

Invited Review:

Natural rubber nanocomposites

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Abstract

Natural rubber (NR) is a valuable and important polymer material that has wide and various applications. Therefore the investigations for NR improvement, particularly for special applications are in continuous development. In this trend, preparation of NR nanocomposites using nanofillers of both organic and inorganic origination is one of leading directions. In this paper, NR nanocomposites with the most popular and promising nanofillers were reviewed. These nanofillers are nanosilica and layered silicate as the most important fillers for NR industry after carbon black, and nanocellulose as a new abundant and environmental friendly filler. Methods of NR nanocomposites preparation were briefly summarized. The main attention was paid to the establishment of nanostructures in NR composites. Based on limited (about 80) references, mostly in recent 15 years, the improvement of NR nanocomposite properties was analyzed in connection with their nanostructure.

Keywords. Natural rubber, nanocellulose, nanosilica, nanoclay, nanocomposite.

ABBREVIATION

CB	– Carbon black
CNF	– Cellulose nanofiber
DSC	– Differential scanning calorimetry
DMA	– Dynamic mechanical analysis
DPNR	– Deproteinized natural rubber
MFC	– Microfibrillated cellulose
NCC	– Nanocellulose crystal
NR	– Natural rubber
NRCN	– Natural rubber-cellulose nanocomposite
NRNC	– Natural rubber nanocomposite
ONR	– Oxidized natural rubber
RNC	– Rubber nanocomposite
SEM	– Scanning electron microscopy
TEM	– Transmission electron microscopy
TGA	– Thermal gravimetric analysis
phr	– per hundred rubber

1. INTRODUCTION

Natural rubber (NR) is one of the biopolymer materials that have very wide applications. Due to such valuable properties as high tensile strength, high deformation, excellent viscoelastic behavior, the use of NR in many economic and technical fields is irreplaceable. According to VPS report [1] the main applications of NR in various fields are:

- Tyre: 65 %
- Tubes and transport belts: 8 %
- Accessory: 7 %

- Medicine: 6 %
- Shoes: 5 %
- Other: 9 %.

NR world production developed regularly, about 4.5 % per year in the period 2002-2012 [1]. Although there was some stagnation in 2008-2009 because of world economic regression NR world production is raised again, about 1.3-1.5 % per year in 2013-2016 years and expected will growth 3 % per year in average in period 2016-2025 [2].

Nanofillers for polymer nanocomposite preparation are in growing utilization [3-5]. These

fillers may be classified by various methods based on:

- The numbers of the size of nanometer scale. There are one-nanosize fillers (layered silicate), two-nanosize fillers (carbon nanotube, cellulose nanowhiskers) or three-nanosize fillers (nanoparticles of metallic oxides or minerals).
- The filler origination: natural or synthetic
- The filler nature: organic or inorganic.

Because of a wide variety of filler, the challenge of rubber nanocomposite preparation is the dispersion of nanofiller in polymer matrix into nanoscale dimension. In many cases, it is beyond the possibility of traditional processing equipment. This point is the main obstacle for industrial application of rubber nanocomposites (RNC).

Although carbon black (CB), one kind of nanofillers, has been prepared and are used in rubber industry from 20th years of XX century, notion RNC is considered as advanced materials only in last 20 years. A number of scientific publications on RNC is also quite modest in the comparison with nanocomposites based on plastic matrix. However, perspective trend in various applications of RNC is obvious, that why the publications on RNC raised rapidly last years.

In this paper, nanocomposites based on NR are considered. Natural rubber nanocomposites (NRNC) preparation and properties, as well as their structure, is discussed.

2. PREPARATION METHODS OF NATURAL RUBBER NANOCOMPOSITES

Like other nanocomposites from thermoplastic polymers, NRNC may be prepared by methods such as solvent-assisted technique, water-assisted technique and melt mixture. *In-situ* polymerization method, often used for the synthetic polymer, is not practiced for NRNC.

2.1. Mixture in solution (solvent-assisted technique)

According to this method, NR is dissolved in some organic solvent while nanofillers are separately dispersed in the same solvent to form a suspension. When two components are mixed, NR molecules and nanofiller particles easily penetrate into each other and form nanocomposite. This method is very effective when nanoclay (layered silicates) is applied. Due to well-swelling capacity of organomodified nanoclay in the organic solvent, silicate layers are pushed apart from each other, creating good conditions for polymer molecules get

into interlayer space and form nanocomposite with intercalated and/or exfoliated structures [6]. For example, in butadiene styrene/nanoclay system with toluene, the interlayer space of nanoclay is expanded more than twice [6]. In some cases, low molecular polymers (for example epoxy or liquid rubber) are used to swell nanoclay before it is mixed with rubber.

The solvent-assisted method may be used to make nanocomposites from both NR and synthetic rubbers.

2.2. Mixture in latex (water-assisted technique)

Latex is the stable emulsion of rubber particles with the dimension in nano-meso range in water media. Nanofiller particles, such as nanosilica, nanoclay etc. may be easily dispersed in water owing to surface active substances to form their suspension. This suspension is mixed with NR latex and then coagulated by common methods to receive NR nanocomposites. This is a very effective method for the preparation of NR nanocomposites with nanofillers of various natures [7].

Another modification of this technique is dispersion of NR in nanomatrix. For example, deproteinized natural rubber (DPNR) latex is dispersed in polystyrene (PS) matrix to create the composite system, in which NR is dispersed phase of average particle size 0.5-0.6 μm , while PS form the continuous phase surrounding NR particles by the film of thickness 15-25 nm [33].

The mixture in latex has advantages for both direct preparations of NRNC and of the masterbatch with the high concentration of fillers. Note, masterbatch from NR-nanofiller allow not only preparation of NRNC but also nanocomposite from the blend of NR with other rubbers or plastic. Besides, using water as dispersion medium instead of organic solvent shows the advantage of this technique due to environmentally friendly character.

