inferred from the SEM observation. Ion implantation gets the surface polished and the flatness is greatly improved. With the increase of energy and dose, the injected ions react with the macromolecules intensely and the surface is probably carbonized to some degree, which may lubricate the surface.

In order to evaluate the influence of ion implantation on the wear resistance of NBR surface, wear resistance tests of unimplanted NBR and NBR treated with nitrogen ions up to energy of 40 keV and dose to $0.2\times10^{17}cm^{-2}$ were performed. Table 1 details the volume loss of NBR before and after nitrogen ion implantation.

Table 1　The volume loss of unimplanted NBR and NBR treated with nitrogen ions by wear test.

Items	Unimplanted			N^+(40 keV, 2×10^{16} cm^{-2})		
	A_1	A_2	A_3	B_1	B_2	B_3
Vs/cm^3	2.5128	2.5042	2.5256	2.5437	2.5233	2.4915
Vt/cm^3	2.2479	2.2547	2.2751	2.2734	2.2444	2.2603
Density/$(g/cm)^3$		1.342			1.334	
$\Delta V/cm^3$	0.197	0.186	0.187	0.203	0.209	0.173
$\overline{\Delta V}$ cm^3		0.190			0.195	

We took three samples from the unimplanted and implanted NBR respectively. Vs represents the volume before test while Vt is the volume after wear test. ΔV represents the variation of the volume after wear test. $\overline{\Delta V}$ is the average of ΔV. The results show that the wear resistance of NBR treated with nitrogen ions is similar to unimplanted ones even a little worse. This is probably caused by the plasticizer leaving the surface of NBR during ion implantation, which has an influence on the ductility and flexibility of the rubber.

3.3　Surface analysis

EDX (Energy Dispersive X-Ray Spectroscopy) analysis of NBR samples before and after implantation was carried out. Fig. 5 shows the weight percentage of surface elements of unimplanted NBR and NBR treated with nitrogen ions in various energy and doses. The injected nitrogen ions mainly influence the content of C, N and O. When the nitrogen ions are implanted with the energy of 40 keV, the N content of the surface is higher than that of unimplanted NBR. However, the N content of the surface is lower than that of unimplanted NBR when the nitrogen ions are implanted with the energy of 30 keV. The reasons why the N content is different in different injected energy need to be further studied. There is nitrile (-CN) in the macromolecules of NBR, which may react with the injected nitrogen ions resulting in the change of N content. According to the simulation of SRIM, the projected range of nitrogen ions with energy of 40 keV in NBR is about

170 nm whereas the electron beam to excited X-Ray can penetrates up to micron depth. So, the EDX not only tests the elements of the implanted surface but also elements of part substrates. No matter what the energy and doses are, the O content of implanted samples is always higher than that of unimplanted NBR indicating that the samples were oxidized during implantation. Jagielski *et al.*[9] thought that the release of hydrogen from organic materials often results in the oxidation of the surface layer.

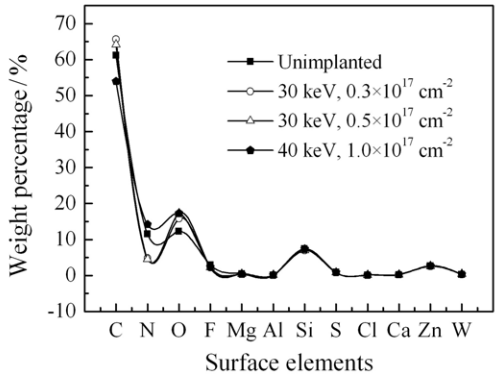

Fig. 5 Chemical composition of NBR before and after implantation with nitrogen ions in different energy and doses.

