

Degradation of Non-vulcanized Natural Rubber – Renewable Resource for Fine Chemicals Used in Polymer Synthesis

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Abstract: In the current scenario, there is growing interest in the products of degradation of rubber (natural and synthetic) for specific applications in different industry sectors, whose benefits in replacing conventionally used products are mainly related to sustainability. Since the degradation products of rubber can be used in different areas, several research groups may have the interest aroused by these products, but are not familiar with the aspects related to the chemical behavior of rubber. This review aims to bring together the key information in the published literature on the degradation of natural rubber, emphasizing metatheses reactions, oxidative damage and splitting of the double bond, in order to serve as a reference source for researchers from different fields interested in obtaining such kind of products. The structures and properties as well as additional chemical transformations resulting in oligomers of isoprene, functionalised oligomers and polymers based on both are also described.

Keywords: *Degradation, depolymerization, natural rubber.*

Introduction

In the current scenario, when the socio-environmental issues are the focus of lawmakers and major polluting industries, recycling of materials, especially waste, has been constantly discussed among the public, private and academia in the search for alternatives for sustainable development. In this context, there is growing interest in the products of degradation of polymers^[1,2]. The growing interest in the exploitation of renewable raw materials for the development of new high value polymer systems makes natural rubber (NR) a material of choice among known rubbers. This is due to its low cost and wide availability, not to mention the set of mechanical properties it bears^[3]. World natural rubber production is forecast to rise 4.3 percent annually to 12.5 million metric tons in 2013. Natural rubber (polymer designation poly(*cis*-1,4-isoprene), empirical formula (C₅H₈)_n) is obtained from the latex of several rubber-yielding plants (e.g., *Hevea Brasiliensis* and *Parthenia argentatum*) by coagulation with chemicals, drying, electrical coagulation, and other processes. Latex is a polydispersed colloidal system of rubber particles in an aqueous phase^[4]. With *Hevea* latex, the dry rubber content varies between approximately 28-40%, although it may rise to 45-50% after a long period of non-tapping. The rubber produced from latex contains, besides the hydrocarbon chains (~93.7%), relatively small quantities of protein (~2.2%), carbohydrates (~0.4%), natural lipids (~2.4%), glycolipids and phospholipids (~1.0%), inorganic materials (~0.2%), other compounds (~0.1%). Among such compounds, the most important are the natural antioxidants that are the proteins^[5-7]. The molar masses of rubber molecules range from 50,000 to 3,000,000 g/mol. Sixty percents of the molecules have molar masses of greater than 1,300,000 g/mol^[4]. In order

to be effectively used in different polymer formulations (as reactive component, co-monomer) the molar mass of the NR has to be lowered to several thousand. Such oligomeric products are easily mixed (dissolved) with other precursors for polymer synthesis.

First, the problem of natural and synthetic rubber degradation appeared after incredible growth of production and application of the vulcanized rubber. The main application of natural rubber vulcanizates is on the tire production for airplanes, trucks, cars, two wheelers etc. However, natural rubber is also combined with other rubbers and thermoplastics to improve some important properties such as thermal degradation solvent resistance, etc. Some of these blends were developed by one of the authors of this review and include ethylene – propylene-diene copolymer (EPDM) with NR in order to improve the thermal resistance of the blend^[8-14]. With similar purpose ethylene – vinyl acetate copolymer was also blended with NR^[15-18].

In this review we will only analyze the papers on degradation of NR through the scission of the polymer main chain (C-C bonds). Decreasing of molar masses of NR can be done through the chemical reactions of C=C double bonds. For example, metathesis reactions of NR molecules are challenging^[19] due to presence of an alkyl group directly linked to the double bond, which can impede the coordination reaction with a metal active center (catalyst). Some methods were applied for degradation of synthetic poly(*cis*-1,4-isoprene), and as far as the chemical structure of this polymer and NR is similar we suppose that these methods can be considered in this review, because they, certainly, can be applied to degrade the NR too.

Table 1. Degradation processes and products obtained from natural rubber or synthetic polyisoprene.

