CHEMICAL ENGINEERING TRANSACTIONS
VOL. 59, 2017
A publication of AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet
Guest Editors: Zhuo Yang, Junjie Ba, Jing Pan

ISBN 978-88-95608- 49-5; **ISSN** 2283-9216
DOI: 10.3303/CET1759028

Swelling Properties of Nitrile-butadiene Rubber with Different Acrylonitrile Content in Isopropyl Nitrate

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Nitrile-butadiene rubber is the sealing material of isopropyl nitrate; however, leakage or vaporization phenomena frequently occur. In order to analyze the causes of leakage and volatilization and study on the various properties of nitrile-butadiene rubber after the swelling of isopropyl nitrate, the author prepared nitrile rubber which contained 20%, 30% and 40% of acrylonitrile respectively, the quality and volume change rate, surface topography, organization structure, mechanical properties of the swollen nitrile rubber were tested separately. The results showed that the mass and volume of nitrile-butadiene rubber increase greatly after swelling; The higher the acrylonitrile content is or the higher the temperature is, the more obvious the swelling effect will be; Small molecules like plasticizers in nitrile-butadiene rubber will be precipitated during swelling process; The mechanical properties of the nitrile rubber decrease severely after swelling. The main cause of swelling lies in the similarity of polarity between NBR and isopropyl nitrate, and it becomes hard for the nitrile rubber to meet the sealing requirements.

1. Introduction

Single-soldier FAE is a novel kind of high energy ammunition, which functions to cause damage by over-pressure shock wave and high temperature caused by fuel explosion (Song et al., 2007; Wan et al., 2013).The FAE equipped in the projectile is the mixture of isopropyl nitrate and magnesium powder, sealed with nitrile butadiene rubber as the sealing material. In long-term storage, it is unavoidable for the isopropyl nitrate in FAE to have contact with the sealing material, nitrile rubber, resulting in the frequent leakage and volatilization of isopropyl nitrate, thus exerting adverse effects on the quality and performance of the munitions (Chen et al., 2014). In addition, as isopropyl nitrate is a colorless, pungent and toxic liquid, its volatile gas also does harm to the managers of the ammunition depots (Wang et al., 2012). Therefore, to study the swelling properties of nitrile butadiene rubber in isopropyl nitrate is of great significance to improving the quality of ammunition.

Due to NBR's application as sealing rubber, a great deal of experimentation has been done at home and abroad to study its solvent resistance. Choi and Ha, (2009) has studied on the influence of swelling temperature and acrylonitrile content on water resistance of NBR containing Silicon Dioxide, with the results showing that the swelling ratio of NBR in water grows with the increase of temperature and acrylonitrile content; Lv et al., (2015) has studied on the swelling properties of nitrile butadiene rubbers with different contents of acrylonitrile in cyclohexane, with results indicating that the performance of NBR has been reduced in all respects after being immersed in cyclohexane, and the swelling ratio of nitrile rubber in cyclohexane becomes lower with the increase of acrylonitrile content. Three kinds of nitrile butadiene rubber are prepared in the experiment of this paper. After three kinds of NBR being immersed in isopropyl nitrate respectively, tests will be carried out on the nitrile rubber soaked for different time periods to study on their quality and volume, mechanical properties, infrared spectrum and thermal decomposition, to find out the influences of acrylonitrile contents on NBR's swelling properties in isopropyl nitrate.

2. Experimental

2.1 Test materials and instruments

NBR DN401, NBR 1051, NBR 1052 of Zeon Inc., Japan; N774 carbon black, N550 carbon black, Quanzhou

Please cite this article as: Lili Wu, Yukui Ding, Jianwei Zhen, Qian Zhang, Siyang Chen, 2017, Swelling properties of nitrile-butadiene rubber with different acrylonitrile content in isopropyl nitrate, Chemical Engineering Transactions, 59, 163-168 DOI:10.3303/CET1759028

Shengda Rubber and Plastic Co., Ltd.; dioctyl phthalate (DOP), Shanghai Lingfeng Chemical Reagent Co., Ltd.; zinc oxide, Guangzhou Zhanfei Chemicals Co., Ltd.; auxiliary agents like vulcanizer, Jiangsu Haixing Chemical Co., Ltd.; isopropyl nitrate (IPN), Yichang Xiangrong Chemical Co., Ltd.