2.3. Melt mixture (Direct melt mixing)

Direct melt mixing is a highly applicable technique from present rubber processing point of view. According to this technique, nanofiller mainly in the form of fine powder, is brought into rubber by mean of two-roll mixing mill [8, 9] or internal mixer [10-12]. Thanks to high shear rate and temperature, nanoparticles are dispersed in the melt rubber matrix until the homogenous mixture is reached. Hence, shear rate and temperature in mixing process have great influence on NRNC properties, particularly mechanical. Besides, the rubber polarity also effects

on properties of received nanocomposites. As NR is the material owing very low polarity, some measures are taken to make the polarities of NR and nanofillers closer. It may be a surface modification of nanofiller that lowers its polarity [12] or NR modification for raising its polarity [13]. Also possible to use low molecular liquid for swell nanofiller, therefore promote the penetration of rubber molecules into the filler. For example, polyethylene glycol is used for dispersion nanoclay in NR in process melt mixing [11].

From above brief resume, one can see the two methods, namely mixing in latex and direct melt mixing; have high possibility to industrial application although they are now in development.

Solvent-assisted technique may be applicable, but only in special cases because of high cost and harmful effect of organic solvents on the environment

3. NANOCOMPOSITES FROM NR AND ORGANIC NANOFILLERS

3.1. Natural rubber-cellulose nanocomposite (NRCN)

The most popular organic nanofiller at present is nanocellulose. As cellulose is the main component in botanical organs, cellulose nanofillers may be extracted from very wide sources (table 1).

Table 1: Example of length (L) and diameter (D) of nanocellulose fillers, extracted from various sources [14]

Source	L (nm)	D (nm)	Experimental technique
Bacterial	100-1000	10-50	TEM
Tunicate	1160	16	DLS
	100-1000	15-30	TEM
Valonia	>1000	10-20	TEM
Cotton	255	15	DLS
	100-150	5-10	TEM
Cotton linter	15-320	6-70	TEM
	300-500	15	AFM
Soft wood	100-150	4-5	AFM
Hard wood	140-150	4-5	AFM
Wheat straw	150-300	~ 5	TEM
Rice straw	117±39	8-14	TEM

Beside of differences in dimensions as shown in table 1, the nanocellulose elements are different in morphology and crystalline state. For example, nanocellulose crystals (NCC) consist almost of the crystals of cellulose while the microfibrillated cellulose (MFC) has alternating structure of crystalline and amorphous parts. In morphology MFC presents a rather stable network structure, but NCC show only rod-like structure. MFC have aspect ratio much higher than NCC have (table 2).

Obviously, with a wide variety in dimension, morphology, and crystallinity, the separation of various kinds of nanocellulose has no significant practical meaning. Therefore in this review, they will be considered together as cellulose nanofiller (CNF) in general.

The main advantages of CNF are low density, renewable nature, high mechanical characteristics, a

wide variety of supplied source, low abrasion of processing equipment [16]. It worth to note, CNF surface is active, so they have the ability to be modified by chemical functional groups for receiving improved properties [16,17]. However, CNF as reinforcement filler has some disadvantages, such as high moisture adsorption, low wetting capability, and low compatibility with most polymer matrices because of the big difference in surface polarity.

The works of French authors [18, 19] may be considered as pioneer report on high reinforcement possibility of NCC for composite materials. The rapid development of a number of publications with keyword "cellulose nano" shows the high level of attention to this material: from total 517 publications in 2000, this number reached 4062 till 2009 [16].

Table 2: Comparison of dimensions of MFC and NCC [15]

Structure	Length, nm	Diameter, nm	Aspect ratio
Microfibrillated cellulose	> 1000	10-40	100-150
Nanowhisker	100-600	2-20	10-100
Microcrystalline cellulose	>1000	>1000	~1

3.1.1. Structure of NR/cellulose nanocomposites

As there are lots of OH-groups on the surface of CNF elements, it is expected that the cellulose-NR interaction will be weaker than cellulose-cellulose one. Also, due to high aspect ratio, CNF form their network with hydrogen bonds inside the polymer matrix [6]. Interaction in the cellulose-cellulose network may remarkably raise the elastic modulus of nanocomposites.

Beside strong interaction of CNF, the modulus enhancement of nanocomposites also is explained by mechanical percolation effect of cellulose fibers [16]. When the CNF content reaches some defined ratio by volume they pass through each other to form the mechanical network that is responsible for abnormal high mechanical properties. This defined ratio is named as percolation threshold and linked with the aspect ratio of fiber (table 3).

Table 3: Aspect ratio (L/D) and percolation threshold (ϕ) of some CNF [16]

Sources	L/D	ϕ , %
Cotton	11.8	5.9
Ramie	28.6	2.5
Sugar beet pulp	42	1.7
Palm tree	43	1.6
Wheat straw	45	1.6
Tunicin	6.7	1.0

Together with cellulose percolation network, in [20] is proposed Zn-cellulose network that coexists with crosslinked NR molecules. According to this model, the 3D-network Zn-cellulose is formed as a result of the reaction of cellulose with activator or accelerator in the pre-vulcanization period. It is assumed that ion Zn forms the loose complex with OH-groups of atoms C2, C3 in glucopyranose group of cellulose. In addition, high polarity of cellulose molecules makes the interaction of this 3D network in the composite structure become stronger.

Unlike NR crosslinked network that takes place in the whole volume, the Zn-cellulose network exists in clusters, and interaction between clusters is rather

weak and easily broken by NR matrix swelling in toluene and *p*-xylene [20].

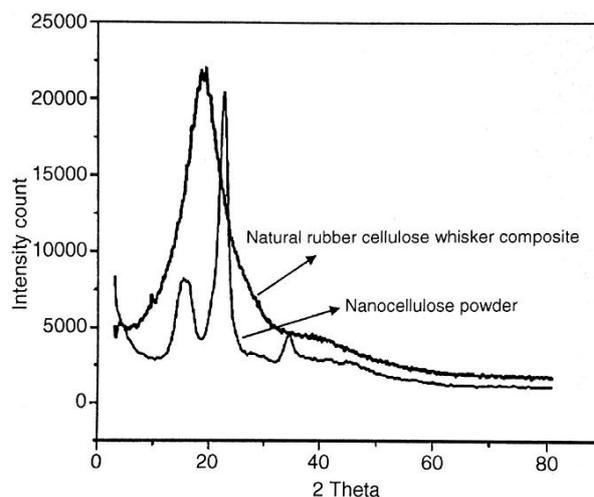


Figure 1: XRD patterns of NR/nanocellulose composites

Nanofiller structures have an obvious effect on NRCN structure. In [21] shown, in the processing work, MFC fillers entanglement is easier than nanowhiskers, that is clear on SEM pictures. In dispersion process, layers in nanocellulose crystals are pushed apart from each other, that shown in XRD patterns [22].