Rubber	Degradation agent	Catalyst	Temperature of degradation, °C	Time of degradation*	The lowest molar mass reached	Chemical structure and Functional groups	Ref.
NR, IR	tungsten hexachloride	tetramethyl tin	80	3 h	5,800	mostly isoprene units	[20]
IR	<i>cis</i> -but-2-ene-1,4-diol	second generation Grubbs catalyst (Ru-complex)	28	8 h	14,000		
IR	<i>cis</i> -but-2-ene-1,4-diacetate	second generation Grubbs catalyst (Ru-complex)	50	8 h	4,480	isoprene units, OH	[21]
NR	<i>cis</i> -but-2-ene-1,4-diacetate	second generation Grubbs catalyst (Ru-complex)	50	2 h	2,500	isoprene units,	[22]
NR	β -pinene	Ru-alkylidene catalyst	50	24 h	850	acetoxy groups	[22]
NR	Ethane (ethylene)	second generation Grubbs catalyst (Ru-complex)	50	28 h	38,000	isoprene units, acetoxy groups	[23]
NR	$H_2O_2/HCOOH/H_3IO_6$	Ru-alkylidene catalyst	45	48 h	695	isoprene and monoterpene units	[24]
NR-latex	$H_2O_2/HCOOH/H_3IO_6$	Ru-alkylidene catalyst	120	3 h	~100-500	isoprene units	[25]
IR	H_3IO_6 ;	–	30-60	6 h	800-860	isoprene units, OH, C=O	[26]
NR	m-chloroperbenzoic acid/ H_3IO_6	–	30-60	30 h	4,600	isoprene units, epoxy, OH, C=O	[27]
NR	$H_2O_2/HCOOH/NaNO_2$	–	30	6 h	3,320	isoprene units, C=O	[28]
NR	H_2O_2/UV ;	–	0 + 30	6 h + 6 h	1,717	isoprene units, epoxy and OH groups	[29,31]
NR	$H_2O_2/sunlight$	–	70	9 h	4,100	isoprene units, COOH, OH, C=O	[32]
NR-latex	oxygen/ozone	–	RT	50 h	4,700	isoprene units, epoxy groups	[33]
NR-latex	Peracetic acid/ $(NH_4)_2S_2O_8$	Propanal	RT	50 h	840	isoprene units, epoxy groups	[34]
NR-latex	$H_2O_2/K_2S_2O_8$	–	0	20 min	18,000	isoprene units, C=O	[35-36]
NR	<i>Nocardia</i> sp. strain 835A	–	10	3 h	68,400	isoprene units, C=O	[37]
NR	<i>Xanthomonas</i> sp. strain 35 Y	–	65	12 h	~7,800	isoprene units, C=O	[38]
NR, PI	<i>S. coelicolor</i> 1A	–	50-55	24 h	~1,300	isoprene units, C=O	[39]
NR, PI	<i>S. lividans</i> TK23	–	–	2 weeks	~7,700	isoprene units, C=O	[40]
NR	Phenylhydrazine	–	–	8 weeks	236	isoprene units, C=O	[41]
NR	RRM**;	–	–	1 week	226, 196, 264	isoprene units, C=O	[42]
NR	Diallyl Disulfide	–	–	6-10 weeks	~12,000	isoprene units, C=O	[43]
NR	Ultra-sound irradiation (40 kHz, 50 W)	–	–	–	51,500	isoprene units, C=O	[44]
		–	–	–	39,600	isoprene units, C=O	[45]
		–	–	–	2,700	isoprene units, C=O	[46]
		–	–	–	4,900	isoprene units, C=O	[47]
		–	–	–	1,13x10 ⁴ -	isoprene units, C=O	[48]
		–	–	–	3,15x10 ⁶	isoprene units, C=O	[49]

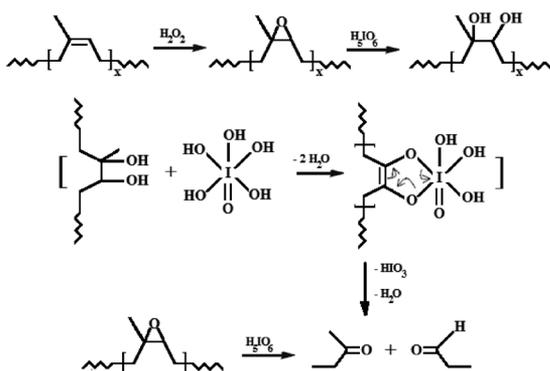
*To achieve the lowest molar mass **Renewable resource material.

Methods of Degradation of NR

The known methods of degradation/depolymerization of natural rubber include: chemical degradation, including metathesis reactions and scission of the double bond; degradation by ozonolysis; biodegradation; photodegradation (sunlight and UV irradiation) and degradation by ultrasonic irradiation. The basic information about the results obtained is collected in Table 1.

Chemical degradation

Numerous publications, as for example^[21,25-35,41-54], are devoted to oxidative methods of degradation natural rubber. The widely used approach is degradation through the epoxidation reaction of isoprene units of the rubber polymer chain. The epoxidation is usually carried out using hydrogen peroxide in the presence of formic acid, as far as the pH of reactive media has to be controlled. The NR latex has to be stabilized before epoxidation. It is considered that the oxidative cleavage reaction takes place via the epoxidized isoprene units of the rubber at its consequent treatment, in most cases, by periodic acid. The molar ratio of [HCOOH]/[isoprene unit] is usually kept as 0.3 at equimolar ratio of [H₂O₂]/[HCOOH]. This reaction is fulfilled in THF^[25], or in latex form^[26]. The main reaction product isolated is oligomeric isoprene terminated by carbonyl groups. Its structure is confirmed by ¹H-NMR, ¹³C-NMR, FTIR techniques. The chemical transformations of isoprene units to epoxidized isoprene units through the reaction with hydrogen peroxide and further to diol functionalized isoprene units via interaction of the epoxidized units with periodic acid are shown below in Scheme 1. The further interaction of the intermediate diol functionalized isoprene units with periodic acid leads to formation of carbonyl terminated isoprene oligomers and liberation of iodic acid (Scheme 1).