LN - 10 Internal mixer, Shanghai Rubber Machinery Factory; SK - 160B open mill, Changzhou No.1 Rubber & Plastic Equipment Factory; plate vulcanization apparatus, XQLB-350 ×350, Shanghai Rubber Machinery Factory; universal tensile testing machine, Model CMT4104 , Shenzhen Xinsansi Experimental Instrument Factory; Electric heating constant temperature blast drying oven, DHG-9146A, Shanghai Shengxin Scientific Instrument Company; electronic analytical balance, CP-214, Shanghai Puchun Electronic Equipment Co., Ltd.; scanning electron microscope, Model S-4800, Hitachi Ltd.; infrared spectrometer, NICOLET6700, Thermo Nicolet Corporation, the USA.

2.2 Preparation of Samples

After plastic practice on raw rubber, various ingredients such as complexing agents were added and the mixture was put into the internal mixer. After being completely mixed, it was put into the open mill to form sheets. Then it went through the process of vulcanization under the condition of 160□ and 10 MPa. According to this process, the nitrile rubber with acrylonitrile content of 20%, 30% and 40% was produced respectively, called N20, N30 and N40. Take N20 as an example, the components and contents of which are shown in Table 1 below.

Table 1: The main components and content of N20 and their mass fractions

Materials	Fractions	Mass/g	Materials	Fractions	Mass/g
DN401	100	0.500	DOP	10	0.050
ZNO	5	0.025	N774	66	0.330
SA	1	0.005	N550	20	0.100

2.3 Test method and performance testing

Swelling test of isopropyl nitrate was carried out on N20, N30 and N40 rubber samples. Full dip device is adopted as the test device, with a sample size of 50mm×25mm×2mm and soak time of 3h, 6h, 12h, 18h, 24h, 36h and 48h respectively. After swelling for certain periods of time, the samples were sucked dry by filter paper, then their quality, surface morphology, organizational structure and mechanical properties were tested. Drying tests on partially swollen rubber samples were performed at 80 °C for 24h, and the quality of samples after drying was recorded. The calculation formula of the mass change rate before and after swelling (*⊿m*), volume change rate (*⊿V*) is as follows:

$$\Delta m = \frac{m_2 - m_1}{m_1} \times 100\% \tag{1}$$

$$\Delta V = \frac{(m_2 - m_4) - (m_1 - m_3)}{m_1 - m_3} \times 100\% \tag{2}$$

In the formula, m1 is the mass of rubber before swelling (g); m2 is the mass of rubber after swelling (g); m3 is the mass of rubber in water before swelling (g); m4 is the mass of rubber in water after swelling (g); m5 is the mass of the dried rubber after swelling (g). The mechanical properties of rubber samples before and after swelling were measured by universal tensile testing machine. The sample belonged to Type II, with the thickness of 2mm, tensile rate of 500mm/min and gauge length of 20mm. The calculation formula about tensile strength (*TS*) and elongation at break (*Eb*) is as follows:

$$TS = \frac{Fm}{Wt} \tag{3}$$

$$Eb = \frac{(L_b - L_0)}{L_0} \times 100\% \tag{4}$$

In the formula, Fm is the maximum force recorded (N); W is the width of narrow part on cutting tool (mm); t is the thickness of the tested part (mm); L_0 is the initial test length; L_b is the test length when it breaks.

Characterization of surface morphology of rubber samples before and after swelling was done by a scanning electron microscope, the organizational structure of rubber samples before and after swelling was characterized by an infrared spectrometer.

3. Results and Discussion

3.1 Quality and volume change rate analysis

As a kind of polymer material, nitrile-butadiene rubber has a loose collection, large molecular clearance and weak intermolecular interaction, for which solvents can easily penetrate the polymer. When the affinity between solvent and polymer is large, solvation with surface macromolecules will take place and solvents will permeate into the inside gaps of the macromolecules due to thermal motion. The solvent molecules that penetrate can also cause the solvation of the macromolecular chains, weakening the force between segments of the macromolecular chains and increasing the spaces, which is called swelling. The swelling of polymer materials is characterized by significant volume expansion and mass increase from the macroscopic perspective.

