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Preparation of graft copolymers from Viet Nam deproteinized natural rubber with acrylonitrile using tetraethylenepentamine and *tert*-butyl hydroperoxide radical initiators

Nguyen Thi Ngoc Anh, Phan Minh Quyet, Vu Trung Nam, Nguyen Quynh Vi,
Than Van Hau, Tran Quang Tung, Nguyen Thu Ha, Nguyen Ngoc Mai, Tran Thi Thuy*

School of Chemistry and Life Sciences, Hanoi University of Science and Technology,
No1. Dai Co Viet Street, Hai Ba Trung District, Ha Noi, Viet Nam

*Email: *thuy.tranthi3@hust.edu.vn*

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Abstract. Natural rubber, known for its high strength, resilience, and elongation, undergoes degradation and exhibits poor thermal stability due to its unsaturation, prompting various techniques to enhance its properties. In this study, the graft copolymerization of acrylonitrile onto deproteinized natural rubber using tetraethylenepentamine and *tert*-butyl hydroperoxide as radical initiators at 30 °C was investigated to increase the thermal and mechanical properties of natural rubber.. The effects of acrylonitrile concentration on the conversion and grafting efficiency were studied. The structural characterization of the obtained graft copolymer was carried out by Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy. The improvement in thermal properties was confirmed by Thermal Gravimetric Analysis/Differential Thermal Gravimetric Analysis, which showed optimal graft copolymerization at 15 wt.% acrylonitrile, where the maximum degradation occurred at 377 °C. The mechanical properties of the products were also studied via tensile testing, where the tensile strength of the 15 wt.% acrylonitrile graft copolymer (1.5 ± 0.5 MPa) nearly tripled when compared to virgin deproteinized NR (3.8 ± 0.9 MPa).

Keywords: Acrylonitrile, deproteinized natural rubber, graft copolymer, thermal gravimetric, tensile strength.

Classification numbers: 1.3.3, 2.9.3, 2.9.4.

1. INTRODUCTION

The development of renewable materials such as natural polymers is becoming a major strategy to protect the environment. Natural rubber (NR) is a renewable resource with high economic value [1]. It is derived from *Hevea brasiliensis*, commonly known as the rubber tree, which is native to the Amazon River basin [2]. Like other plant materials, the latex comprises various growth-related substances. Specifically, NR is a colloidal system comprised of rubber particles that are stabilized by a thin layer of phospholipids and proteins. NR consists of approximately 40 - 45 % rubber (poly(cis-1,4-isoprene)) by weight, along with 4 - 5 % nonrubber constituents, including proteins, lipids, carbohydrates, and sugars. Additionally, it contains approximately 50 % water [3]. It has many outstanding advantages such as high tensile strength, high elongation, and high elasticity [4 - 8]. Due to its remarkable elastic properties, natural rubber is extensively and widely utilized in the manufacturing industry for various applications, ranging from vehicle tires and elastic bands to the production of cushions, blankets, and other related products. However, it contains 93 - 95 % cis-1,4-polyisoprene, resulting in poor oil resistance due to its low polarity and long hydrocarbon chains [9, 10]. In addition to the high content of C=C double bonds, it is easy to make the chain of natural rubber aging when exposed to oxygen, heat, ozone, and sunlight [11 - 13]. These disadvantages and the emergence of synthetic rubber have limited the commercial application of NR. Therefore, it is necessary to overcome the disadvantages and enhance the advantages of NR.

In fact, there are many methods that have been used to overcome the disadvantages of NR such as incorporating new functional groups into natural polymers, hydrogenation [14 - 17], epoxidation [18], and copolymerization with vinyl monomers [19]. Among those, the graft copolymerization is a commonly used technique. This is because it is a well-known method for creating hybrid polymers with distinctive structures required for a variety of applications by employing multiple monomers [20 - 22]. Typical monomers that have been successfully grafted onto the NR chain include methyl methacrylate (MMA) [23 - 26], maleic anhydride (MA) [8, 27], styrene (ST) [28, 29] and acrylonitrile (AN) [30]. AN is an attractive monomer to improve the mechanical, thermal properties and oil resistance of NR because of its highly polar nitrile group in its structure. In the reported works, graft copolymerization of AN onto NR latex has been carried out, and the structure and morphology of graft copolymer have been fully reported [30]. However, the thermal and mechanical properties of the graft copolymers of AN have not been fully reported.

