

Nitrile rubber and carboxylated nitrile rubber resistance to soybean biodiesel

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Abstract

Biodiesel has been considered a suitable substitute for petroleum diesel, but their chemical composition differs greatly. For this reason, biodiesel interacts differently than petroleum diesel with various materials, including rubbers. Therefore, the resistance of some elastomers should be thoroughly evaluated, specifically those which are commonly used in automotive industry. Nitrile rubber (NBR) is widely used to produce vehicular parts that are constantly in contact with fuels. This paper aimed to assess the resistance of carboxylated nitrile rubber (XNBR) with 28% of acrylonitrile content to soybean biodiesel in comparison with non-carboxylated nitrile rubber samples, with high and medium acrylonitrile content (33 and 45%). NBR with medium acrylonitrile content showed little resistance to biodiesel. However, carboxylated nitrile rubber even with low acrylonitrile content had similar performance to NBR with high acrylonitrile content.

Keywords: nitrile rubber, crosslink density, biodiesel, mechanical properties.

1. Introduction

Nitrile rubber (NBR) represents a rubber for special purposes and it is highly resistant to mineral oils and non-polar solvents, due to the presence of nitrile groups in its structure. One of its main applications is in the automotive industry, in parts that require constant contact with fuels.

The degradation of nitrile rubber can occur via different ways, including changes in the crosslink network and reactions with free carbon double bonds¹⁻⁴. Carbon black can also accelerate the thermal oxidation process of NBR compounds¹⁻⁵.

Some studies^{4,6-17} have tested the compatibility of many elastomers to biodiesel, including nitrile rubber (NBR), whose degradation process is often assessed observing changes in the mechanical properties after static and/or dynamic immersion in different types of media at different temperatures.

Biodiesel is a liquid bio-fuel considered to be an environmentally friendly source of energy, and a feasible alternative to petrol-diesel. It is chemically defined as a mixture of mono-alkyl esters obtained from vegetable oils or animal fat.

There are many vegetable sources for biodiesel production, such as soybean oil, palm oil, and rapeseed oil, among others. Some differences in physico-chemical properties are observed depending on the feedstock used for the biodiesel production^{18,19}.

Petroleum diesel and biodiesel interact differently with various materials, as both are chemically different. For this reason, the properties of biodiesel should be further studied. To date, biodiesel compatibility with materials that are used widely in diesel engines has not been fully assured.

Usually nitrile rubber presents low resistance to biodiesel from different sources. Trakarnpruk and Porntangjitlikit⁶, and Dubovský et al.¹³ suggested that the deterioration in mechanical properties were due to the plasticization effect of biodiesel. However, the use of a biodiesel/diesel 10% blend (B10) should not be of concern⁶.

Haseeb et al.^{7,8} inferred that the degradation process occurs due to reactions with the crosslink network, and with the free double bonds in the polymer chains. Linhares et al.¹⁰ concluded that an increase in the acrylonitrile content increases the nitrile rubber resistance to biodiesel. Akhlaghi et al.^{4,14} showed that the biodiesel attacks the filler-elastomer interfaces, which affect the mechanical properties; in addition, biodiesel would decrease the crosslink network of elastomer compounds. Akhlaghi et al.¹⁴ also suggested that a prolonged exposure to biodiesel can promote the hydrolysis of nitrile groups of NBR by Zn²⁺ cations. Moreover, the chemical differences of biodiesel obtained from different sources can affect the biodiesel solvent power, and, hence, its degradation power¹⁵.

However, most of the authors did not specify the acrylonitrile content in the nitrile rubber samples nor which formulations were used during the tests, impeding a thorough comparison of the results.

Considering that biodiesel is an actual fuel option, and nitrile rubber is largely used for automotive parts production, the need to study the interaction between biodiesel and elastomers is urgent.

This paper aimed to evaluate the resistance of different nitrile rubber samples to soybean biodiesel. The novelty of this paper lies on the assessment of carboxylated nitrile rubber performance after immersion in soybean biodiesel,

and of the relation of different types of crosslink network with elastomer resistance to soybean biodiesel.