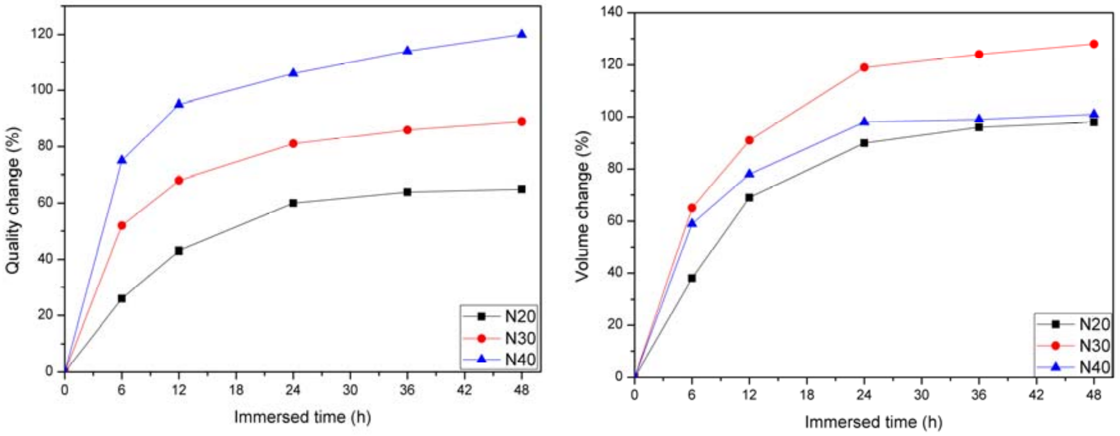


Figure 1: Variation of quality and volume change rates of swelling NBR with immersion time

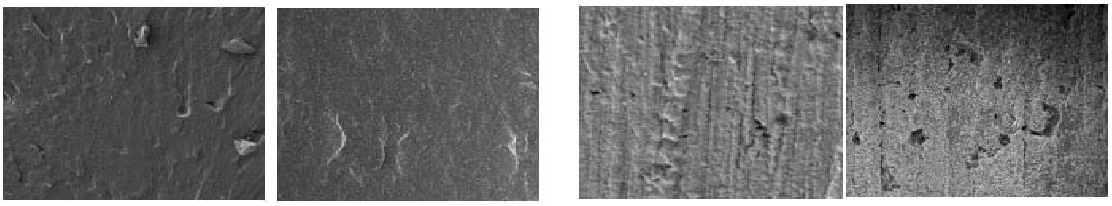
Figure 1 shows the quality and volume change rate curves of N20, N30 and N40 after swelling in isopropyl nitrate for different time periods. As can be seen from the figure, the mass of NBR increases significantly after being immersed in isopropyl nitrate. Within 6h before immersion, rapid increase in rubber mass growth rate can be observed. After 24h of immersion, the change rate of the sample mass increment of the NBR decreases obviously and finally become stable. This is due to the maximum difference in solvent concentration inside and outside the rubber during the initial swelling period, for which the solvent can quickly enter the gaps of macromolecular network inside the rubber. Then the solvent in the macromolecular network will move the molecular chain outwards resulting in easier access of solvent molecules to molecular networks and another increase in swelling capacity (Chen and Ding, 2015; Zhang et al., 2014). Due to the interaction force between molecular chains, the size of gaps between the macromolecular networks is limited. Therefore, the rate of swelling increment gradually slows down and becomes stable at last.