This study aims at obtaining a better insight into the preparation of graft copolymerization of AN onto deproteinized natural rubber (DPNR) and fully addressed how improving of the thermal and mechanical properties of modified NR. Specifically, the graft copolymerization of AN onto DPNR utilized the redox initiator system tetraethylenepentamine/*tert*-butyl hydroperoxide (TEPA/TBHPO) in latex. The structural and chemical compositions of the DPNR, graft copolymer (DPNR-graft-PAN) was investigated by ATR-FTIR. The thermal properties of those samples were studied via TGA-DTGA and DSC. The mechanical properties of the products were determined via tensile testing.

2. MATERIALS AND METHODS

2.1. Materials

High ammonium natural rubber latex (HANR, 60 wt.% of dry rubber content (DRC)) was provided by Merufa Company (Ho Chi Minh city, Viet Nam). Sodium dodecyl sulfate (SDS, 99 wt.%) and AN (98 wt.%) were supplied by Tokyo Chemical Industry Co., Ltd, Japan. Urea was obtained from Nacalai Tesque, Inc (Kyoto, Japan). TEPA and TBHPO, and other chemical products for copolymerization preparation were purchased from Sigma-Aldrich Chemie Gmbh (Munich, Germany).

2.2. Methods

2.2.1. Deproteinization of NR

Before grafting copolymerization, the urea deproteinization was performed to increase conversion in the graft copolymerization [31]. HANR latex with a DRC of 60 % was used to create DPNR by incubating the latex with 0.1 wt.% urea and 1 wt.% SDS for 60 minutes at room temperature, followed by centrifugation at 10.000 rpm for 30 minutes at 15 °C. After the first centrifugation, the cream fraction was separated and dispersed in 0.5 wt.% SDS solution. Then the cream fraction was separated and dispersed in 0.25 wt.% SDS solution. The final DPNR, which had DRC of 30 %, was dispersed and preserved in a 0.1 %. wt. SDS solution.

2.2.2. The graft copolymerization of DPNR

The DPNR with DRC = 30 % was stirred at 250 rpm to remove any dissolved oxygen in the latex by bubbling with argon gas for 1 hour at 30 °C. Then TEPA/TBHPO initiator system with molar ratio of 1:1 (10^{-5} mol kg^{-1} dried rubber/10^{-5} mol kg^{-1} dried rubber) and AN were added to the reaction vessel. The stirring speed was increased to 400 rpm, keeping the reaction mixture at 30 °C for 2.5 hours. After the grafting reaction was finished, the unreacted monomer was removed by rotary evaporator under reduced pressure at 77 °C. The obtained latex was poured into a glass Petri dish to dry at 40 °C for a week. Then, homopolymers were removed by Soxhlet extraction the dried products with acetone solvent, and the samples were dried again for a week. This process was performed with different amounts of AN, respectively: 10, 15, 20 and 25 wt.% per kg dried rubber.

2.3. Characterization of the materials

The gravimetric analysis was used to determine Conversion and Grafting efficiency of AN. They were calculated by gravimetric method following these equations [32, 33]:

$$\text{Conversion (\%)} = \frac{\text{weight of PAN in gross polymer}}{\text{total weight of monomer}} \times 100\% \tag{1}$$

$$\text{Grafting efficiency (\%)} = \frac{\text{weight of PAN linked to NR}}{\text{total weight of polymer formed}} \times 100\% \tag{2}$$

The chemical structure of the obtained materials was confirmed by attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectroscopy (Thermo Scientific Nicolet iS5 FT-IR).