2. Materials and Methods

2.1 Compounding

Nitrile rubber samples with different acrylonitrile content (33 and 45%) and carboxylated nitrile rubber (with 28% of acrylonitrile content) were used. The rubber samples were generously given by Nitriflex S/A Indústria e Comércio. The compositions were prepared in a roll mill, at 50 °C ± 5°C (323K ± 5K), as per ASTM D3187, using the formulation presented in Table 1. The carbon black sample was given by Cabot do Brasil Indústria e Comércio S.A..

For identification purposes the compositions prepared were labelled according to the elastomer used in the formulation: *NBR33* for the composition prepared with nitrile rubber with 33% of acrylonitrile; *NBR45* for the composition with nitrile rubber with 45% of acrylonitrile; and *XNBR* for the compositions prepared with the carboxylated nitrile rubber with 28% of acrylonitrile content. Further information on the nitrile rubber samples is given in Table 2.

A small sample of each composition was analysed on a Tech Pro MDPT moving die rheometer (MDR), for one hour, at 160°C (433K) to establish the optimum cure time (t_{90}) of each composition. The compositions were vulcanised in a hydraulic press using their respective t_{90} to obtain testing specimens for the mechanical tests.

2.2 Crosslink density

Crosslink density of the samples was calculated by equilibrium swelling with acetone, using the Flory-Rehner equation^[20,21] (Equation 1), at room temperature.

Table 1. Formulation of the NBR compositions, as per ASTM D3187, in phr^a.

Component	Amount in phr ^a
Nitrile rubber	100
Zinc oxide	3
Stearic Acid	1
Sulphur	1.5
TBBS ^b	0.7
Carbon black (SP6630)	40

^aparts per hundred parts of rubber; ^bN-tert-butyl-2-benzothiazyl sulphenamide.

Table 2. Main properties of the nitrile rubber samples*.

Property	Nitrile rubber sample with 33% of acrylonitrile	Nitrile rubber sample with 45% of acrylonitrile	Carboxylated nitrile rubber sample with 28% of acrylonitrile
Bound acrylonitrile (%) – ASTM D3533	32	46.7	27.8
Mooney viscosity (MML1+4 @373K) – ASTM D1646	45	55	45
Ash content (%) – ASTM D5667	0.1	0.1	0.1

*given by the supplier Nitriflex S/A Indústria e Comércio.

$$\eta = \frac{-\left[\ln(1-v_r) + v_r + \chi(v_r^2)\right]}{\left[V_0\left(\frac{1}{v_r^3} - \frac{v_r}{r}\right)\right]} \quad (1)$$

wherein η is the crosslink density; v_r is the volume fraction of rubber in equilibrium swollen vulcanizate sample; V_0 is the molar volume of the solvent (73.40 mL.mol⁻¹); χ is the interaction parameter between the solvent and the elastomer.

The volume fraction of rubber in equilibrium swollen gel (v_r) was calculated according to Equation 2. It is worth mentioning that the filler volume was subtracted of the rubber volume in the calculation.

$$v_r = \frac{\frac{M_1 - f_f M_1}{\rho_c}}{\frac{M_1 - f_f M_1}{\rho_c} + \frac{M_2 - M_3}{\rho_s}} \quad (2)$$

wherein, M_1 is the initial sample mass; f_f is the filler fraction volume; ρ_c is the calculated composition density; M_2 is the swollen sample mass; M_3 is the deswollen sample mass; ρ_s is the solvent density (0.79 g.mL⁻¹).

The interaction parameter (χ) for each composition was calculated according to the Equation 3^[22].

$$\chi = \beta_1 + \left(\frac{V_0}{RT}\right)(\delta_s - \delta_p)^2 \quad (3)$$

wherein, β_1 is the lattice constant^[22] (0.34); R is the universal gas constant; T is the temperature in Kelvin; δ_s is the solubility parameter of the solvent (9.9 for acetone^[23]); δ_p is the solubility parameter of the polymer (varies for each rubber sample^[23]).

The calculated interaction parameter (χ) for *NBR33* was 0.3507; for *NBR45* was 0.3474; and for *XNBR* was 0.3640.

The dried compositions density (ρ_c) was calculated following the Arquimedes' principle, in which consider the mass of the sample in air, the apparent mass of the sample immersed in the solvent, and the density of the solvent. The apparent mass of the sample is measured using a proper apparatus, which measures the mass of the sample submerged in the solvent (acetone) held by a thread. The density was, then, calculated according to Equation 4.

$$\rho_c = \frac{M_1}{(M_1 - M_4)} \times \rho_s \quad (4)$$

wherein, M_4 is the apparent mass of the sample immersed in the solvent.

