



Mini Review

Modification of Natural Rubber as a Resistant Material to Dimethyl Ether

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Abstract

The aim of this study is to investigate the prospect of Natural Rubber (NR) as a seal to dimethyl ether (DME). Natural Rubber (NR) as a renewable material would probably become part of a variety of kinds of products with distinctive NR elasticity, tensile strength, adhesion to metal and flexibility at low temperature. Acrylonitrile (AN) and styrene (ST) monomers give a good contribution in improving the chemical and mechanical properties of NR. Acrylonitrile as a polar monomer has resistance towards organic solvent, good heat and abrasion resistance. Styrene as a good co-monomer potentially reduces crosslink, thereby decreasing diffusivity of solvent. Dimethyl ether (DME) is a fuel substitute for LPG. The DME is an organic solvent which has high permeability to rubber and plastic; therefore, it is easy to dissolve and destroy the material. The previous researches have developed seal materials which are resistant to DME with synthetic rubber. The graft copolymerization of NR-g-AN/PS is expected to improve the resistance of NR to DME. The preliminary experiment was investigated. The results showed that modified NR proved by Fourier Transform Infrared Spectroscopy (FTIR). The presence of the functional group C≡N and benzene indicated AN and ST which grafting onto NR, respectively. The result shows that NR-g-AN/ST can reduce the mass change in solvent equivalent DME. From approach of the theory solubility parameter, it proved that NR-g-AN/ST can decrease of the diffusion of DME. These results are a new discovery prospect of natural rubber as a material seal to DME.

Key words: Acrylonitrile, dimethyl ether, graft copolymerization, natural rubber, styrene

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INTRODUCTION

The Natural Rubber (NR) is one of the most important commodities in Indonesia. Natural rubber has a good property, i.e., higher elasticity, tensile strength, adhesion to metal and flexibility at low temperature than synthetic rubber. Furthermore, NR has also the potential for seal material to infrastructure supporting materials in the gas distribution system of DME. However, NR is low resistant to organic solvent such as DME. The weakness of NR can be eliminated by modifying it. The most effective method for modifying NR is the graft copolymerization with a monomer. The graft copolymerization is a method in which monomers are covalently bound to the backbone of rubber¹. The grafting method is the most widely used methods for modifying the natural rubber into the design product of rubber. Natural rubber is an unsaturated rubber, therefore it easy to interact with the monomer².

The process of graft copolymerization of NR with a monomer has been developed by the previous researchers. This article represents a literature review on the modification of NR with the graft copolymerization method. Some monomers are grafted onto the natural rubber to make changes in both the physical and chemical properties of natural rubber. Acrylate monomer and its derivatives are compounds that are often grafted with natural rubber and take effect on resistant properties in organic solvent. Styrene is a co-monomer that helps the process of copolymerization.

On the other hand, dimethyl ether (DME) acts as a promising alternative fuel also to conventional diesel oil. The properties of DME include high oxygen content, high cetane number, quick atomization, non-toxic and environmental benignity, as this material potentially reduces exhaust emissions of diesel engines by maintaining high fuel efficiency³⁻⁶. However, DME is a polar gas and has high permeability for organic compounds, such as rubber and plastic and easily swells or dissolves rubber and plastic. In the previous study, a mixture of DME and diesel 20/80%-v (D20) causes a corrosive effect on the rubber seal and causes leakage problems³. Several studies have used synthetic rubber, such as chloroprene rubber (CR), acrylate rubber (ACM), nitrile butadiene rubber (NBR), fluorocarbon rubber (FPM), fluorosilicone rubber (FMQ), ethylene propylene-diene monomer rubber (EPDM) with durability testing to DME^{3,7,8}.

In this study, the advantages of grafting acrylonitrile and styrene onto polymers, process of graft copolymerization of natural rubber with acrylonitrile and styrene and the effects of dimethyl ether (DME) on rubber are described. The initial experiment has been performed with the equivalent solvent

of DME. From the theoretical calculations, mixture DEE/MEK 50/50%-v is equivalent of DME. The swelling test is measured by immersion of samples in the solvent for several days. The samples are natural rubber and copolymer NR-g-AN/ST vulcanized. In the future, acrylonitrile and styrene monomers grafting onto natural rubber are expected to change the physical and chemical properties of natural rubber and to increase resistance to dimethyl ether.