Interaction of NR and cellulose is realized through hydrogen bonds between their molecules. As mentioned above, these bonds are weak, so NR-cellulose interaction is much weaker than cellulose interaction. In any case, the NR-cellulose interaction may limit the mobility of NR molecules, as reported in publications [21, 24, 25].

3.1.2. Properties of NR/Cellulose nanocomposites

Mechanical properties

Thanks to nanocellulose elements dispersed in NR matrix, NRCN have improved strength, modulus etc. in comparison with initial NR, while their elastic properties are almost unchanged.

In [23] the changes of stress-strain curves of NRCN with nanocellulose whiskers content were studied (figure 2).

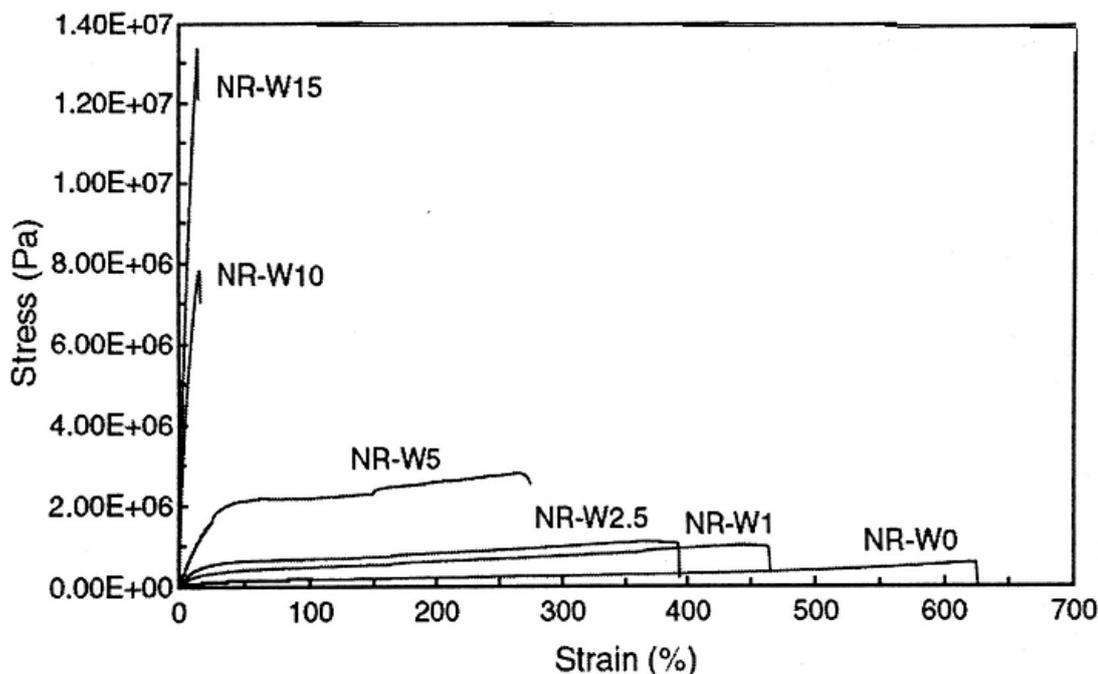


Figure 2: Stress-strain curves of NR/cellulose whisker nanocomposites [23]; $T = 25^{\circ}\text{C}$ (the numbers in codification show whisker content)

One can see when whisker content rises till 5% the nanocomposites have remarkably enhanced strength and modulus, while the curves show obvious elastic character. However, when whisker content reaches 10%, materials behave like typical brittle body.

Morphology of CNF also effect on mechanical properties of NRCN. Bendahou A. et al [21] show, when 10% nanowhisker can make NRCN become brittle, then 5% of MFC is enough to bring the same effect. Tensile strength and modulus of NRCN reinforced with MFC are also higher than that of whisker filled composites. It may be explained that higher MFC aspect ratio results in lower percolation threshold of MFC than that of NCC; hence the reinforcing effect of MFC higher than nanowhisker at the same concentration [16, 21].

Besides, in MFC there are some non-cellulose substances such as lignin, hemicellulose, that enhance adhesion of MFC to NR in comparison with nanowhiskers containing almost only cellulose [21].

In other research [24] it is suggested that added

value in percentage of mechanical properties owing to nanoreinforcement depend remarkably on properties of matrix materials. In case of NR, it depends on processing and vulcanization conditions. This dependence could be seen when stress-strain curves of NRCN with nanowhisker content to 10% are investigated: for all considered nanowhisker contents, the tensile stress rises drastically only after 400% deformation and the forms of curves stayed the same (figure 3).

This means nanowhiskers have almost no effect on strain-induced crystallization of NR composite that is responsible for the high strength of NR, and effect of NR crosslinking have an advantage over reinforcement effect of nanowhiskers.

The fact that proves NR-cellulose bindings are weaker than bindings in vulcanization network are results of successive tensile testing: at first loading-unloading cycle, nanocomposite has modulus notable higher than that of original NR, but after fourth cycles, these values become almost the same (table 4).

Table 4: Tensile modulus E_i , in MPa, of NR and NRCN in successive test [21]

Sample	E_1	E_2	E_3	E_4	E_5	E_6	E_7
NR	0.64	0.58	0.36	0.27	0.20	0.17	0.16
NR-W ₁	1.58	0.75	0.38	0.27	-	-	-
NR-MF ₁	1.50	0.79	0.32	0.22	-	-	-

Note: NR-W₁ and NR-MF₁ are nanocomposites reinforced with nanowhisker and microfibrillated cellulose respectively, with filler content 1 phr.