Scheme 1. Scheme of oxidation process of polyisoprene^[26].

Certainly, all the researchers noted that they did not reach a complete epoxidation of the polyisoprene and the resulting products contained isoprene units, epoxidized isoprene units and carbonyl terminal groups^[25-28,42].

However, Phinyocheep et al.^[26] suggest that the degradation of the epoxidized natural rubber (ENR) by periodic acid does not take place by the cleavage of the epoxy-containing isoprene fragments, but via C=C of the isoprene unit through the formation of the intermediate *vis*-diols. They compared the molar mass of the degradation products obtained from the ENR with different content of epoxy groups and did not find significant changes. However, in the same paper they postulate that the degradation rate of NR by periodic acid is much lower than that of the ENR. They explain this fact by higher polarity of ENR compared to NR that is important because the reaction was carried out in a latex phase.

By performing the reaction in solution, Mauler et al.^[55] observed that the NR can be degraded by periodic acid without previous epoxidation and the extent of degradation depends on the temperature and solvent nature. They observed that the velocity of degradation was faster in chloroform than in toluene or n-hexane. Recently, Bafica and Soares^[56,57] studied the efficiency of periodic acid on the cleavage of natural rubber by performing the experiments in THF, at room temperature. The amount of H₅IO₆ exerted significant influence on the degradation process, as indicated by the molar mass reached after 60 min of reaction at room temperature. Table 2 illustrates this effect.

Considering all publications in this subject, we may suppose that both the mechanisms may be happened with the utilization of periodic acid for degradation of NR.

Gillier-Ritoit et al.^[27] degraded poly(*cis*-1,4-isoprene) (PI) using two agents to obtain the carbonyl terminated oligomers: periodic acid (1 step process) and *m*-chloroperbenzoic acid (MCPBA) + periodic acid (2 step process). The authors consider that in both the cases the first stage of the process is epoxidation. Then in a case of MCPBA the periodic acid has to be added for cleavage of the epoxidized units of PI. The molar mass of the products obtained varied from 4,000 to 9,000 g/mol.

Isa et al.^[28] degraded NR using the combination of H₂O₂, HCOOH and NaNO₂. They studied the structure of the product by FTIR and ¹H-NMR techniques. The polymer chain of the product contained isoprene units, isoprene units containing epoxy groups and isoprene units containing hydroxyl groups. The authors studied the influence of temperature and reaction time on efficiency of degradation of NR latex. They have found that the longer process and the higher temperature provide

Table 2. Effect of the amount of periodic acid on the molar mass of the degraded NR.

H ₅ IO ₆ (mg)	H ₅ IO ₆ / NR weight ratio	H ₅ IO ₆ / double bond molar ratio	Mn	Mw	Mw/Mn
5.1	0.51	0.07	193,500	974,000	5.0
10.0	1.00	0.13	137,700	794,300	5.8
14.6	1.46	0.19	124,700	644,500	5.2
63.5	6.35	0.81	6,900	50,100	7.2
130.2	13.02	1.66	1,700	18,300	10.6

formation of the product of lower molar mass. The lowest molar mass reached was 1,717 g/mol after heating for 9 hours at 70 °C.

Saetung et al.^[25] obtained the oligomeric product with molar mass between 2,000 and 3,000 g/mol. Phinyocheep et al.^[26] reached molar mass around 500 g/mol after 21 h of processing with periodic acid.

Epoxidation of fresh natural rubber latex was carried out^[33] with freshly prepared peracetic acid. The oxidative depolymerization of the epoxidized rubber without loss of epoxy groups was fulfilled with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in the presence of propanal. The resulting epoxidized liquid natural rubber with molar mass around 10^4 was found to have well-defined terminal groups: aldehyde groups and α - β unsaturated carbonyl groups. The degree of epoxidation in degradation products varied from 3.9 to 38 %. Authors^[33] have studied the effect of proteins removal on degree of epoxidation and they did not observe any significant differences after epoxidation in the same conditions. Interestingly, increase in epoxidation degree led to increasing glass transition temperature from 212 °C for initial NR to 245 °C for ENR with 38 % of epoxidation as well as gel fraction content from 8.9 % for NR to 61 % for the same ENR. Authors^[33] explain these facts by possible side reactions and by ring-opening of epoxy groups with formation of three dimensional network structure that, as it is well known, provides increasing T_g and gel fraction content. In the world patent^[21] the combination of $\text{K}_2\text{S}_2\text{O}_8$, sodium dodecyl sulphate and H_2O_2 was used for depolymerization of NR latex. After 24 h processing at 50-55 °C the average relative molar mass of the product was around 68,000 g/mol.

Metathesis reactions

Metathesis reaction is a catalytically induced reaction, in which carbon-carbon double bonds undergo cleavage and reforming processes as schematically shown in Scheme 2. This reaction is induced by a wide range of transition metal complexes, but most important and practical catalysts are based on tungsten, molybdenum or rhenium with either tin or aluminum alkyl compound as co-catalyst^[22,58-63].