2.3 Immersion tests

Pure soybean ethylic biodiesel, kindly donated by CENPES/Petrobras (Brazil), was used for the immersion tests. The biodiesel properties were within the Brazilian regulations, and its main components are ethyl esters derived from mono and poly-unsaturated acids^[18,19].

2.4 Change in mass

Small rectangular specimens were cut from the vulcanised sheets to assess the change in mass after immersion according to ASTM D471. The specimens were weighed, in air, in a balance with 0.1 mg accuracy. The immersed samples had their surfaces dried with filter paper before they were weighed. The results were the average change in mass from the tested specimens. The immersion was conducted for 22h at 100 °C (373K) in an oven with forced air circulation.

2.5 Mechanical tests

Stress-strain tests were performed on a testing machine EMIC, model DL2000, as per ASTM D412, using Die C dumbbell specimens, i.e., 115mm length, and bench mark distance of 25.4 mm. The rate of grip separation was 500 mm/min (± 50 mm/min). Tear strength tests were conducted on the same testing machine according to ASTM D624, using Type C test specimens, i.e., an unnicked test piece with a 90° angle on one side, and 102 mm length. The rate of grip separation was also 500 mm/min (± 50 mm/min). Hardness tests were performed on a durometer Shore A, from Parabor, following ASTM D2240, and the testing

2.6 Scanning electron microscopy

After the mechanical tests, the fracture surfaces of the immersed and the non-immersed samples were sputtered with a gold film and analysed by scanning electron microscopy (SEM), using 15 keV electron beam acceleration voltage in a JSM 6510LV microscope from JEOL.

3. Results and Discussions

3.1 Change in mass

Change in mass of the compositions after the immersion in the bio-fuel is shown in Figure 1. *NBR33*, with medium acrylonitrile content (33%), absorbed the fuel in the highest extent, increasing in over than 50% its mass. On the other hand, *XNBR*, with only 28% of acrylonitrile content, swelled around 30%, and *NBR45*, as expected, absorbed the oil in much lower extension, increasing in less than 15% of its mass.

Differently from these results, Akhlaghi et al.^[14] found an increase in mass between 10 to 15% for nitrile rubber compositions with 34%. The difference in the results can be assigned to the different biodiesel source used (rapeseed in their study and soybean in this study), and also to the lower temperature employed in the cited reference. Nonetheless, the tendency that increasing the acrylonitrile content, decreases the biodiesel uptake was similar in both studies.

The bio-fuel swelling by the *NBR33* sample is usually attributed to the “like dissolves like” principle^[4] since biodiesel presents some polarity due to its ester nature. The closeness

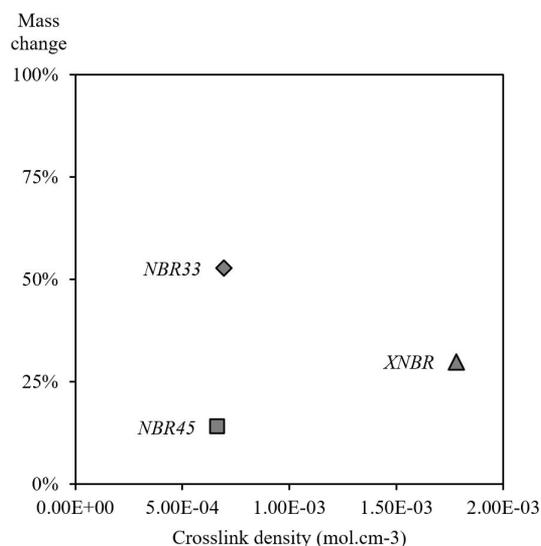


Figure 1. Change in mass after 22h of immersion in soybean biodiesel as function of crosslink density of the nitrile rubber compositions.

of polarity between the fluid and the elastomer eases the diffusion of the fuel into the polymer.