Thermal gravimetric analysis (TGA) was performed by a Linseis STA PT1600 analyzer with a heating rate of 10 °C/min under a nitrogen atmosphere and a temperature scan of 30 - 600 °C. Meanwhile, Differential Scanning Calorimetry (DSC) measurement was carried out using a DSC 7020 Exstar analyzer. The samples were cooled down to –150 °C using liquid nitrogen and heated up to 120 °C at a constant rate of 10 °C/min.

The tensile strength was used to evaluate the mechanical properties of the products. It was conducted using a Toyo Seiki Strograph VG10E according to JIS K6251 with a crosshead speed of 200 mm/min. The obtained samples were cut from solution-casted films with a Dumbbell-shaped No. 7.

3. RESULTS AND DISCUSSION

3.1. Graft copolymerization of AN

The effect of AN concentration, from 10 to 25 wt.% per kg dried rubber, on the conversion and graft efficiency of AN onto DPNR is presented in Figure 1. The grafting efficiency of copolymerization reached the highest value at (35.32 ± 2.01 %) at which the conversion gains (60.16 ± 1.72 %), corresponding to concentration of 15 wt.% AN. At the content of 20 and 25 wt.% AN, the conversion continuously increased but the grafting efficiency decreased. This is because at a high AN concentration, monomers are more likely to react with each other to create homopolymer than with DPNR's backbone [34, 35]. Therefore, the optimal condition for graft copolymerization is the 15 wt.% concentration of AN. This sample was selected to investigate the structure, thermal and mechanical properties of the material.

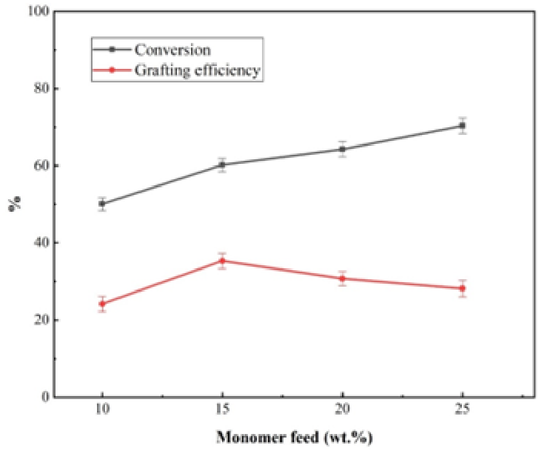

Figure 1. Effect of AN concentration, (wt.% per kg dried rubber), on graft copolymerization.

3.2. Structural characterization of the graft copolymer

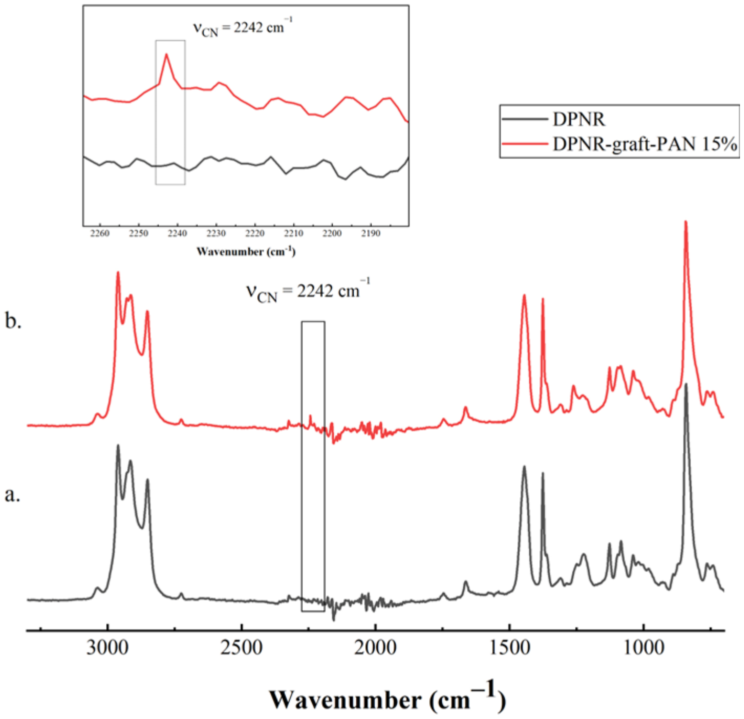

Figure 2. FT-IR spectra of (a) DPNR and (b) DPNR-graft-PAN copolymer sample.