Relatively few reports exist on the metathesis reactions of natural rubber, NR, or poly(*cis*-1,4-isoprene), IR^[22,58-63]. This may be explained by the fact that NR is a very sensitive to the side reactions and this polymer with trisubstituted unsaturations degrades much slower than poly(*cis*-butadiene) and other polyalkenamers with disubstituted unsaturations^[58]. Alimuniar et al.^[20] described metathesis degradation of NR and synthetic IR using the tungsten hexachloride – tetramethyl tin catalytic system. Using gel permeation chromatography (GPC) method authors showed that molar mass of polymers decreased considerably. Even at 28 °C, NR was degraded with drastic change of molar mass from 1.2×10^6 to 1.4×10^3 g/mol. The higher was the temperature, the lower became the molar mass. Authors^[24] consider that their successful results are based on purification of NR by



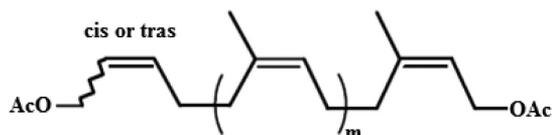
Scheme 2. General scheme of metathesis reaction.

several times precipitation, and selection of the catalyst system.

Using both the ^1H -NMR and ^{13}C -NMR (proton and carbon 13 nuclear magnetic resonance) techniques, the authors^[20] tried to follow the structural changes in addition to molar mass decreasing. Finally, they concluded that

[...] very complicated products were resulted from various reactions, i.e., inter- and intramolecular cyclizations, branching, gelation, and isomerization.

Hence, sterically hindered substrates require highly stable and selective metathesis catalysts. The development of highly active Ru-alkylidene catalysts opens new possibilities in olefin metathesis and their application to controlled synthesis of desired products^[62,63]. Since ruthenium-based catalysts show a high tolerance to a wide variety of functional groups^[64] they allow more freedom in terms of the choice of functionalities that can be incorporated by the chain transfer agent at the end of the polymer chain. Telechelic oligomers can be synthesized by selective cleavage of polymer chain with synchronous functionalization of isoprene units. Solanky with co-workers^[22] first investigated a model polymer degradation reaction using Grubbs catalysts^[64] to achieve low molar mass telechelic isoprenic oligomers from synthetic polyisoprene and then extended the reaction to high molar mass natural rubber in order to evaluate the efficiency of these catalysts in the latex. First attempts with synthetic polyisoprene were performed in an organic solvent (dichloromethane) using bis(tricyclohexylphosphine)benzylidene ruthenium(IV), a first generation Grubbs catalyst, and *cis*-but-2-ene-1,4-diol as chain transfer agent (CTA). These attempts were not successful in the range of [Isoprene]/[CTA] ratio from 20 to 200. The authors^[22] explained this failure of the metathesis reaction under the conditions applied by a slow efficiency of the first generation Grubbs catalyst towards tri-substituted alkenes. Then the process was fulfilled in the same conditions but using tricyclohexylphosphine [1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene] benzylidene ruthenium(IV) dichloride, second generation of Grubbs catalyst. It appeared possible to reach the lowest molar mass of the telechelic oligomers obtained in the range of 4,700-5,500 g/mol. Molar mass decreased with increasing the catalyst concentration and the reaction time and decreasing CTA content. The chemical structure of the degradation products was confirmed on the similar experiments with low molar mass hydroxyl telechelic polyisoprene using *cis*-but-2-ene-1,4-diacetate as CTA and a second generation Grubbs catalyst. For the product of metathetic degradation of poly(*cis*-1,4-isoprene) the ^1H -NMR analysis confirmed the presence



Scheme 3. Structure expected from the metathetic depolymerization of poly(*cis*-1,4-isoprene)^[22].

of acetoxy telechelic polyisoprene with characteristic *cis* and *trans* chain end ethylenic protons: 5.78 ppm (*cis* HC CH), 5.61 ppm (*trans* HC CH), 5.31 ppm (isoprenic HC CH), 5.1 ppm (isoprenic HC CH), 4.6 and 4.5 ppm (end chain CH₂). In addition, the FTIR spectrum presented a strong peak centered at 1,741 cm⁻¹ corresponding to the carbonyl stretching. Authors^[22] proposed the chemical structure of the product as follows (Scheme 3):

Authors^[22] found the well correlated molar mass by ¹H-NMR and size exclusion chromatography (GPC) analysis's of the acetoxy telechelic polyisoprene structures. In the same conditions it was carried out the controlled degradation of high molar mass synthetic polyisoprene from 330,000 to ~8,000 g/mol with yield ≥ 80 %. It worth to note that when the reaction time was longer than 1 h molar mass of the degradation products decreased to 850-2,500 g/mol, but yield also decreased to 30-40 %. Then they used the same ratios of [isoprene]/[CTA] and [isoprene]/[catalyst], which were effective for poly(*cis*-1,4-isoprene), for NR latex phase experiments. As a result no polymer degradation was observed, according to authors due to catalyst poisoning by proteins and catalyst insolubility^[22]. Thus they further used deproteinized rubber latex and succeeded with some addition of acetonitrile as a co-solvent, which did not induce latex coagulation, to obtain a liquid natural rubber with $M_n = 38,000$ g/mol, but not lower. Presence of the acetoxy groups in the resulting product was confirmed by a peak at 1,728 cm⁻¹ of the carbonyl stretching in the FTIR spectrum.