INFLUENCE OF GRAFTING ACRYLONITRILE AND STYRENE ONTO POLYMERS

Acrylonitrile is the polar monomer which is higher than other monomers⁹. According to Nagaty *et al.*¹⁰ and Bhattacharya and Misra¹, the reactivity order of acrylonitrile is greater than that of ethyl acrylate and methyl methacrylate^{10,11}. Acrylonitrile is contained in Nitrile Butadiene Rubber (NBR). The greater the acrylonitrile content in NBR can improve its physical properties, such as tensile strength, hardness, abrasion resistance, resistance to gas permeability, heat resistance and oil resistance¹¹. The previous studies have used acrylonitrile monomer grafted onto natural rubber since 1969 by Beniska and Staudner¹² and Claramma *et al.*¹³. Further research was conducted by Yamamoto *et al.*¹⁴ and Prukkaewkanjana *et al.*¹⁵. Grafting acrylonitrile in natural rubber increases the mechanical properties of natural rubber.

Styrene (ST) is the non polar monomer. Grafting ST onto natural rubber increases resistance to oxidation and obsolescence. Styrene can also reduce the cross-link of the vulcanized rubber¹⁶. In the graft copolymerization, styrene acts as a co-monomer in the process which is assisting the process. The previous study have used styrene as a co-monomer in the graft copolymerization monomer onto polymer. Styrene was assisted in the process of the grafting of Maleic anhydride (MA) onto natural rubber^{17,18} and onto isotactic polybutene-1¹⁹. The presence of styrene in the grafting reaction increases both grafting efficiency and grafting yield¹⁸⁻²⁰. Styrene also acts as a co-monomer for the grafting of acrylonitrile onto ethylene-propylene-diene monomer (EPDM)²¹; onto natural rubber^{20,22,23} and onto chlorinated polyethylene (CPE)²⁴.

In the process of grafting, polyacrylonitrile (PAN) and polystyrene (PS) are formed as a grafted homopolymer onto natural rubber and as a free homopolymer. The presence of free polyacrylonitrile (PAN), which is formed in the mixture, will also improve the insolubility and resistance to organic solvent, where DME also includes organic compounds²⁵. The presence of free polystyrene (PS), which is formed in the mixture, can increase resistance to high temperature²⁶. In the previous study, acrylonitrile and styrene monomers were

grafted onto polymers (Natural rubber and other polymers). The researchers of those studies have listed the data of the advantages after grafted in Table 1.

GRAFT COPOLYMERIZATION OF NATURAL RUBBER WITH ACRYLONITRILE AND STYRENE

Graft copolymerization is a method of transplantation of the main chain of the rubber with a monomer which correlates with the desired improvement of the product properties. This method has been used since the 1930s. Graft copolymerization has been performed in the liquid rubber phase, a phase of solid rubber and latex form. Graft copolymerization in a latex form is called a copolymerization latex emulsion. It is the most economical and practical method because the stages of the process are shorter than others³⁴.

The grafting method is the most effective method used to modify natural rubber into the desired rubber good mechanical properties or chemical properties. Monomers in the grafting of natural rubber are acrylonitrile, maleic anhydride, styrene, methyl methacrylate, ethyl methacrylate, vinyl compounds and other monomers. The grafting of monomer has an important role in determining the chemical and mechanical properties of the new copolymer². Table 2 below lists the previous studies on the grafting process of acrylonitrile and styrene onto natural rubber.

There are various elements that influence the graft copolymerization process, i.e., temperature, protein content and time of reaction. The dependence of the graft copolymerization reaction to temperature is expressed in the form of the Arrhenius equation (Eq. 1) which states that the reaction rate constant is directly proportional to the reaction of temperature⁹:

$$k_i = A \exp\left(\frac{-E_i}{RT}\right) \quad (1)$$

Rising temperature will cause decomposition of the increased initiator, thereby increasing the amount of free radical and rate of reaction. In the copolymerization reaction of natural rubber with the monomer, the temperature rising above 80°C will cause gel fraction and it is not desirable to happen in the reaction⁴¹. Deproteinized natural rubber latex has been studied previously. The presence of the high protein makes inefficiency in the grafting process because the protein can act as a catcher of free radicals and as a terminator, thus slowing the reaction^{36,42}. Grafting efficiency increases with increasing reaction time^{41,42}. However, in several studies, copolymerization increased in the early hours of the reaction; after that the reaction became slow and at the end of the reaction time, delta conversion was close to zero³⁹. Table 3 shows the reaction time of the process ranging from 2-10 h.