Table 1. Signals of functional groups on the FT-IR spectra.

Stretching vibration and bending vibration (cm^{-1})	DPNR	DPNR-graft-PAN
$\nu_{\text{C-H olefin}}$	3040	3040
$\nu_{\text{C-H alkyl}}$	2962	2962
ν_{CN}	-	2242
$\nu_{\text{C=C olefin}}$	1664	1664
$\delta_{\text{C-H alkyl}}$	1442, 1376	1442, 1376
$\delta_{\text{C=C olefin}}$	840	840

The FTIR method was used to confirm the presence of AN on the DPNR-graft-PAN copolymer obtained after Soxhlet extraction. The characteristic absorption bands of DPNR and DPNR-graft-PAN with 15 wt.% AN were presented in Table 1 and Figure 2. There are five mentioned characteristic peaks attributed to NR structure: C-H olefin stretching vibration at 3040 cm^{-1}, C–H alkyl stretching vibration at 2962 cm^{-1}, C-H alkyl bending vibration at 1442, 1376 cm^{-1}, C=C olefin bending vibration at 840 cm^{-1} and C=C olefin stretching vibration at 1664 cm^{-1} [36 - 38]. Besides, the IR spectrum of DPNR-graft-PAN copolymer showed additional signal, which is suitable functional groups and structure of grafted monomer. The additional peak appearing at 2242 cm^{-1} was assigned to the valence vibration of the −C≡N group in the PAN molecule [39]. This confirms the presence of the PAN segment in DPNR-graft-PAN. This indicates that the graft reaction has occurred.

3.3. Thermal properties

3.3.1. DSC

The glass transition temperature (T_g) of NR was studied by differential scanning calorimetry (DSC) method. The curves of DPNR and DPNR-graft-PAN 15 wt.% samples are presented in Figure 3. The T_g of DPNR is – 65.14 °C, which corresponds to the cis-1,4 polyisoprene structures of the DPNR. This result has also been reported in Derouet’s study [40]. Meanwhile, the T_g of DPNR-graft-PAN increased to – 60.51 °C.

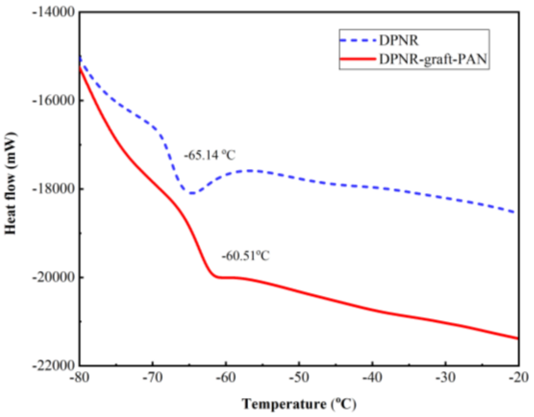

Figure 3. DSC curves of DPNR and DPNR-graft-PAN 15 wt.%.

The increase in T_g of co-polymer products can be interpreted as an increase in the hardness of chemically modified NR materials. Because T_g is a parameter that reflects the flexibility of the polymer segments. This variation may be due to interactions between the chains of the PAN branch. When the AN monomer is grafted to the NR chain, the intermolecular forces in the copolymer increase due to the presence of polar nitrile groups in PAN. This force is stronger, leading to stronger interactions between polymer chains. Another reason that can cause the increase in T_g of modified NR is the cross-links formed between the polymer chains of NR. As can be seen in Figure 3, the selection of AN monomer to denature NR has shifted T_g significantly, shifting by 4.63 °C compared to the T_g of DPNR. According to Dung's research, the copolymerization of ST onto DPNR shifted T_g from − 63.90 °C to − 63.14 °C, which is a slight change in T_g of NR after the modification [9]. Another study of Hieu *et al.* indicated that the combination of AN and ST in DPNR copolymer has a rather large impact on the T_g of DPNR, which increased by 6.44 °C [33].