Much lower molar mass of the resulting oligomers was reached by Gutiérrez and Tlenkopatchev^[23] via cross-metathesis with β-pinene using a similar Ru-alkylidene catalyst (Figure 1).

It was noted^[23] that both the initial components for metathesis reaction (natural rubber and β-pinene) were selected from the renewable products. β-Pinene relates to the class of monoterpenes. The reaction was carried out in bulk (a small amount of 1,2-dichloroethane was added with the catalyst) under the nitrogen atmosphere

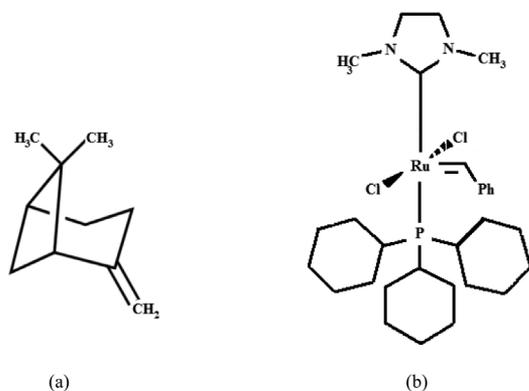
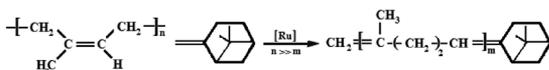


Figure 1. Chemical formula of: (a) β-pinene and (b) 2nd generation Grubbs catalyst [1,3-dimethyl-4,5-dihydroimidazol-2-ylidene (PCy₃)Cl₂Ru=CHPh]^[23].



Scheme 4. Metathesis reaction of NR with β-pinene as CTA^[23].

at 45 °C. The molar ratio NR/catalyst was kept equal to 1,000, and the molar ratios of NR/CTA were equal to 1, 5 and 10. The reaction was terminated by adding of ethyl vinyl ether. The reaction is shown in Scheme 4.

The main product (42 %) was oligomers with the chain of isoprene units ($m=1-3$) terminated by one vinyl group and one monoterpene unit, as shown in a Scheme 4. Simultaneously the authors^[23] noted that some amount of short chain ($m=1-3$) isoprene oligomers terminated by two vinyl groups (11 %) and by two monoterpene units (17 %) were obtained. The total yield of 80-90 % of the degradation product of natural rubber was fixed. The oligomers with different amount of isoprene units and end groups were isolated and their ratio was determined with a help of gas chromatography coupled with mass spectrometry analysis (GC/MS). The experimental molar masses of oligomers obtained were determined by gel permeation chromatography (GPC) and end-group analysis using ¹H-NMR spectroscopy. Authors concluded that molar mass could be varied by changing the ratio of NR and β-pinene, and duration of the process. The molar mass was varied from ~700 to ~3,000 g/mol with a polydispersity from 1.6 to 2.5.

Wolf and Plenio^[24] reported the metathesis degradation of the natural rubber using ethenolysis in the presence of the recently developed Ru-indenylidene and Ru-benzylidene complexes (NHC) (NHC_{ewg})RuCl₂(CRR'), where NHC = *N,N'*-bis(2,4,6-trimethylphenyl)imidazolynilidene, as well as Grubbs-Hoveyda complex. Authors noted that unlike other NHC ligands, NHC_{ewg} were characterized by electron-withdrawing substituents, which render their electron donation comparable to that of trialkylphosphines^[65,66]. The process was carried out in Büchi miniclave using ethene and solution of natural rubber and catalyst in toluene at 120 °C and ethene pressure of 7 bar for 3 h. Importantly, the reaction mixture was transferred to a millipore cell and filtered over a nanofiltration membrane ($M_w = 500$ g/mol, flow = 1 mL/min, $\Delta p = 3$ bar) to remove residual polymers^[24]. First, the linear triterpene squalene (C₃₀H₅₀) was used as a model for NR. Twelve different Ru-containing complexes were tested in various solvents such as C₆D₆, toluene, CH₂Cl₂, pentane, C₆H₁₂ at different reaction temperatures (100, 120, 140 °C) and varying

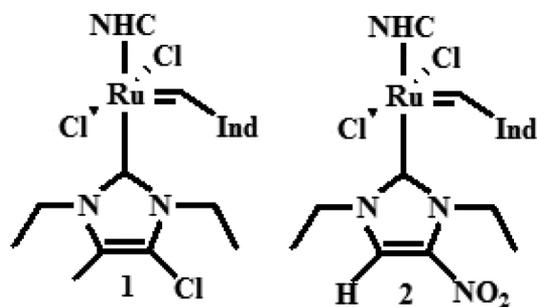
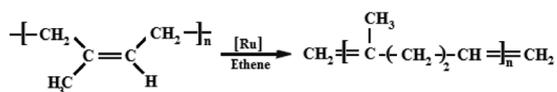


Figure 2. The most effective Ruthenium complexes in squalene ethenolysis (Ind = 3-phenylidenylid-1-ene, NHC = *N,N'*-bis(2,4,6-trimethylphenyl)imidazolynilidene)^[24].