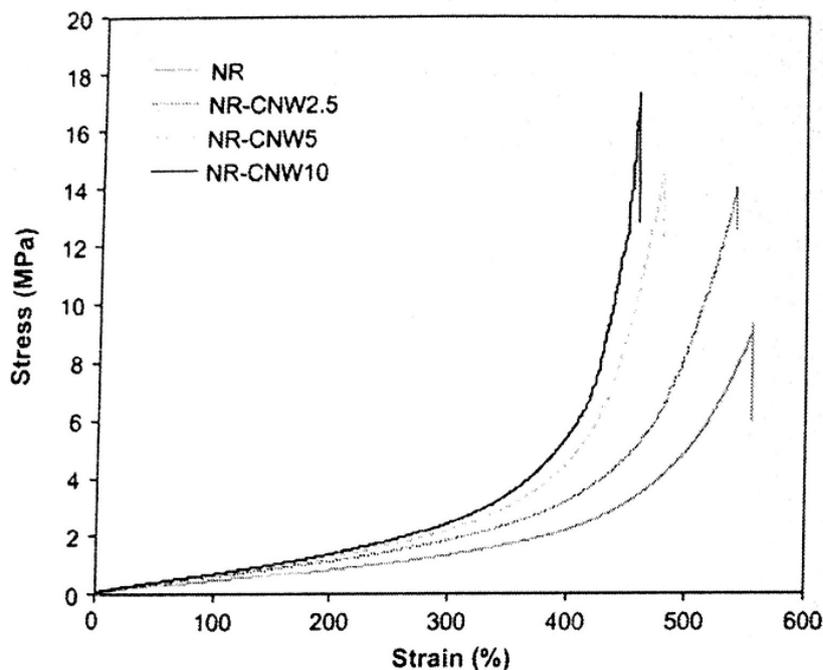


Figure 3: Stress-strain curves of NR/cellulose whisker nanocomposites [24]

For improvement of NR-cellulose interaction, some researchers have oxidized NR by KMnO_4 [25]. The surface of oxidized NR (ONR) is supposed richer of OH groups than NR, so NR-cellulose interaction would be improved thanks to increasing number of hydrogen bonds. This improvement may be seen through successive tensile test results: decreasing of modulus after two loading-unloading cycles of ONR composites is less than that of NR-composite. However, this improvement is not so remarkable, maybe because of decreasing of molecular weight of ONR when the degree of oxidation increases. And this molecular weight decreasing may compensate the influence of increasing hydrogen bonds.

NCF also have the effect on dynamic properties of NRCN because of limitation of molecular NR mobility in presence of NCF. At the temperature below glass transition temperature T_g the movements of molecules are restricted, so storage modulus of NR and NRCN are approximately same. When the temperature higher T_g , mobility of NR molecules increases, then effect of NCF begins to be observed: the storage modulus of NRCN (E') is higher for 5-6 times in comparison with NR composites [21, 24, 25]. If the NCF content is high enough to pass mechanical percolation threshold, the strong network is formed then E' increase hundred times [21].

Thermal properties

The thermal properties of NRCN are

investigated through TGA, DSC or DMA curves. In [20, 24] researchers observed the higher heat resistance of NRCN than that of NR. It is shown in increasing of beginning decomposition temperature T_0 and maximum degradation temperature T_{\max} of NRCN. Although the NR-cellulose interaction is assumed rather weak due to a low compatibility of two components and thermal stability of cellulose lower than that of NR, these results prove the existence of some strong interaction of these materials.

The main reason for improved thermal stability of NRCN is suggested that around nanocellulose elements, the mobility of NR molecules is decreased [20, 21, 24, 25]. In [24] it is shown, the higher CNF content (to 10 %) the higher T_{\max} . However, the other picture is shown in [20]: when CNF content is low (2.5 %), formed networks such as Zn-cellulose or percolation may raise thermal stability of NRCN. But when CNF content is high enough (5-10 %), the thermal stability of NRCN is a little lower in comparison with NR. The reasons of this may be: the presence of low-molecular-weight bioorganic fiber, the cellulose aggregates create the non-homogeneous distribution of filler in NR matrix and oxygen in cellulose backbone.

Increasing NR-cellulose interaction by oxidation of NR has no significant influence: the T_{\max} of NRCN is only 380 °C while T_{\max} of NR is 377 °C. Suggested, the enhanced interaction by increasing number of hydrogen bonds is compensated by decreasing of molecular weight of NR molecules

resulted from oxidation [25].

Note, the glass transition temperature T_g of NRCN does not change remarkably than that of NR. This proves that reinforcement effect of NCF displays mainly at temperatures higher than T_g , as mentioned above.

Other properties

Barrier properties of nanocomposites in, particularly of a new class of biodegradable nanocomposites, such as NRCN, are attracting great attention. These types of nanofillers may impart, apart from barrier properties, other smart properties such as antimicrobial or biosensing etc. [16].

For NRCN, barrier properties are estimated firstly by swelling behavior and diffusion coefficient of organic solvents. Typically, they are toluene,

good solvent for NR and water, non-solvent medium for NR but have high affinity to cellulose [20, 21, 25]. In toluene, NRCN have much lower swell than NR, and the higher NCF content the lower swell of NRCN: from 92-93 % of 1 % NCF composite reduced to 84-86 % of 5 % NCF one, in comparison with 2233 % of neat NR [20]. The reason may be, beside tortuosity of path or void reduced with the increase of nanofiller contents, the formation of Zn-cellulose network by percolation mechanism of cellulose. Indeed, this result is quite suitable to the calculation: with the aspect ratio 10-50, NCF (whiskers) have percolation threshold in the range of 4.6-5.9 %. Besides, this network may lead to increasing of the whole crosslinking density of NR (table 5).

Table 5: Dependence of crosslinking of NRCN on nanofiller loading [20]

NCF loading in NRCN, %	V_r	Crosslinking density $\times 10^{-6}$
0 (NR matrix)	0.7432	0.8592
2.5	0.7813	0.9023
5.0	0.7992	0.9249
7.5	0.8052	0.9356
10.0	0.8078	0.9394

Note: V_r – volume fraction of rubber phase in the swollen gel of vulcanized rubber.