Table 1: Advantages of the grafted acrylonitrile and styrene onto polymers

Monomers	Polymer grafted	Advantage	References
Acrylonitrile and styrene	Butadiene	Enhancing strength and chemical resistance; increasing product toughness and strength	Ebewele ⁹ and Simpson ¹¹
Acrylonitrile	Casein	Increasing wet-rub resistance and susceptibility to microbial attack	Dong and Hsieh ²⁷
Acrylonitrile and ethyl methacrylate	Cellulose	Altering the physical and chemical properties of the cellulose	Gupta and Sahoo ²⁸
Acrylonitrile and styrene	EPDM	Improving the heat resistance and rheological property	Qu <i>et al.</i> ²¹
Acrylonitrile	Butadiene	Improving polymer quality	Vega <i>et al.</i> ²⁹
Acrylonitrile	<i>Ipomoea dasysperma</i> seed-gums	Improving thermal stability	Singh <i>et al.</i> ³⁰
Acrylonitrile	Natural rubber	Improving the mechanical properties and oil resistance of NR/NBR vulcanized	Angnanon <i>et al.</i> ²⁰
Acrylonitrile and styrene	Polyethylene	Improving in the impact strength of the ACS resin	Luo and Wu ²⁴
Acrylonitrile	Natural rubber	Improving the oil resistance and tensile strength	Yamamoto <i>et al.</i> ¹⁴ and Prukkaewkanjana <i>et al.</i> ¹⁵
Acrylonitrile	Chitin	Enhancing the adsorptive property of chitin	Hanh <i>et al.</i> ³¹
Acrylonitrile	Starch	Enhancing stability of latex	Misman <i>et al.</i> ³²
Acrylonitrile	Polyethyleneglycol	Improving thermal stability	Sarier <i>et al.</i> ³³

Table 2: Graft copolymerization of acrylonitrile and styrene monomer onto natural rubber

Monomers	Grafting method	Temperature/pressure of reaction	Time of reaction (h)	Reference
Acrylonitrile	Emulsion	35°C/1 atm	2	Yamamoto <i>et al.</i> ¹⁴
Acrylonitrile and methyl methacrylate	Emulsion	60°C/1 atm	6	Okieimen and Urhoghide ³⁵
Styrene	Emulsion	30-60°C/1 atm	2-10	De Silva <i>et al.</i> ² , Tho <i>et al.</i> ³⁶ , Pukkate <i>et al.</i> ³⁷ , Suksawad <i>et al.</i> ³⁸ , Songsing <i>et al.</i> ³⁹ and Sittiphan <i>et al.</i> ⁴⁰
Acrylonitrile and styrene	Emulsion	70°C/3 atm	8	Prasassarakich <i>et al.</i> ²²

Table 3: Hansen solubility parameters for the solvent and polymer^{51,50}

Solvent	Solubility parameter, δ (MPa ^{1/2})			
	δ_D	δ_P	δ_H	δ
Dimethyl ether	15.20	6.10	5.70	17.34
Benzene	18.40	0.00	2.00	18.51
Toluene	18.00	1.40	2.00	18.16
Xylene	17.60	1.00	3.10	17.90
Ethyl benzene	17.80	0.60	1.40	17.87
Cyclohexane	16.80	0.00	0.20	16.80
Methyl cyclohexane	16.00	0.00	1.00	16.03
n-pentane	15.60	0.00	0.00	15.60
n-hexane	14.90	0.00	0.00	14.90
n-heptane	15.30	0.00	0.00	15.30
n-octane	15.50	0.00	0.00	15.50
n-nonane	15.70	0.00	0.00	15.70
Acetone	15.50	10.40	7.00	19.94
Cyclohexanone	17.80	6.30	5.10	19.56
n-butyl acetate	15.80	3.70	6.30	17.41
1,4-dioxane	19.00	1.80	7.40	20.47
Chloroform	17.80	3.10	5.70	18.95
Chlorobenzene	19.00	4.30	2.00	19.58
Carbon tetrachloride	17.80	0.00	0.60	17.81
Methanol	15.10	12.30	22.30	29.61
Ethanol	15.80	8.80	19.40	26.52
n-propanol	16.00	6.80	17.40	24.60
Diethyl ether	14.50	2.90	5.10	15.64
Methyl ethyl ketone	16.00	9.00	5.10	19.05
DEE/MEK 50/50%-v	-	-	-	17.35
Natural rubber	16.00	4.00	6.00	17.55
Polyacrylonitrile	21.70	14.10	9.10	27.43
Polystyrene	22.30	5.80	4.30	23.44