In addition to the monomer choice directly affecting T_g, the method selection is also important. When compared with other methods, it was found that graft copolymerization resulted in a clear shift of T_g. According to Mahittikul's study, the transfer hydrogenation of HANR shifted T_g from − 62.3 °C to − 61.9 °C, with a small change in HANR's T_g after transfer hydrogenation [15]. According to another report by Ha *et al*. in 2015 that showed that transfer hydrogenation to DPNR shifted T_g from − 67 °C to − 65.8 °C [41]. The T_g of NR did not shift significantly when NR was modified by the transfer hydrogenation method. This is because the replacement of a C=C double bond by a C-C single bond in the transfer hydrogenation process does not influence the mobility of copolymers chains resulting in doing not shift in T_g [33].

3.3.2. TGA-DTGA

The decomposition temperatures (T_d) of DPNR and DPNR-graft-PAN 15 wt.% were investigated by thermal gravimetric analysis and differential thermal gravimetric analysis (TGA-DTGA). TGA-DTGA of obtained materials were displayed in Figure 4 and Figure 5. The T_d of DPNR was 371 °C, while DPNR-graft-PAN decomposed at higher temperature, 377 °C. This demonstrates that AN grafting improved the thermal stability of DPNR.

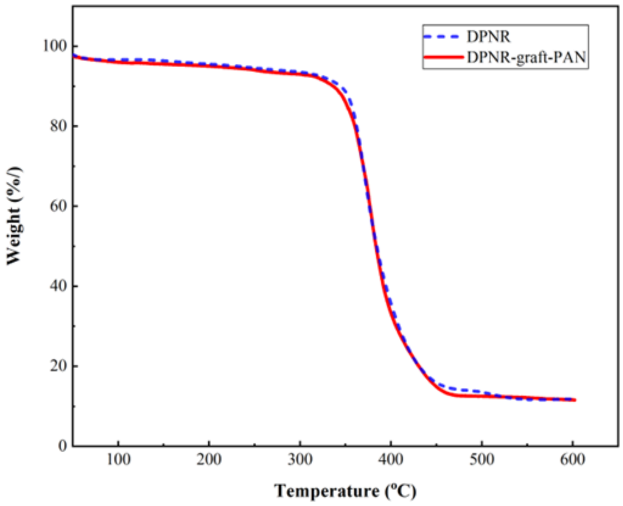

Figure 4. TGA curves of DPNR and DPNR-graft-PAN 15 wt.%.

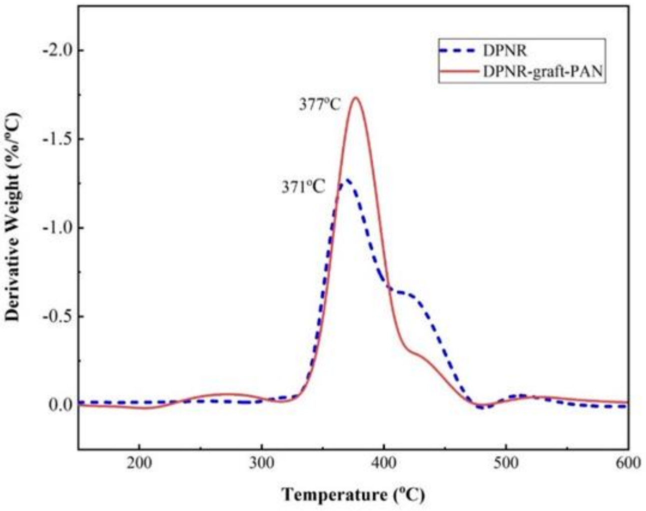

Figure 5. DTGA curves of DPNR and DPNR-graft-PAN 15 wt.%.