It is remarked in [21] that no visible difference in toluene uptake of NRCN with MFC or nanowhiskers, although these fillers have quite different morphology, resulting in their different interaction with NR: rod-like whiskers seem to have interaction through hydrogen bonds and percolation network, while MFC-to entangle. Because NR-cellulose interaction is expected rather weak, the authors [21] come to the conclusion that the reduction of swelling in toluene is most probably result from the cellulose-cellulose interaction.

Opposite to swelling in toluene, water uptake of NRCN increase with filler contents [25]. It is supposed, the reduction of water uptake by increasing surface interaction between NCF and NR is compensated by high affinity to water of cellulose. It is shown, when the water uptakes of NRCN with nanowhiskers and MFC are compared: MFC, having lower affinity to water due to presence of residue of lignin, fatty acid, etc. on surface, impart lower water uptake to NRCN than nanowhiskers, having almost all cellulose in their content (table 6).

The electrical properties of NRCN also attract attention. Studies by dielectric spectroscopy show that the conductivity of NRCN rises with cellulose contents till 15 phr. The dependence of conductivity on temperature is obvious: at low temperatures, the

degree of conductivity increasing is rather low, while at the elevated temperature (100-150°C), the conductivity increases remarkably [26]. However, the author notice that composite conductivity is limited by NR one. Because of lack of physical contact between nanocellulose particles, the electron tunneling mechanism is hindered.

Table 6: Toluene uptake (TU) and water uptake (WU) of NRCN [21]

Materials	TU (%)	WU (%)
NR	2223	15.5
NR-W1	93	-
NR-W2,5	92	65.7
NR-W5,0	84	83.0
NR-W10	80	82.3
NR-W15	79	119.7
NR-MFC1	92	-
NR-MFC2,5	86	21.7
NR-MFC5,0	91	20.9
NR-MFC10	89	-
NR-MFC15	70	37.9

Note: NR-W and NR-MFC are nanocomposites with nanowhisker and microfibrillated cellulose respectively. The numbers indicate the NCF content in phr.

The temperature dependence of NRCN conductivity is studied deeper in [27]. At low temperatures, conductivity increase is supposed due to moisture increase by OH groups on cellulose surface. At elevated temperature, this increase is dominated by the crystalline degree of cellulose: composites filled with cellulose nanocrystals have the higher conductivity of one with MFC.

Surface interactions between NR and cellulose fillers have a certain effect on NRCN conductivity. The interface acts as nanopore that allows movement of ion-carrying elements to form a complete circuit. This will be more favorable when nanocellulose crystals (NCC) form a percolation network in NRCN volume. In contrast, the surface of MFC with the presence of residue of lignin and fatty acid may reduce the formation of hydrogen bonds between NR and cellulose, As a result, NRCN with MFC have conductivity lower than that of composites filled with NCC [27].

Although NCF increase the NRCN conductivity, in some applications this increase seems to be not

enough. For more conductivity increase, in [28, 29] were prepared NRCN with hybrid carbon black/nanocellulose filling by latex assembling technology. In these materials, carbon black (CB) particle adhere onto nanocellulose crystals, thanks to which the conducting percolation network from low content of NCC (1.65 %) is reached. This carbon black/ nanocellulose percolation network increase the conductivity of composite to 12 orders: from 4.8×10^{-13} S/m for CB/NR composites to 3.5×10^{-1} S/m for CB/NCC/NR composites at the same CB loading (3.75 v. %). It is a very promising direction to the preparation of conducting CB/NR material with low CB contents.

3.2. Other nanocomposites NR/organic filler

Beside CNF, some other nanofillers of organic origination such as chitin or starch are also studied. Their TEM images are shown in figure 4. For comparison, MFC and NCC also presented.

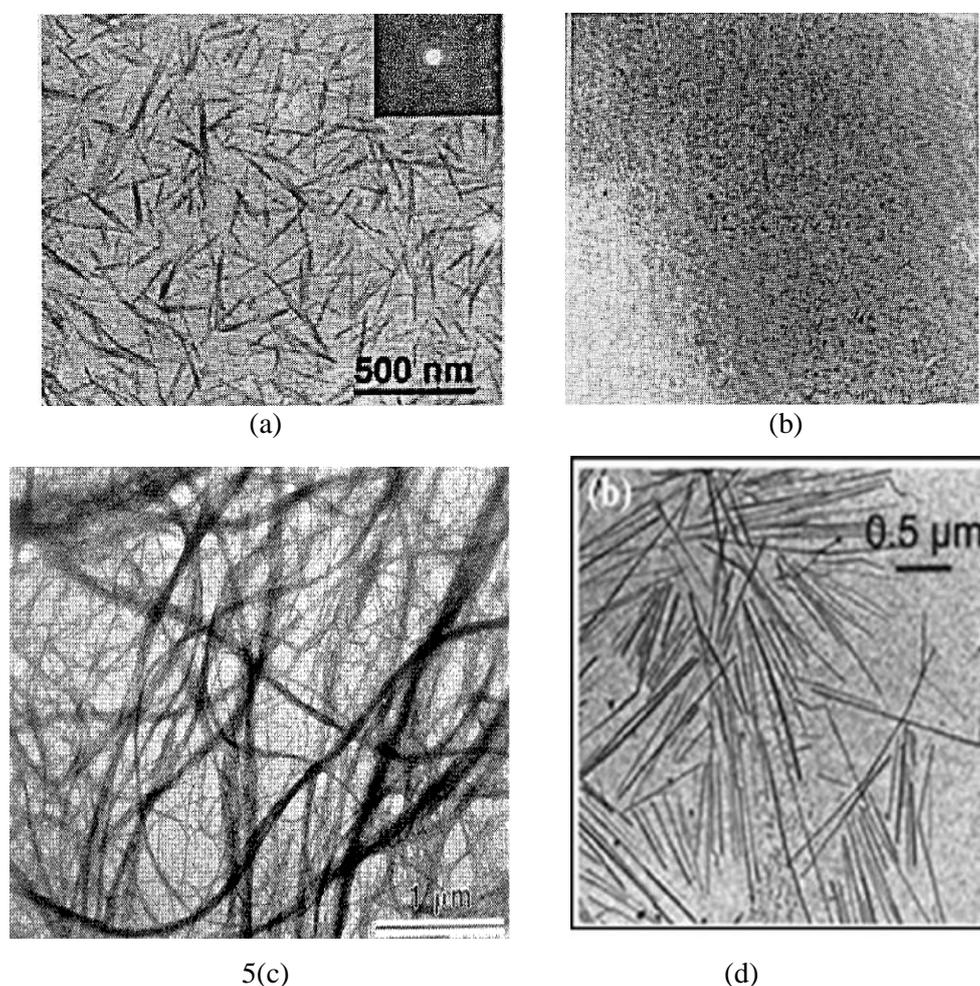


Figure 4: TEM images of some organic nanofiller [30] (a) Chitin whiskers; (b) Waxy maize starch nanocrystals; (c) Microfibrillated cellulose; (d) Cellulose nanocrystals