EFFECTS OF DIMETHYL ETHER (DME) ON RUBBER

Dimethyl ether (DME), which has the chemical formula of CH_3OCH_3 , at room temperature is odorless and colorless gas and it is fairly easy to process it into a liquid phase. The potential of DME as an alternative fuel for diesel engine vehicles is expected because it has a cetane number of 55-60; therefore, it is ideal for use in a Compression Ignition (CI) engine⁴. The DME is gaseous at normal pressure and temperature, with a boiling point of -25.1 and the vapor pressure of 0.6 MPa. The physical properties of DME are very similar to Liquefied Petroleum Gas (LPG), so it can be distributed and stored using the same technology as the handling of LPG⁴³. The DME has high content of oxygen, a low level of sulphur or other NO_x content, low-carbon, therefore making it have clean burning. The DME can be produced from many sources, such as biomass, organic waste and agricultural products⁴⁴.

The DME is sufficiently polar and has a high permeability for organic compounds, such as rubber and plastic, hence easily dissolving rubber and plastic. The DME with a percentage of 20% in diesel oil (D20) causes corrosion on the product seal and causes leaks. In the study comparing the DME with diesel oil, DME viscosity values are lower than those

of diesel oil, so this easily causes leaks and the injection system is dependent on clearance (cavity) from sealing^{8,3,45,46}. According to Wu *et al.*⁷, in the previous study, DME is powerful solvent and can dissolve the plasticizer compounds, one of the constituents of vulcanized rubber, which can damage crack resistance and cause the loss of the seal on the cable⁷.

Permeability is a trait where the gas velocity or steam enters the polymer. Permeability consists of three processes: (1) The absorption of the compound into the polymer, (2) Diffusion through the polymer and (3) Compound desorption from the surface of the polymer, causing it to disappear. The factors that cause the permeability of the polymer are solubility and diffusivity of small molecules in the polymer, the chain block and the complex group, polarity, crystallinity, filler, humidity and plasticity⁴⁷.

The absorption of DME to the rubber causes changes of volume and mass. This is induced by the similarity of polarity and solubility parameter between the rubber and DME. In most cases, swelling occurs due to absorption of fluid. Diffusion speed of liquid into the pores of the rubber determines the time required to reach equilibrium. Then the fluid diffusion speed slows down. The lower the viscosity of the fluid is, the higher the speed of diffusion. When the liquid enters onto the rubber, liquid rubber

surface can be chemically attacked. Assault fluid diffuses into the rubber can lead to a reduction in volume/mass and it is called shrinking⁴⁸. Swelling of events can lead to some changes of the physical properties and make possible changes of the chemical properties. Fluid in the swelled material enables attack or reaction of the ingredient in the material and causes the material to be diffused out. Saputra *et al.*⁴⁹ investigated of natural rubber vulcanized in DME. They concluded that DME possibility attacked some ingredients in natural rubber and can cause high swelling and shrinking⁴⁹.

SOLVENT EQUIVALENT TO DIMETHYL ETHER (DME)

Determination of the solvent type for resistance testing of rubber can be predicted based on the equation 2 and solubility parameters in Table 3. The Eq. 2 is the formula hilde brand solubility parameter (δ) which δ_D is dispersion cohesion, δ_p is polar cohesion, δ_H is hydrogen bonding cohesion⁵⁰:

$$\delta^2 = \delta_D^2 + \delta_p^2 + \delta_H^2 \quad (2)$$

Table 3 shows the calculation of the δ value. From the calculation of the d, show that n-butyl acetate approximating DME. However, the value δ_D , δ_p and δ_H of n-butyl acetate are different from DME. Moreover, n-butyl acetate properties are different from DME. Diethyl ether as an ether group is quite similar to DME, with δ_D and δ_H approximates to DME, although the values of δ of 15.64. From Table 3, methyl ethyl ketone has also δ_D and δ_H approximating to DME, although the values of δ of 19.05. The combination of two solvents, diethyl ether and methyl ethyl ketone is expected similar to DME properties. The mixture of DEE/MEK 50/50%-v has δ of 17.35 MPa^{1/2}. It is similar to DME which has δ of 17.34 MPa^{1/2}.