Figure 1 also matches the crosslink densities of each composition with the oil mass uptake after 22h. Some authors^[7,8] proposed that an increase in acrylonitrile content would increase the crosslink density, which would lessen the bio-fuel swelling. Our results disagreed with these propositions. Crosslink density presented no relation with the compositions’ acrylonitrile content, as *NBR45* and *NBR33* had similar crosslink density. *XNBR* can form additional non-sulphur crosslink bonds through the carboxyl groups^[24], which explains the highest crosslink density achieved. These crosslinks are formed by the interaction between carboxyl groups and zinc^[24].

In addition, the biodiesel swelling was also not related to the crosslink density of the compositions. Carboxylated nitrile rubber (*XNBR*) absorbed less oil than *NBR33*, but swelled more oil than *NBR45*.

We could observe that the crosslink density of the compositions solely does not rule the degree of biodiesel swelling. Based on these results, differences in biodiesel absorption should be assigned to a contribution of both the acrylonitrile content and the type of crosslink.

3.2 Mechanical tests

The mechanical test results from the different NBR compositions after the immersion in pure soybean biodiesel were presented as the relative change after the immersion in comparison with those non-immersed ones, and are depicted in Figures 2 and 3.

NBR33 presented very low resistance to soybean biodiesel, given that the losses of the mechanical properties were 66% on average. *NBR45*, however, experienced less significant losses, 38% on average, after immersion in biodiesel. Previous tests already showed better resistance

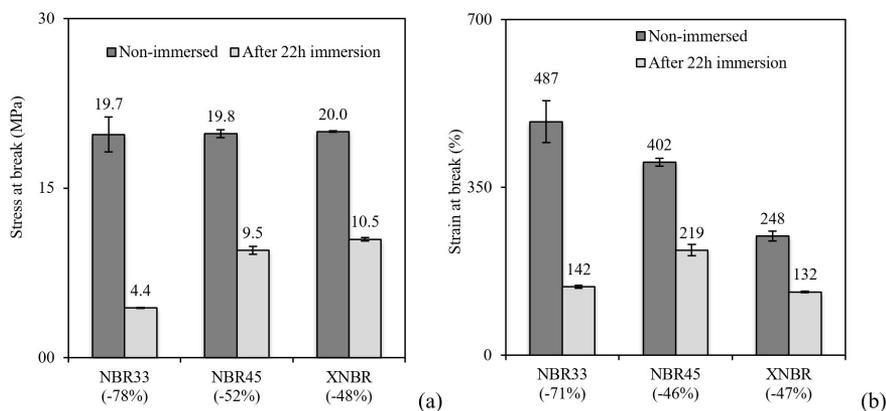


Figure 2. (a) Stress at break, and (b) strain at break of nitrile rubber compositions: non-immersed, and after immersion in soybean biodiesel for 22h at 100 °C. Between brackets the percentage of loss of the properties.

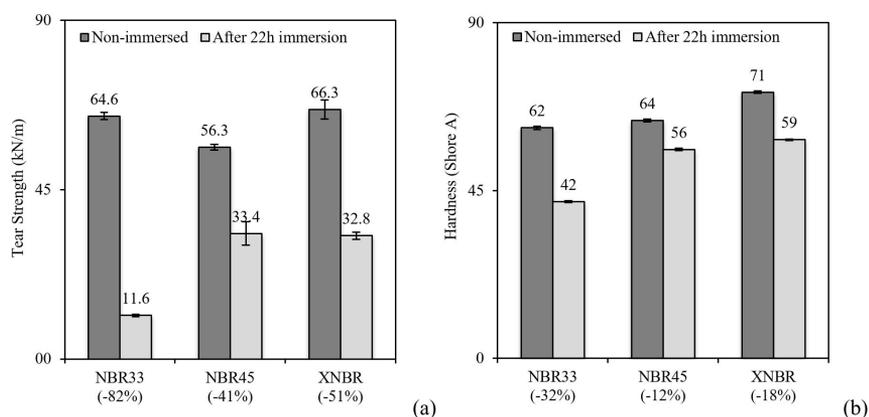


Figure 3. (a) Tear strength, and (b) hardness of nitrile rubber compositions: non-immersed, and after immersion in soybean biodiesel for 22h at 100 °C. Between brackets the percentage of loss of the properties.

to biodiesel for samples with higher acrylonitrile content^[10], in spite of they had been conducted at different conditions.