The average length and width of chitin whiskers are around 240 and 15nm respectively [31]. Starch nanocrystals consist of platelet-like particles with the thickness of 6-8 nm, length of 40-60 nm and a width of 15-40 nm. Such nanocrystals are generally observed in the form of aggregates with an average size 4.4 μm [30]. Despite this size they can be brought to nanoscale fillers because at least one of their dimensions is at the nanometer scale.

Nanocomposites from NR and above mentioned nanofillers show some properties analogous NRCN ones. For example, their toluene uptake decrease with increasing filler contents [30]. The reason for decreasing toluene uptake is assumed thanks to formation of chitin or starch network that pass through vulcanization network of NR.

The effect of filler percolation network on properties of NRNC is observed in dependence of NRNC dynamic properties on their processing technique. The composite samples prepared by the hot pressing method have much lower relative relaxed modulus than that prepared by evaporation have. This may be because, in evaporation method, there is much more time for formation percolation network based on filler–filler interaction, as

evaporation process is much slower than hot pressing process [32]. Note, the reinforcement effect of fillers is observed more clearly in unvulcanized samples than in vulcanized ones. It may be explained that vulcanization process interferes the formation of percolation filler network.

The other type of organic NR nanocomposites is one in which NR particles are dispersed in polymeric matrix. In [33] were prepared composites NR/PS, in which dispersed NR particles with the size of 500-600 nm covered by polystyrene continuous film of thickness about 15nm (figure 5).

The followed studies on morphology and mechanical properties of NR/PS nanocomposites show the increase of PS content make general mechanical properties and storage modulus increasing, as well as decreasing of mechanical loss $\text{tg}\delta$ in comparison with neat NR. These have resulted from the interaction of brittle PS with elastic NR on both micro- and nanoscale [34,35]. The analogous results are obtained for composites based on dispersed NR in nanomatrix of polybutylacrylate (PBA) [36]. The difference is, because PBA is softer than NR, the modulus and $\text{tg}\delta$ of NR/PBA nanocomposites are lower than that of NR.

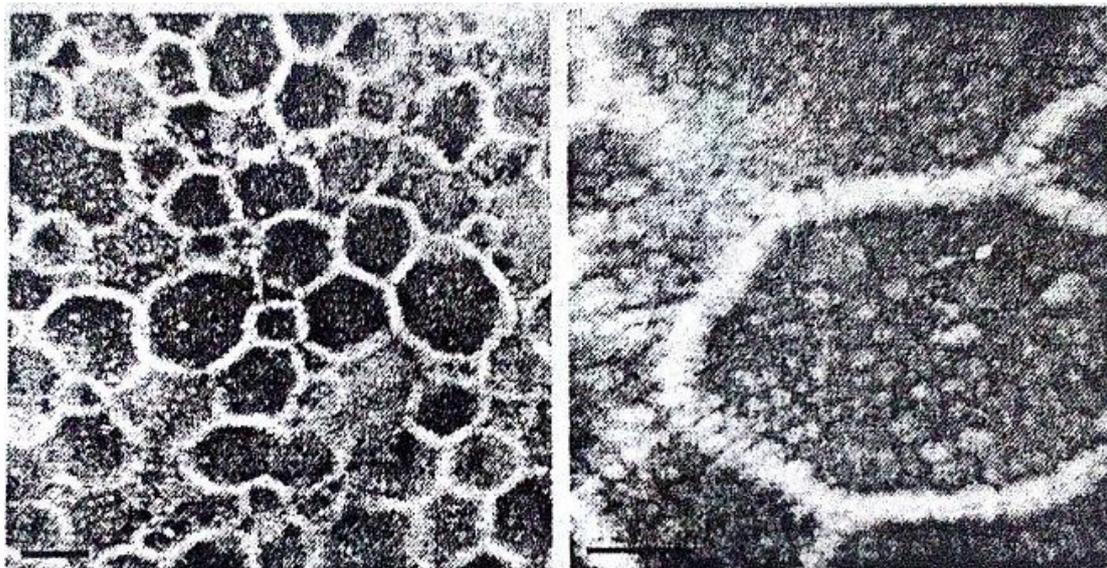


Figure 5: TEM images of deproteinized NR/PS composite [34]

Reinforcement effect of NR nanoparticles dispersed in PP matrix is presented in [37]. The vulcanized NR particles with the size of 100-200 nm are introduced into PP by melt compounding. These nanoparticles increase crystalline degree as well as impact resistance of PP matrix. However, NR is material softer than PP, so if NR content exceeds 1% the mechanical strength and modulus of nanocomposite decrease.

4. NANOCOMPOSITES FROM NR AND INORGANIC FILLERS

A lot of inorganic nanofillers are studied as reinforced fillers for NR, such as CaCO_3 [38], Al_2O_3 [39], ZnO [40], or carbon nanotubes [41] and SiC particles [42]. A new class of inorganic nanofiller for rubbers – layered double hydroxide (LDH) – also shows promising perspective, which summarized in

review [43]. In this paper, we focus only on two most popular nanofillers for rubber at present, namely nanosilica and nanoclay.

4.1. Nanocomposite NR/nanosilica

At present, silica, or SiO_2 , is the most important after CB in the rubber industry. Due to chemical nature of surface, silica has higher filler-filler interaction and lower affinity to rubber in comparison with CB. Therefore, dispersion of silica into rubber, especially on nanoscale is difficult.