Table 2 shows the solubility parameters of the polymers. These data indicate the possibility that NR will be degraded by DME, because NR has d similar to DME. The presence of polyacrylonitrile and polystyrene in natural rubber will increase δ of natural rubber. Increasing of the solubility parameter of natural rubber causes the power to resist the solvent diffuses into the network of the rubber. It can decrease of the mass change at the wet measurement. This is coherent with the phenomenon "Like dissolve like"³. The decreasing in the mass change allows may reduce degradation of natural rubber.

The material used was natural rubber from South Sumatera, Indonesia. Measurement after the immersion has been performed on wet and dry condition (after 24 h at room temperature). The change of mass is specified in percentage (%) by using this mathematical^{3,7,52} Eq. 3:

$$\text{Percentage mass change} = \frac{m_f - m_i}{m_i} \times 100\% \quad (3)$$

where, m_f (final mass) is the mass of the sample after immersion at time t and m_i (initial mass) is the mass of a dry sample before immersion. After measuring changes of the mass, the samples were measured again to discover the tensile strength, elongation and hardness. The second measurement result was compared with the first measurement (before immersion). The changing chemical properties can be evaluated by Fourier Transform Infrared (FTIR) after immersion.

FUTURE RESEARCH ON GRAFTING COPOLYMERIZATION OF NATURAL RUBBER AND ITS PROSPECT RESISTANCE TO DIMETHYL ETHER

Acrylonitrile and styrene monomers have the potential to change the properties of natural rubber. The graft copolymerization AN and ST onto NR was investigated but the application of this material for resistance to DME has not been developed. The addition of styrene in natural rubber can also lower the cross-link of the natural rubber vulcanized, thereby decreasing diffusivity of DME into natural rubber. Polystyrene and polyacrylonitrile as a free homopolymer in the mix will make the vulcanized rubber become more resistant to organic solvent and high temperature.

There is a problem with dimethyl ether (DME) as a fuel substitute for LPG. The DME is an organic solvent which has high permeability to rubber and plastic; therefore, it is easy to dissolve and destroy the material. Modification of the natural rubber is expected to solve this problem. There is a good prospect to modify natural rubber to increase resistance to DME as organic solvent.

Based on previous studies, preliminary research was conducted. The preliminary research was carried out by process graft copolymerization NR with AN/ST monomers and immersing the vulcanized rubber grafting with mixed results of DEE/MEK50/50-v. The results can be viewed in Fig. 1 and 2.

Figure 1 indicates that the spectrum of (a) NR and (b) NR-g-PAN/PS. The spectrum of (b) shows the functional