Despite having low acrylonitrile content (28%), the carboxylated nitrile rubber composition presented an average loss of 41%, which was close to those observed for high acrylonitrile content composition (*NBR45*). Moreover, *XNBR* had a better resistance to biodiesel than medium acrylonitrile content composition (*NBR33*). This suggests that the resistance of nitrile rubber samples are not merely assigned to the acrylonitrile content of the samples.

The losses of stress at break after immersion were matched with the samples' crosslink densities (Figure 4a) and with the mass change of each composition (Figure 4b).

Once again, we could observe that crosslink density solely does not rule rubber resistance to biodiesel (Figure 4a). *NBR33* and *NBR45*, which have similar crosslink density, presented remarkably different mechanical resistance to biodiesel, which, for these compositions, may be assigned to the difference in the acrylonitrile content. On the other hand, *XNBR*, with the highest crosslink density, had similar loss to *NBR45*. As already mentioned, carboxylated samples can form different kinds of crosslink bonds, because of the presence of carboxyl groups.

This additional type of crosslink improved the rubber resistance to biodiesel, despite the fact that *XNBR* has the lowest acrylonitrile content among the compositions. The crosslink networks of the compositions *NBR33* and *NBR45* were mostly composed by polysulfide crosslinks, which are less resistant to thermal and chemical oxidation.

We could infer that the presence of different types of crosslink network compensates the lower acrylonitrile content.

Comparing the stress at break losses with the change in mass after 22h (Figure 4b), we could highlight that *XNBR* has a superior resistance to biodiesel, since these samples had similar mechanical performance to *NBR45* after immersion in biodiesel, despite of having had a larger oil uptake.

The mechanical losses observed could be attributed to the reduction of the polymer chains entanglement^[6], oxidation of free double bonds, and reduction of polymer-filler interaction^[4,7,14,25], which were provoked by the diffusion of the biodiesel into the samples. The detrimental effects of the oil also come from its low oxidative stability, which is due to the high presence of unsaturated components^[4,18,26]. The oxidation of biodiesel results in the formation of carboxylic acids as well as water^[4], which can detrimentally react with the rubber network.

3.3 Scanning Electron Microscopy (SEM)

SEM analyses were also conducted to give further support to the observations already drawn. The fracture surfaces from all tensile tests specimens' compositions are shown in Figure 5.

NBR33 showed a highly deteriorated surface after the immersion compared to the non-immersed specimen. Many clusters on the surface of the immersed samples could be observed. The modified surface suggests a strong, yet destructive, affinity between the biodiesel and the elastomer.

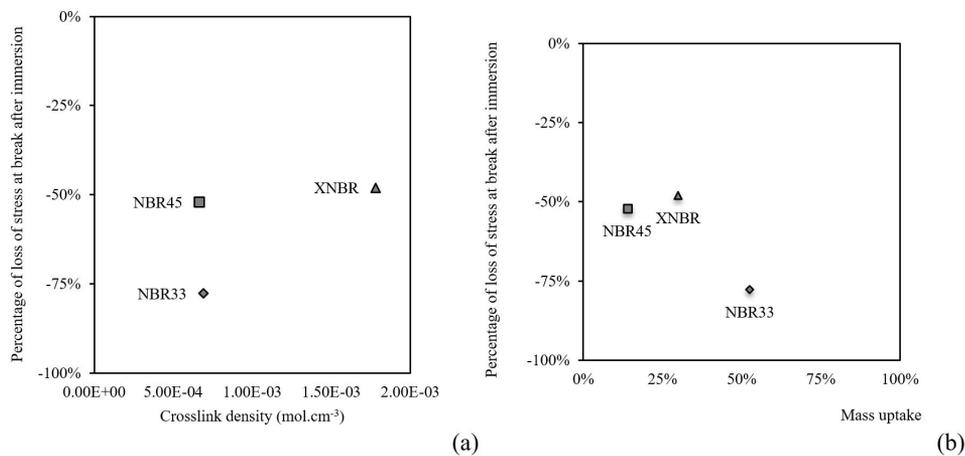


Figure 4. Percentage of loss of stress at break after 22h of immersion in soybean biodiesel of the nitrile rubber compositions as function of: (a) crosslink density (a); and (b) mass uptake.