Scheme 5. Scheme of natural rubber ethenolysis, where $n = 3-6$ ^[24].

amount of catalyst (0.005, 0.01, 0.05, 0.1 mol%) and reaction time (1, 3, 6, 20 h). Interestingly, depending on the conditions used the conversion calculated^[24] according to conversion = $\text{squalene}_{\text{end}}/\text{squalene}_{\text{start}}$ was from 1 to 99 %. The optimized procedure with the best catalysts 1 and 2 (see Figure 2) was applied for degradation of NR.

Finally, several oligomeric products were separated by simple gravity chromatography. Oligoisoprenes with $n=3-6$ were obtained in > 90% purity (HPLC, NMR) and characterized by ¹H- and ¹³C-NMR spectroscopy, and high resolution mass spectrometry. The reaction scheme is presented in Scheme 5.

Scission of the double bond

NR was chemically degraded by scission of double bond induced by chloranil / iron (III) chloride^[67] or phenylhydrazine / iron (II) chloride^[39,68,69] systems. Curti et al.^[67] used 2-methyl-2-butene as a model for the reactions; they found that reactions were characterized by second-order kinetics, independent of the catalyst. The value of the rate constant decreased significantly when the reactants were diluted 10-fold. The presence of chloranil did not alter the chromatogram profile obtained by GC-MS for the thermal degradation of NR. It was concluded that chloranil decreased the activation parameters for the degradation because the degradation products were the same as those obtained thermally in absence of chloranil. Activation parameters such as energy, enthalpy, entropy and Gibbs energy were determined. Activation energies (in kJ/mol) for the degradation of NR were calculated to be 60.1 for NR/chloranil and 41.9 for NR/FeCl₃. From the values of activation parameters, it was suggested that the activation step of the reaction induced by chloranil is more thermally dependent than the reaction induced by FeCl₃ that, otherwise, was found to be more entropically dependent. Bualek^[39] degraded NR using phenylhydrazine / iron (II) chloride system and obtained the product with molar mass around 50,000 g/mol as the lowest one. Nitrobenzene has appeared to be not very effective chemical degradation agent for natural rubber too^[70]. De et al.^[40] used diallyl disulfide (DADS) as well as the renewable resource material (RRM), which was a vegetable product having the major constituent DADS, for chemical degradation of sulfur cured natural rubber vulcanizate. Process of reclaiming was monitored by estimating the sol and gel portions and molar mass determination of sol portion. The lowest molar mass of sol fraction reached was around 5,000 g/mol.

Ozonolysis

Nor and Ebdon^[32] used an oxygen/ozone stream from ozonizer passed through the NR solution in chloroform at 0 °C for oxidation degradation of NR. They determined the molar mass of the products using GPC technique

and calculated the average number of chain scissions, S . After 1 min of ozonolysis the molar mass of the natural rubber decreased to 5,390 g/mol with the calculated $S=49$ and finally, after 20 min ozonolysis, the molar mass distribution curve of ozonolysed NR becomes essentially unimodal with M_n of 840 g/mol, and the value of S was calculated to be around 321. The authors proposed a two stage mechanism of NR ozonolysis: in a first stage the authors observed formation of relatively stable polymeric ozonides and peroxides during a fast and diffusion controlled reaction between the NR and ozone; then only in a second, slower stage such products undergo scission and possibly, only after reaction with further ozone, form oligomers with functional, oxygenated end-groups. The FTIR results confirmed the main bands of initial NR and of the ozonolysed product after 20 min of ozonolysis. The main changes observed in FTIR spectra were as follows. The intensity of characteristic bands of the polyisoprene chain at 2962, 2928 and 2855 cm⁻¹ decreased in the FTIR spectra of the degradation product and the new peaks appeared at 3440, 1720 and 1084 cm⁻¹, confirming formation of hydroxyl, carbonyl and ester groups, correspondingly. Authors^[32] indicated that more than one type of carbonyl group may be present in the ozonolysed NR. Three types of carbonyl groups are in fact possible: aldehyde, ketone, and/or carboxylic acid.