Figure 1 clearly shows that the mass increment of N40 is the largest while that of N20 is the least after swelling in isopropyl nitrate. That is, with the increase of acrylonitrile content in nitrile rubber, NBR’s resistance to isopropyl nitrate becomes weaker and its swelling capacity in isopropyl nitrate becomes larger. The higher the acrylonitrile content is, the greater the polarity of NBR molecule becomes. In addition, isopropyl nitrate is also a kind of polar solvent. Based on the principle of similarity and intermiscibility, which means it is easier for substances with similar polarity to dissolve with each other, the higher the acrylonitrile content is, the smaller the difference between polarity of the nitrile rubber and isopropyl nitrate is and the larger the swelling capacity will be.As can be seen from the figure, N30 and N20 has the maximum and minimum volume expansion rate respectively, which is slightly different from the figure of swelling mass change. The trend of volume change rate of NBR in isopropyl nitrate is similar to that of mass change rate; that is, the longer the swelling time is, the higher the volume expansion rate will be. Within 6h before swelling, the volume expansion rate of N40 is close to that of N30. After 6h of swelling, the volume expansion rate of N40 gradually approaches that of N20, and the rate of N30 becomes much larger than that of N40 and N20. Due to the highest acrylonitrile content in N40, its polarity is also relatively the highest and the intermolecular force is relatively larger, making it hard to stretch outward. Therefore, although the mass change rate of N40 in isopropyl nitrate is the largest, its volume expansion rate is lower than N30. N20 has the lowest acrylonitrile content; however, due to its largest polarity difference with isopropyl nitrate, solvation effect is the least obvious, leading to the lowest volume change rate.

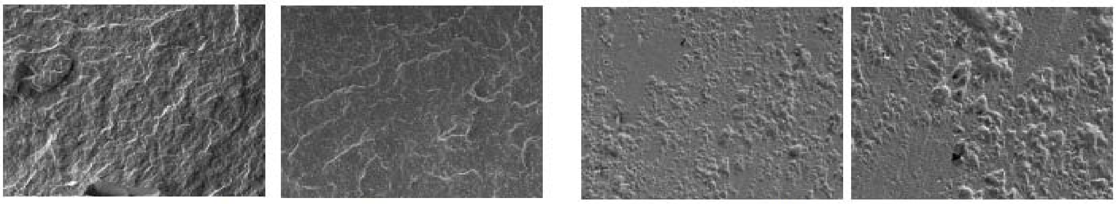
3.2 Analysis on surface morphology

Figure 2 represents the surface morphology of N20, N30 and N40 at original stage and after swelling for 24h in isopropyl nitrate. It can be seen that the morphology of original N20 without swelling in isopropyl nitrate appears even more flat, with uniformly doped small molecular particles. While more sulcus lies on N30 surface, with uniformly doped small molecule particles as well. And N40 is similar to N30 in terms of sulcus and uniformly doped small molecule particles. After swelling in isopropyl nitrate for 24 hours, obvious corrosion can be observed on N20 surface, cracks arising and many large aperture holes occurring. Similar corrosion phenomenon appears on the surface of N30 but is significantly lighter compared with N20. Similarly, holes appear on the surface of N40, the number of which is significantly less than that on N20 and N30 surface, which are relatively smoother.

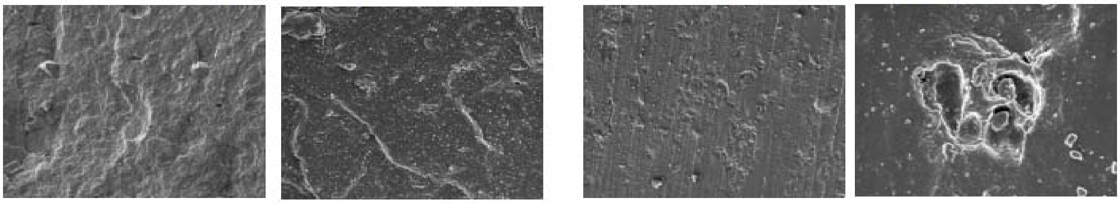
Due to the similar polarity of NBR and isopropyl nitrate, when the former swelled in the latter, corrosion on rubber surface is inevitable, and the precipitated small molecules from the rubber also causes surface pits and holes. With the increase of acrylonitrile content, intermolecular force of rubber becomes stronger, making it too hard for small molecules to precipitate, which accounts for the smooth surface and less holes of N40.