3.4 Hardness

The modification of hardness has relationship with the energy and doses of injected ions. Fig. 6 shows the hardness curves of NBR treated by hydrogen ions with doses of 2×10^{15}, 5×10^{15}, 1×10^{16}, and 2×10^{16} cm^{-2}. It is clear that the hardness of NBR treated with hydrogen ions is higher than that of unimplanted samples. What's more, the hardness increases with the increase of injected energy. And the hardness increases with the decreasing doses of injected ions when the injected energy is constant. The results are beneficial for industrial applications of ion implantation, for the

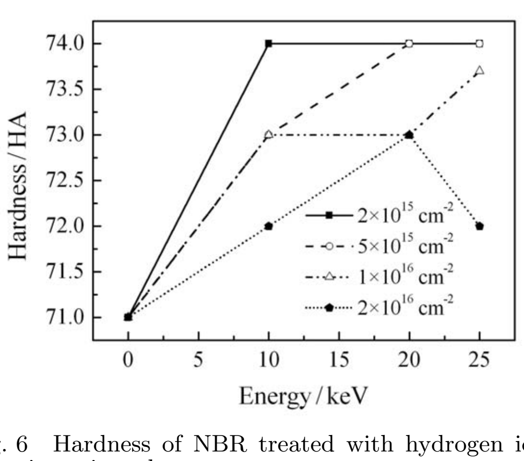

Fig. 6 Hardness of NBR treated with hydrogen ions in various doses.

NBR can get higher hardness while the treatment time is shorter. Bielinski *et al.*[10] made a research about improving hardness of several kinds of polymers by implantation of He^{+} and Ar^{+} ions, and found that the light He^{+} ions are the most efficient to make the surface layer harder, which is probably the result of additional crosslinking of macromolecules[10]. It may have relationship with the crosslinking of macromolecules that implanted hydrogen ions can improve the hardness of NBR. And the crosslinking of macromolecules of NBR seems easy to occur when the injected energy is higher and the doses are lower.

Thermal aging may influence the modification of ion implantation. Fig. 7 shows the hardness increments of NBR treated with various ion doses after thermal aging. It is obvious that the hardness increment of NBR treated with hydrogen ions is smaller compared with unimplanted one. And the hardness increment decreases with increasing energy. Under the same injected energy, the hardness increment decreases with decreasing doses. Integrated with Fig. 6, it is obvious that injected hydrogen ions with higher energy and lower doses not only improve the hardness of NBR but also enhance the thermal aging resistance.

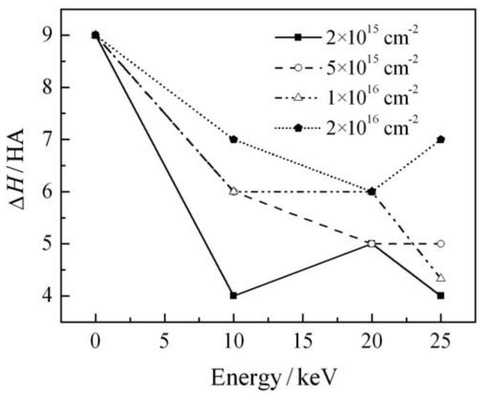

Fig. 7 Hardness increment of NBR treated with hydrogen ions in various doses after thermal aging.

4 Discussion and outlook

Ion implantation modifies the surface of NBR greatly. Wrinkle and patch network can be observed by implanting nitrogen ions with lower energy and doses. The formation of wrinkle may have relationship with the "cross-linking" and "chain-scission". And hydrogen release as well as part deformation of substrate due to heating up results in the patch network. When the energy and doses of injected nitrogen ions are higher, the surface of NBR seems to be polished and becomes much flatter, which may lead to an about 64% reduction of friction coefficient. Nitrogen ions implantation has little influence on the wear resistance.

The injected nitrogen ions react with nitrile of NBR molecules, which may change the N content. And the reaction mechanism needs further studies. Injected hydrogen ions with higher energy and lower doses improve the hardness as well as the thermal aging resistance of NBR, which is beneficial for the industrial application of ion implantation. It has a great significance that ion implantation improves the surface properties of NBR although many mechanisms are still unclear. More studies will be carried out in the near future.

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低能强流离子注入丁腈橡胶的表面改性

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摘要： 丁腈橡胶是一种广泛使用的合成橡胶，目前应用于各种非轮胎制品。离子注入被认为是一种提高丁腈橡胶表面特性的有效手段，比如降低摩擦系数、提高耐抗性等。最近，为了理解辐照效应对于硫化橡胶的功能特性如摩擦系数和硬度等的影响，利用北京大学离子源测试平台将 N^+ 和 H^+ 注入丁腈橡胶表面进行研究。离子注入完成以后，对丁腈橡胶表面的摩擦系数、硬度、耐热老化性能、摩擦特性以及耐磨损性能进行了分析。

关键词： 丁腈橡胶；离子注入；表面改性

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