To overcome this difficulty, the silane-modified silica is used. Thanks to silane layers on surface, the energy for the destruction of the filler-filler interaction of silica in rubber matrix is reduced, even less than that of CB. This results in more easy dispersion of silica in rubber [44].

The effect of silane modifiers on properties of NR/silica nanocomposites is reported in some works, for example [45, 54]. In [45] it is shown, at temperature not very high ($< 120^\circ\text{C}$), γ -mercaptopropyltrimethoxy silane (MPTS) reduced scorch time of rubber, while bis(triethoxysilylpropyl)tetrasulphide (TESPT) raise one. It is because TESPT increase activation energy while MPTS reduce. However, at temperatures higher 120°C , this effect is less clear. The analogous results were reported in [54].

Nanosilica may be introduced into NR by various techniques: sol-gel process [46, 47], mixing in latex [48-51] or melt mixing with NR [44, 52]. Therefore, degrees of dispersion of nanosilica in NR are different, depending on preparation methods. Sol-gel method (in-situ) creates the best dispersion: the average size of silica particles is 20-40 nm. Mixing in latex also can disperse nanosilica till particles with size of about 40 nm. However, due to strong filler-filler interaction, silica nanoparticles may aggregate to form clusters with almost double size – 75-80 nm if the filler content exceeds 4 % [48]. For melt mixing, observed mainly clusters or aggregates of about 100 nm [52]. Due to aggregation, nanoparticles in melt mixing method have the smaller aspect ratio (~ 1.78) in comparison with one prepared by sol-gel method (~ 2.02) [53].

Properties, particularly mechanical, of NR/silica nanocomposites are obviously improved in comparison with microcomposites of the same composition. For example, the improvement of mechanical properties is reported in [47, 48, 54, 55], the reduction of abrasion and friction coefficient – in [57], the increase of heat resistance – in [48,49]. Worth to note, in contrast with other nanofillers that increase viscosity of material, dispersion of

nanosilica into the nanometer scale makes material viscosity down [58]. However, NR/silica nanocomposites have some disadvantages: hardness, T_g and $tg\delta$ of nanocomposites are raised because the mobility of NR molecules is limited by silica nanoparticles, increased heat accumulation [49] or some decreased fatigue resistance [56] under dynamic loading.

As mentioned above, the size of silica nanoparticles depends on dispersion technique. It leads to the fact that properties of NR/ silica nanocomposites suffer from a certain influence of preparation methods. In [53, 58] reported that in-situ method limits filler-filler interaction, so the aspect ratio of nanoparticles is raised. Also, in [48] reported about the suppression of formation of heavy aggregates in latex mixture method, which leads to smaller particles size. As a result, the degree of property improvement may be changed when different preparation methods are used. For example, in comparison with nanocomposites prepared by melt mixing, the latex mixture method gives composites with higher mechanical properties, lower abrasion and friction coefficient [57] and higher activation energy of vulcanization [54].

At present, the using hybrid fillers in nanocomposites based on elastomers is of increasing attention [59]. In this trend, it worth to remark CB/silica dual phase systems in which silica finely distribute in carbon phase within aggregates and/or within the particles of dual phase aggregates. The silica domains are estimated to have dimensions similar to ones of carbon crystals, namely in the range of 0.4-4 nm [60]. CB/silica dual phase systems obviously increase reinforcement effect for NR composites [61]. Besides, these systems may enhance the stability of NR composite at an elevated temperature in comparison with CB only NR composites [62].

4.2. Nanocomposites NR/nanoclay

Nanoclays are the most studied layered silicate as nanofillers for polymeric composites. The reason is they are rather cheap and available in big quantity natural materials. Besides clay chemistry and modification have been carried out from 1970 years. [5].

Nanoclays may have the structure 2:1 or 1:1 [63]. As nanofillers for polymer composites, nanoclays with 2:1 structure are much more popular owing to the fact that polymeric molecules more easily introduce in between clay layers.

4.2.1. Structure of NR/clay nanocomposites

Nanoclay may be introduced into NR by all dispersion methods applied for polymer nanocomposite preparation: via solvent, via latex and melt compounding [6]. Note, although the dispersion via solvent is reliable method, it is less interesting in practice because of the presence of expensive and no environmentally friendly organic solvents. The most present promising methods are dispersion via latex and melt mixing (compounding). There are some modifications for rising effectiveness of dispersion, for example, freeze-dried latex compound to form NR latex/clay aerogel [64].

The most important structures that cause effective reinforcement of nanoclay are intercalated-exfoliated. In these structures, gallery space between nanoclay layers (d-space) often widen from about 1 nm of initial clay to some nanometers (intercalated structure) or to complete separation of layers (exfoliated structure). Two techniques that are used preferably for examining intercalated/exfoliated structures are X-ray diffraction (XRD) and transmission electron microscopy (TEM). XRD with the scanning angle $2\theta < 10^\circ$ give the information about intercalation: the larger d-space the smaller scanning angle corresponding to characteristic peak on XRD pattern. This peak usually disappears when the exfoliated structure is formed. However, because XRD intensity often reduced at small scattering angles and at partial exfoliation, the disappearance of characteristic peak is not enough for proving of exfoliation. Then, the additional methods, such as TEM or dynamic mechanical thermal analysis (DMTA) are needed.

DMTA, even though indirect method, but is rather effective for determination of intercalation/exfoliation. The indicator for this is strong decreasing of $\text{tg}\delta$ intensity due to reduced mobility of rubber molecules [6].

Beside intercalated/exfoliated structures, there are nanoclay particles which co-exist in the form of tactoids [65, 66]. For DPNR nanocomposites with nanoclay content less than 10 %, tactoids consist of 7 platelets in average and have dimension about 2-20 nm. With higher nanoclay contents (20-30 %) the tactoids have the dimension in range 2-35 nm and include 11-14 platelets/tactoid. Hence, though tactoid concentration is raised with nanoclay content, their average size changes not so much [65].

Type and concentration of organic modifiers of nanoclays have a certain influence on their ability to disperse in NR matrix. In [67] they reported that under the same conditions, aromatic phosphonium modifier causes the lower degree of intercalation of nanoclay than aliphatic one due to the steric effect of

the aromatic ring. For one modifier, for example octadecylamine, the high concentration – 1.5 times of cation exchange capacity (CEC) causes d-spacing 33.9 Å while low concentration (0.5 times of CEC), d-space is only of 17.7 Å [68].