Original N20 Swelled after 24h of N20



Original N30 Swelled after 24h of N30



Original N40 Swelled after 24h of N40

Figure 2: Surface topography of NBR before and after the swelling

3.3 Infrared spectroscopic analysis

Figure 3 is the infrared spectrogram of N20, N30, N40 and IPN at original stage and at the stage after swelling for 24h. After comparison, it can be observed that the infrared absorption peak of N20, N30 and N40 at 1720 cm^{-1} weakens significantly while that at other places strengthens to some extent. Before swelling, no infrared absorption band is tested in original pure IPN at 1720 cm-1, while after swelling it turns turbid, forming a weak peak at 1720 cm^{-1} and a relative decrease at other places compared with the number of the original pure IPN. The infrared absorption peak at 1720 cm^{-1} is the stretching vibration of C=O.

According to the NBR components in Table 1, the presence of dioctyl phthalate (DOP) caused the infrared absorption peak at 1720cm cm^{-1} (Liu et al., 2013; Wang et al., 2015). Due to swelling effects, small molecules of DOP are precipitated, resulting in a great decrease in the absorption peak of NBR at 1720 cm^{-1} is and an occurrence of infrared absorption peak at 1720 $cm-^{1}$ in the IPN after swelling. Small molecules transfers from NBR to IPN, increasing the content of other NBR groups while reducing the content of other groups in IPN. Therefore, NBR's infrared absorption peak enhances after swelling while IPN's infrared absorption peak decreases to a certain extent.

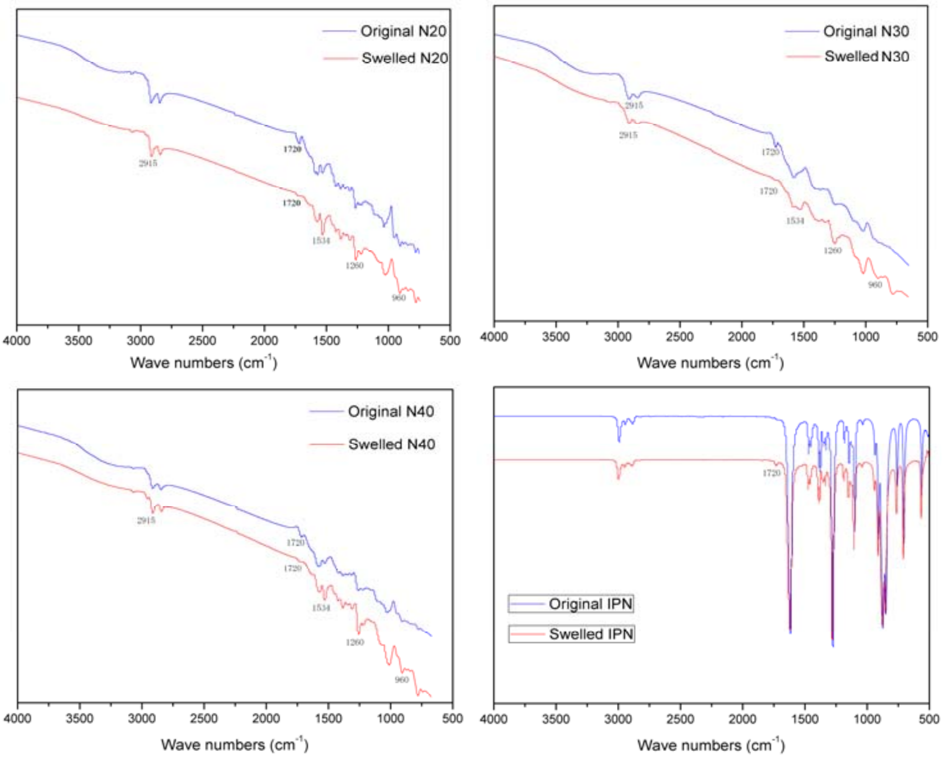


Figure 3: Infrared spectrum of NBR and IPN before and after the swelling

3.4 Mechanical properties analysis

The strength and ability to resist damage of polymer materials are important aspects of their mechanical properties, of which tensile strength is an important ability of rubber to resist damage and one of the most important bases for evaluating the quality of rubber as well (Zhang et al., 2016). The strength of rubber materials is related to the molecular structure, for the main chain chemical bond force and molecular force determine the strength limit of rubber material (Li et al., 2016).