Biodegradation

It is interesting to note that the known rubber degradation by microorganisms starts by an oxidative attack at the double bonds of the polymeric chains too^[43]. Two different groups of microorganisms can be distinguished according to their decomposition strategies. Bacteria and strains belonging to *Corynebacterium*, *Mycobacterium*, *Nocardia* group need direct contact to the rubber material showing adhesive growth^[44]. The bacteria from the genus *Gordonia*^[45] shows good rubber degradation activities in submerged culture, but do not grow and do not form clear zones on latex overlay agar plates containing rubber as the sole carbon source. Members of the second group show weaker growth in submerged culture but grow and form clear zones on NR latex overlay agar plates. These bacteria belong to *Streptomyces* and related genera^[46,47]. From the several microorganisms isolated and tested *Actinomycetes* showed the ability to degrade NR and to use it as carbon source^[48]. Both *Nocardia* strain^[34] and *Xanthomonas* strain^[35] led to accumulation of oligomers with molar mass around 100 g/mol. In the review^[71] Rose and Steinbüchel collected the information about the molar masses of the products obtained by biodegradation of NR by different bacteria. The number of isoprene units in the oligomers produced varied from 2 to 190, and the molar mass varied from ~200 to ~13,000 g/mol. Similarly to the chemical oxidation degradation processes of NR described above in the last cases the oligomers terminated by carbonyl groups were obtained as well that was confirmed by FTIR and NMR spectroscopy. The possible mechanism of the biodegradation of polyisoprene chains has been suggested^[71]. Shah et al.^[44] studied 12 bacterial species for their capacity to degrade rubber. Best

properties were shown by *Bacillus* sp. S10. The effect of different pretreatments like extraction of rubber pieces with acetone, UV or sunlight irradiation, temperature and pH was studied as well. The efficiency of rubber degradation was analyzed through FTIR technique. The best effect was demonstrated in a case of the rubber acetone pretreatment, the optimized temperature was 37 °C and pH 7. Unfortunately, authors^[44] do not give any information about molar mass of the products obtained.

Photochemical degradation

Ravindran et al.^[29], Mathew et al.^[30], and Radhakrishnan Nair et al.^[31] carried out the photochemical degradation of NR (5 wt. % solution in toluene) in sunlight or using UV-irradiation in the presence of H₂O₂ for 50 h. In some cases^[29] the reactive mixture (NR, toluene, H₂O₂) was homogenized to a certain extent by the addition of methanol or tetrahydrofuran. The extent of degradation was slightly higher when THF was used. The extent of depolymerization was found to increase with decreasing concentration of NR, increasing amount of H₂O₂ and also by longer exposure time. The molar mass reached for liquid NR obtained in these works was in a range of 4,000-9,000 g/mol^[29-31]. The products contained isoprene units, epoxy and hydroxyl groups in their structure. The liquid NR (LNR) recovered from the solution after distillation of the solvent under reduced pressure^[29] was almost clear and colorless, but when this material was kept for a few days, its viscosity gradually increased. To solve the problem hydroquinone (0.2 wt. % for removal of radicals, which may be present) and Santowhite MK (0.5 wt. %, as an antioxidant) were added and then the LNR product was found to be stable.

Degradation by ultrasound irradiation

Magalhães and Feitosa^[41] observed the reduction of molar mass of natural rubber (*Hevea brasiliensis*) submitting their solutions in toluene by ultrasound irradiation. In this work it was investigated the effect of temperature (range 15-55 °C) and the irradiation time (range 30-600 min) on the irradiation process, and the products were assessed by GPC. Evaluating the kinetics of degradation it was observed that the peak molar mass decreases fastly during the early stages of degradation and afterwards, this decrease is less fast, tending to a limiting value. The dependence of degradation with temperature was evident. The degradation rate was lower in sonication at 55 °C than at 15 °C and this effect was more clearly defined for longer periods of irradiation. After 120 minutes of sonication, it was observed a difference of 1.4×10^5 g/mol between the molar masses of natural rubbers radiated at 55 to 15 °C. In this work, materials were obtained with molar mass around 10^4 g/mol and it was also observed molecules around 10^3 g/mol, identified by shoulders present in the molar mass distribution curves, specifically, for the system at 15 °C.

Application of the Products of Degradation of NR

One approach to minimize the problem of rubber waste is to use the ground tire rubber in formulations

with other polymers^[72-76] and also with asphalt^[77]. Other interesting solution is the devulcanization of the NR to produce lower molar mass products. Many papers and reviews^[78-81] are devoted to reclaiming processes of post-consumer vulcanized rubber, as, for example, ground tire rubber^[78-87].

Specifically about the products of the degradation of the non-vulcanized NR, many applications are already found in the literature, as following.

Synthesis of oligomers with functional end groups

Many publications used the carbonyl-terminated oligomers obtained from NR to synthesize other oligomers with different functional end groups as potential precursors of a very wide range of polymers. The telechelic oligoisoprenes with terminal and side hydroxyl groups were synthesized^[25,42,49,50] as well as with amino and quaternary ammonium groups^[41,51-54], ethoxy groups^[42], mesyl and azido groups^[28], N,N-diethylthiocarbamate groups^[50]. In some works the mechanisms of chemical transformations of functional end groups are discussed.