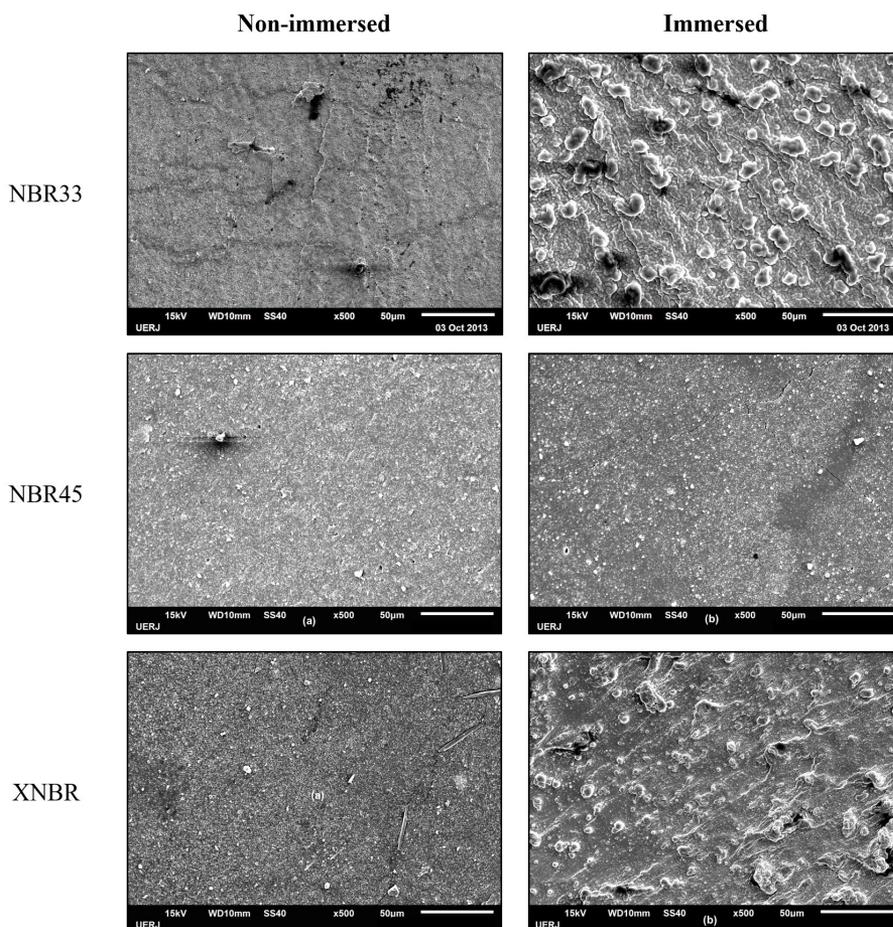


Figure 5. SEM Photomicrographs of fracture surfaces from the nitrile rubber samples. Non-immersed samples, and after immersion in soybean biodiesel for 22h at 100 °C.

On the other hand, the surface of *NBR45* sample was not much attacked after the immersion, as no modification was observed, which suggests weak affinity between the fuel and the composition with high acrylonitrile content. This suggestion is corroborated by the low oil uptake by that composition. This behaviour is beneficial considering the use of this type of nitrile rubber in some applications.

The photomicrographs from *XNBR* fracture surface only presented a few small clusters formed, indicating a moderate chemical interaction between the elastomer and the biodiesel. The different nature of the crosslink bonds might have contributed to lower detrimental interactions, despite the lower acrylonitrile content.

Furthermore, the SEM photomicrographs corroborates the results observed in Figure 1. It was observed that the compositions which absorbed more biodiesel presented a more modified fracture surface after immersion.

4. Conclusions

Based on the results from the mechanical tests and the SEM analyses, we could conclude the compositions *NBR45* and *XNBR* presented similar mechanical performance after immersion in soybean biodiesel. Moreover, despite having lower acrylonitrile content (28%), the carboxylated nitrile rubber exhibited a better performance after immersion in soybean biodiesel compared to the medium-acrylonitrile-content composition (*NBR33*). Furthermore, other conclusions could also be drawn from our results:

- 1) Increasing the acrylonitrile content of the elastomer improves the resistance of nitrile rubber samples to biodiesel;
- 2) Different crosslink systems also enhance the resistance to biodiesel, despite the acrylonitrile content;
- 3) The stress and strain losses were not directly affected by the amount of biodiesel absorbed by the compositions.

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