The improvement of T_d of graft copolymer compared with DPNR can be explained by three main reasons. Firstly, it is possible that graft copolymerization with AN, which is a vinyl monomer, increased the saturation of the DPNR chain [4, 25, 42]. The second reason is the interactions of dipole-dipole of polar functional groups of PAN chains grafted onto the DPNR's backbone, which are stronger than those of London interaction of non-polar functional groups of the DPNR [30]. Finally, the graft copolymerization of AN can help to form crosslinks between NR polymer chains, which increase intermolecular forces.

Acrylonitrile has improved well the thermal properties of NR, which is evident when compared with other monomers. According to Hieu *et al*. study, the graft copolymerization of ST/AN onto DPNR improved T_d from 367.1 to 371.5 °C, which increased by 4.4 °C [33] [12]. Another study of Nhan *et al*. showed that the T_d of DPNR improved from 365.36 to 373.77 °C in the presence of MMA, which increased by 8.41 °C [25]. In the present study, the T_d of denatured NR was increased to 6 °C after graft copolymerization with AN monomer. Thus, the ability to improve the thermal properties of NR when using each AN is better than using both ST and AN, but not as good as using MMA.

3.4. Mechanical properties

Tensile strength is an important characteristic of polymeric materials because it indicates the limit of final stress in most application [43]. The stress-strain curves of unvulcanized DPNR and DPNR-graft-PAN 15 wt.% are shown in Figure 6. The tensile strength of the DPNR sample is about (1.5 ± 0.5 MPa), which corresponds to the cis-1,4 polyisoprene structures of the DPNR. Similar result has also been reported in our previous study [44]. After grafting the monomer onto the DPNR chain, the tensile strength increased by nearly tripled when compared to DPNR (3.8±0.9 MPa). The significant increase in the tensile strength of DPNR-graft-PAN compared to DPNR may be explained by the effect of polyacrylonitrile layer, which was chemically linked and encapsulated NR particles [30, 33, 44]. The polyacrylonitriles are grafted around the NR core in the form of branches leading to increased intermolecular interactions, resulting in increased tensile strength of DPNR. Nhan *et al*.'s report presented that the graft copolymerization of MMA onto DPNR increased the tensile strength about 2 times compared with DPNR [25]. In another study of our group, the combination of AN and ST in DPNR copolymer increased the tensile strength about 2 times compared to DPNR [44]. Thus, when compared with other monomers, it was found that AN improved the mechanical properties of natural rubber well.

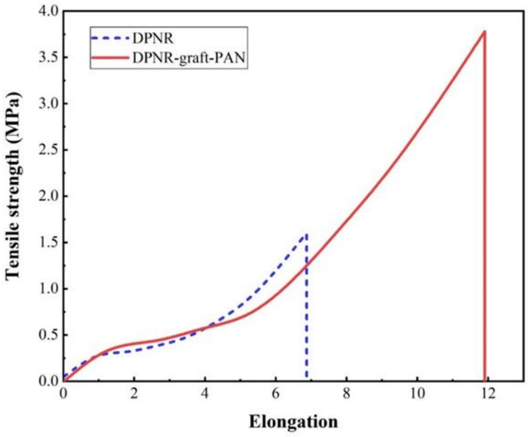

Figure 6. Stress-strain curves of unvulcanized DPNR and DPNR-graft-PAN 15 wt.%.

4. CONCLUSIONS

The graft copolymerization of AN onto DPNR in latex stage with TEPA/TBHPO as the organic redox initiators was performed productively. This was proved by ATR-FTIR spectra. The effects of the content of AN on the conversion and grafting efficiency have been studied and the highest grafting efficiency was observed at AN 15 wt.% per kg of rubber, where the grafting efficiency and the conversion were achieved (35.32 ± 2.01 %) and (60.16 ± 1.72 %), respectively. The improvement in thermal properties of the obtained products has been verified by TGA/DTGA and DSC measurements with a remarkable increasing value in both T_d (377 °C) and T_g (–60.51 °C). Besides that, the mechanical properties of graft copolymer have been significantly improved, where the tensile strength of it was increased by nearly triple compared to DPNR. This improvement in thermal and mechanical properties revealed a promising method in modification of untreated NR.

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Declaration of competing interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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