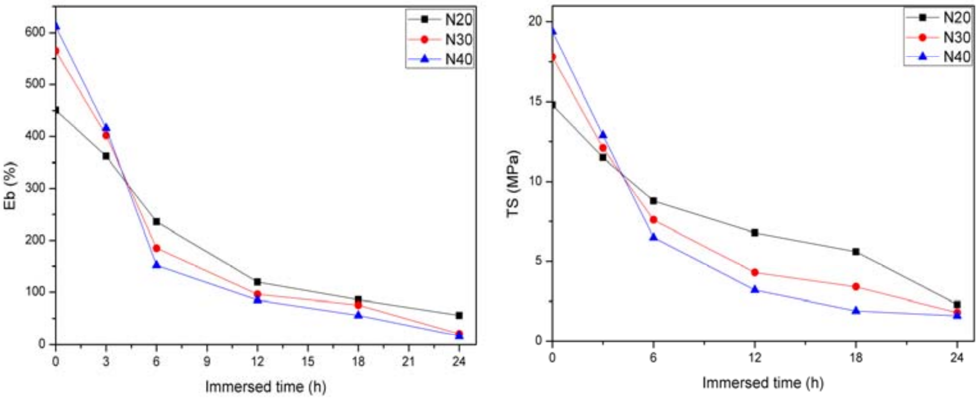


Figure 4: Tensile strength and tensile elongation of NBR with immersion time

Figure 4 is the tensile strength and tensile elongation curve of N20, N30 and N40 in isopropyl nitrate with different swelling time. From the graph, tensile strength and elongation at break share the similar changing trend with swelling time. Before swelling, the tensile strength and elongation at break of N40 are the greatest, followed by N30 and N20. Within 6h before swelling, the tensile strength and tensile elongation of the three kinds of test specimens reduces sharply, among which N40 has the largest falling amplitude, followed by N30 and N20, and then the decline trend becomes a little gentle; Within 3h before swelling, the tensile strength and elongation at break of the three samples gradually become close to each other, and then turn the same after swelling for 3 to 6h, after which the tensile strength and elongation at break of N20 become the largest, followed by N30 and N40. After 24h of swelling, the tensile strength and elongation at break of three kinds of test specimens greatly decline.

The increased acrylonitrile content and -CN group content added to the polarity of rubber molecules and the force of molecular chains, leading to a gradual increase in the difficulty of relative sliding between molecular chains, hence enhancing tensile strength and elongation at break. In the swelling process, as the solvent enters the rubber macromolecular chain gaps, chain structure deforms, physical crosslink fractures and cracks and holes occur in network structure, causing a reduction in chain density and an increase in average end distance, thus a decrease in modulus and tensile strength and elongation at break (Lu et al., 2016; Qin et al., 2013). With the increased acrylonitrile content, the higher the swelling degree of NBR sample in IPN is, the larger the tensile strength and elongation at break becomes. After swelling in IPN for 24h, due to complete reduction in the mechanical properties of the sample, tensile strength and elongation at break become rather low.

4. Conclusions

(1) Swelling effect occurs in NBR and IPN, leading to precipitation of small molecules from NBR; according to the principle of similarity and intermiscibility, the higher the acrylonitrile content is, the larger the quality and volume growth rate of NBR in IPN will be.

(2) Obvious corrosion effect occurs on NBR surface, causing pits and holes on the surface; with larger acrylonitrile content, it becomes harder for small molecule to precipitate, leading to smoother NBR surface with less holes and pits after swelling.

(3) Based on the contrastive analysis of infrared spectrum, the small molecules precipitated after swelling are mainly plasticizers like DOP.

(4) After swelling, NBR’s tensile strength and elongation reduced at break drop significantly, and the larger the acrylonitrile content is, the greater the decrease is; the mechanical properties of the swollen NBR decrease severely, making it hard to meet the sealing requirements.

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