Another way to enhance NR-nanoclay interaction is the suitable modification of NR. It was determined, when using maleic anhydride modified NR [69] or epoxydized NR [70] as a compatibilizer, the dispersion of nanoclay in NR matrix become much better. As a result, the NR composite properties such as cure characteristics or mechanical properties are improved obviously.

4.2.2. Properties of NR/clay nanocomposites

With the addition of layered silicates (bentonite, fluorohectorite etc.) a number of rheological properties of NR latex change remarkably: viscosity, stress to be applied for initiation of flow increase, and pseudoplasticity index strongly decrease. This phenomenon is almost not observed when non-layered silicates are used. That means, intercalated/exfoliated structures form the clay network in latex when layered silicates are introduced [71].

Nanoclays also may change cure characteristics of NR in NR/nanoclay systems. In the presence of nanoclay, curing process occurs earlier, and the higher degree of dispersion the faster curing process, the higher crosslinking density as well [67, 68]. Well-dispersed nanoclays have catalytic action on vulcanization of NR that is proved by reduction of activation energy of vulcanization with the presence of nanoclay. Moreover, the more intercalated/exfoliated structures are formed, the more activation energy of vulcanization is reduced [67].

At low deformation, the intercalated/exfoliated structures are supposed to be the main factor for improvement of mechanical properties of NR. The reinforcement effect is reached when NR molecules interact with nanoclay in interlayer area and reduce their mobility. It results in an increase of network density of NR. Therefore, mechanical loss $\text{tg}\delta$ of nanocomposites decrease [68], as well as specific heat capacity decrease [65] with increasing nanoclay content. However, at high deformation, the reinforcement effect is due to the alignment of nanoclay particles into ordering network without distinction of morphology (exfoliated or tactoid) [65]. Note, at the low nanoclay content (about 5 phr) the strain – induced crystallization of NR still exists, but at higher nanoclay contents, this crystallization is suppressed [72]. However, it is compensated by

reinforcement effect of clay network, and in total the strength of NR nanocomposit is higher than that of neat NR.

Nanoclays have synergistic effect with some other filler, for examples, with CB or carbon nanotubes (CNT). In [73,74] reported that in NR filled simultaneously by CB and nanoclay, there is a formations-ternary filler architecture, in which nanoclay associated with small aggregates of CB to form “nano blocks”, or with free CB particles to form “nano channels”. These structures, formed from favorable electrostatic interaction, induce better filler dispersion and stress transfer from matrix and result in improved static and dynamic mechanical, abrasion and viscoelastic properties of nanocomposites: increment of 18 % in tear strength, 326 % in storage modulus, reduce wear loss by 75 % under severe wear condition in comparison with ordinary CB/NR composites. They also significantly reduce CB loading. Combination nanoclay-CNT allows regulating dynamic properties of NR nanocomposites. This is a new, attractive direction in preparation of damping materials from rubbers [75].

NR/clay nanocomposites have superior barrier properties than that of ordinary NR composites. In [72] shown excellent gas barrier capacity of NR/clay nanocomposites: with clay content 5% their nitrogen permeability reduce about 25 %, and when clay content reaches 40 % - reduce till 64 % in comparison with NR. This is also the reason for considerably lower prolonged air ageing of NR/clay nanocomposites than that of NR/CB ones.

Enhanced barrier properties are supposed due to tortuous path of diffusive media as well as the decrement of transport areas in polymers [72, 76]. In [76] they also pointed out that higher activation energy of diffusion and lower diffusion coefficient of liquids in NR/clay nanocomposites result from the weakening of polymer-solvent interaction at the presence of nanoclay. This leads to anomalous liquid sorption by nanocomposites and the diffusion of the liquid has non-fickian behavior.

Interestingly, nanoclay may act as the compatibilizer in blends of NR with other rubbers including the rubbers that have very low compatibility with NR [6]. The nature of this effect is reported in [58]. Some indirect evidence shows the improvement of properties of rubber blends, that means the better phase interaction in the presence of nanoclay. For examples, blend NR/BR/nanoclay has an increment of twice in tensile strength, 40 % in tear strength than that of NR/BR blend [77]. Blend NR/carboxylated styrene butadiene rubber (NR/XSBR) has a decrement of diffusion coefficient

of benzene from $12 \times 10^{-7} \text{ cm}^2/\text{s}$ to $1 \times 10^{-7} \text{ cm}^2/\text{s}$ when 5 % of nanoclay is added [76]. For incompatible blends such as NR and polyurethane (PUR), using nanoclay through latex mixture enhance tensile strength and modulus remarkably, especially after ageing at 70 °C in 7 days [78]. Blend NR/EPDM rubber with an addition of nanoclay show improved hysteresis parameters under cyclic loading than blend without nanoclay [79].

5. CONCLUSIONS

NR nanocomposites with two kinds of nanofillers: organic (nanocellulose) and inorganic (silica, nanoclay) were introduced. They may be prepared by mean of all methods for polymer nanocomposite preparation. However, the most promising for industrial use are mixing in latex and melt compounding technique.

The most important in NR nanocomposite understanding is the formation of nanostructures inside NR vulcanization network. In the case of NR/cellulose nanocomposites, this may be cellulose percolation network that is responsible for reinforcement. Besides, the Zn-cellulose network, interconnecting with crosslinked NR, may be formed. For NR/nanoclay composites, the most important are intercalated/exfoliated structures. However, it should take into account the coexistence of tactoid structures with the dimension in range 20-40nm that form filler network together with intercalated/exfoliated structures. Note, the reinforcement effect in NR/clay nanocomposites at high deformation is due to alignment of nanoclay particles, no discerning exfoliated or tactoid structures. NR/silica nanocomposites show the more simple structure where SiO_2 particles link to each other or with NR network through hydrogen bonds, or in some case, silane bonds. The improvement of NR nanocomposite properties is believed due to confinement of rubber molecules by nanofillers as well as by filler network, formed pass through crosslinked NR. This needs, however, further careful investigations.

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