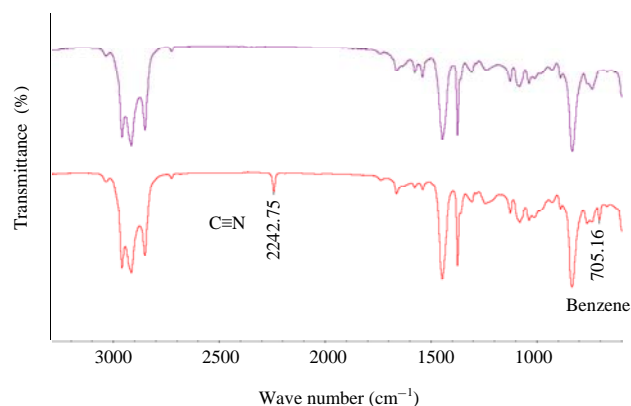


Fig. 1: Spectrum of NR and NR-g-PAN/PS

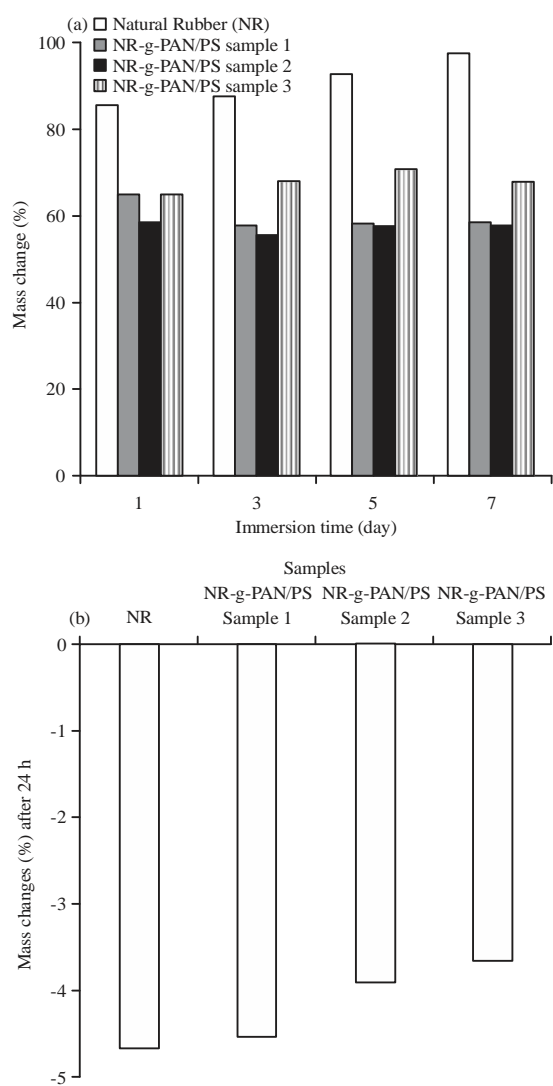


Fig. 2(a-b): Percentage change of mass of NR vulcanized compared with NR-g-PAN/PS vulcanized at the ratio NR/monomer 65/35, (a) Wet measurement and (b) Dry measurement (after 24 h)

group of $C\equiv N$ at the wave number 2242.75 cm^{-1} and benzene at the wave number 705.16 cm^{-1} . The functional group of $C\equiv N$ and benzene show that the grafting acrylonitrile and styrene onto NR, respectively.

Figure 2a shows the change of the mass from the samples after 1, 3, 5 and 7 days. The samples were taken directly from the reagent bottle and measured using an analytical balance. The results in the Fig. 2a are called the wet measured. The change of mass NR vulcanized is greater than the mixture of NR-g-PAN/PS, PAN and PS vulcanized at each measurement point. This is consistent with the theory that PAN and PS onto NR can block the diffusion solvent in the rubber vulcanized. The addition of AN and ST onto the chain of natural rubber so they will be better, especially at being resistant to organic solvent, such as dimethyl ether.

The results in Fig. 2b are called the dry measured. It shows the mass change of samples percentage, after 24 h dried in the atmosphere. This Fig. 2b indicated that decreasing of mass after immersion in solvent. In Fig. 2a solvent diffusion occurs in and out of the rubber network until the equilibrium state. Solvent diffusion in and out of the network caused the shrinking rubber. There are several possibilities may causes of mass reduction. The first, the reaction occurs between solvents and some ingredient in the rubber to form a new compound in the liquid phase that carried out the rubber network⁴⁹. The second, there was no reaction but the solvent that is causing erosion of the free compound in rubber. It is caused reduction of the mass rubber.

CONCLUSION

Established along the review of previous studies, it is possible to continue the research by applying the modified natural rubber. The copolymer NR-g-PAN/PS can be expected

to decreased the diffusivity of DME, therefore can increased resistance rubber to DME. Grafted acrylonitrile and styrene onto the natural rubber have been studied in the previous research but the potential material for resistance towards DME has not been developed. Therefore, it is necessary to further study the resistance of this material towards DME. The preliminary experiment showed that modified NR proved by Fourier Transform Infrared Spectroscopy (FTIR). The present of the functional group $C\equiv N$ and benzene indicated AN and ST which grafting onto NR, respectively. The result shows that NR-g-AN/ST can reduce the mass change in solvent equivalent DME. From approached of the theory solubility parameter, it proved that NR-g-AN/ST can decrease of the diffusion of DME. These results are a new discovery prospect of natural rubber as a material seal to DME.

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