Polyurethane and polyurea materials

Kebir et al.^[51-53] studied the potentialities of hydroxyl telechelic oligomers obtained from natural rubber as precursors for thermoplastic polyurethanes, crosslinked polyurethanes (PUs)^[42] and polyurethane foams^[26]. Similarly, they used the well defined amino telechelic oligomers obtained by transformation of carbonyl telechelic oligomers synthesized by oxidative degradation of natural rubber as precursors for polyurethane or polyurea materials^[49]. In all the cases the polymer products were synthesized by reaction with diisocyanate. For example, by reacting of the new hydroxytelechelic poly(*cis*-1,4-isoprene) oligomers prepared from natural rubber with toluene diisocyanate the new crosslinked polyurethanes with well-defined structure and properties can be obtained by controlling the chemical structures and the functionalities of the telechelic precursors^[42].

Epoxy modification

Mathew et al.^[30] used the low molar mass liquid natural rubber (LNR) obtained by photochemical degradation of NR for modification of epoxy resins. The formation of two-phase microstructure, consisting of spherical particles of LNR strongly bonded to the surrounding matrix, has been observed. Particle in particle morphology was evidenced from the scanning electron microscopy (SEM) measurements, that is, subinclusions of crosslinked epoxy as secondary particles in the elastomer domains, which were dispersed in epoxy matrix. At LNR content in the epoxy-matrix of 5 wt. % the rubber domains appeared as small spheres of size of 1 µm. Increase of the rubber concentration up to 20 wt. % led to formation of the domains of around 9 µm in diameter. As far as Mathew et al.^[30] carried out their study with just one LNR sample, we do not have any information about the influence of molar mass of LNR on morphology and properties of the LNR modified polyepoxides.

Poly(vinyl chloride) formulations

Egharevba et al.^[88] degraded the NR to LNR using phenylhydrazine and then epoxidized the LNR obtained with combination of H₂O₂ and HCOOH. The epoxidized LNR with 30 mol. % epoxidation (ELNR-30) was used in PVC formulations. The blends of PVC containing 20 and 30 wt. % of ELNR-30 presented lower values of tensile strength and elongation at break when compared to the pure PVC sample.

Radhakrishnan Nair et al.^[31] synthesized ELNR-50 and ELNR-20 from natural crumb rubber using H₂O₂ and sunlight and studied the effect of degree of epoxidation on thermal stability of the liquid natural rubber and its compositions with PVC. Thermogravimetric data have shown that the values of temperature onset of degradation (T_0^1) and temperature of the maximal rate of the degradation (T_{max}^1) for the first degradation stage of liquid natural rubber increase with increasing the epoxy content, indicating that the presence of epoxy group delays the breakdown of the liquid rubber molecules. For the PVC/LNR blends, the thermal stability data correspond to those of the constituent polymers irrespective of the sample composition suggesting that the degradation pattern of one constituent is not influenced by the presence of the other. The authors^[31] explain this by the lack of interaction between the blend components.

Solid polymer electrolyte

The novel epoxidized liquid natural rubber (ELNR) was applied^[33] to transport Li⁺ as an ionic conducting medium, that is, solid polymer electrolyte (SPE). The ionic conductivity of the resulting rubber was 1.98×10^{-6} S/cm at 323 K, reflecting its high polarity and mobility. This demonstrates the possibility of using ELNR as a SPE.

Artificial skin

Recently, Lewis patented^[21] the method and system for producing artificial skin. In the field of medical science, one of the most important products is an artificial skin manufactured from synthetic rubber. Artificial skin has various applications such as for educational media, for making training aids and phantoms and for covering surfaces of prosthetic limbs. However, producing of artificial skin from synthetic rubber is expensive. The invention^[21] relates to the utilization of natural rubber for producing artificial skin of lower cost. Author noted that for producing artificial skin the natural rubber in latex form was depolymerized to the one of desired average molar mass between 60,000 and 100,000 g/mol. Then pH of the depolymerized latex was adjusted to 9. After that the latex obtained was compounded, pre-vulcanized, and finally the artificial skin was produced. The mechanical properties of the pre-vulcanized rubber heated at 70 °C for 10 h were as follows: shore hardness (Shore A) = 42, tensile strength = 4.03 MPa, elongation at break = 434 %, and stiffness = 21.81 N/mm.

Conclusions

The review of works published on degradation of natural rubber shows a growing interest of researchers in

this area because natural rubber is a renewable resource, promising raw material for producing various oligomers and monomers for polymer synthesis, replacing the oil products. Among the numerous methods of depolymerization and degradation of natural rubber the most interesting are those, which use natural products or cheap simple chemicals as well as the biological objects as degrading agents. From our own experience the natural rubber is not easily soluble in organic solvents, that is the methods of NR degradation applied for NR in latex are easier carried out in the laboratory. Oligomers of different functionalities were obtained from natural rubber and characterized; such polymers as polyureas, crosslinked polyurethanes, polyurethane foams based on these oligomers have been synthesized and studied. These oligomers were used for modification of the epoxy network and thermoplastic PVC polymers as well.

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