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Tannin Treated Water for use in the Emulsion Polymerization of SBR

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Abstract: The toxicity of residues formed during water treatment is mainly a function of the chemicals used. The inorganic flocculants, when used, give rise to compounds harmful to humans and to the environment. An alternative solution is the use of tannins. However, despite the environmental benefits, when using tannin-based products in the treatment of industrial water, modifications may be imparted to the final product. In this work, tannin was evaluated as flocculating agent to treat the water used in the emulsion polymerization to produce SBR. The results show that good stability of the latex and acceptable color in the rubber can be achieved.

Keywords: *Emulsion polymerization, biodegradable, renewable resources, rubber.*

Introduction

Water covers 75% of the planet surface, in the form of oceans, rivers, lakes, etc. However, only a small part of this water – in the order of 113 trillion m^3 - is available to life on Earth[1]. In addition to surface water, water resources can also be found in underground lands which are the main reservoir of fresh water available for humans. In addition to the human consumption, water is supplied to the cities and is also used in industries and in agriculture for irrigation[2]. The waste generated by the industries, cities and agricultural activities can be found in the solid or liquid form, and has a very large potential for pollution. The industries produce large amounts of waste in their processes, with a portion being retained by the treatment facilities of the industry itself, and partly released into the environment. Thus, despite the large volume of water available, as consumption has continuously exceeded its recuperation process, there has been the so called water stress, or lack of fresh water brought about mainly by the pollution of water from domestic and industrial sewage.

The water treatment is composed of a set of processes with the goal to provide water with the necessary physical, chemical and biological characteristics either to the human or the industrial consumption. Amongst these processes, the following can be cited: coagulation, flocculation, decantation, filtration, disinfection, neutralization, dechlorination, demineralization[3].

Coagulation is a chemical pre-treatment process intended to remove colloidal substances responsible for turbidity. The sedimentation difficulty of colloidal particles under the action of their own weight is due to the electrical charges of equal sign they carry, which impart repulsion among the particles by means of electrostatic forces[3]. Upon coagulation these electrical charges are partial or totally neutralized so that, under gravitational forces the particles may get together giving rise to heavier agglomerates, the flakes, which decant spontaneously.

The flocculation of suspended matter in water to enhance clarification rates is an important aspect of industrial and municipal water treatment[4]. Various kinds of water-soluble inorganic or organic substances may be used as a flocculating agent[5]. Inorganic coagulants such as aluminum sulfate, polyaluminum chloride, ferric sulfate, ferric chloride and sodium aluminate have traditionally been used. These inorganic coagulants are relatively inexpensive and generally effective for water clarification. However, they tend to generate large amounts of sludge, which are difficult to dewater. Also, such inorganic coagulants are only effective within a particular pH range and therefore require proper adjustment of the water pH during treatment. In addition, residual iron and aluminum ions in the treated water may affect downstream operations such as cooling and boiler treatments and may also cause health and environmental concerns when the water is finally discharged[6].

Due to the health and environmental hazards generated by the accumulation of potentially toxic waste, there have been worldwide movements towards the establishment of legislations concerning the disposal of such materials. Various types of waste are regulated under federal and state environmental laws, including

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disposal of waste water and disposal of both liquid and solid toxic or hazardous chemicals[7].

The fundamental difference from the traditional method to that using tannin is based on the fact that the latter need not hydrolyze with the medium to promote the neutralization of charges present in the water, thus not modifying the pH of the water. The coagulation/flocculation process will occur by direct reaction of the cationic fraction of the molecule with the charges present in the medium, destabilizing them and promoting agglomeration and decantation[8].

Water clarification can be brought about by using water soluble amphoteric tannins which, after combining with suspended clays coprecipitate, leaving no residual salts or ions in the treated water. One of the advantages of these flocculants is that they do not affect the pH of the suspension[4-6]. Another advantage is the form of the produced flakes. Their irregular shape allows greater surface contact and thus more efficiency of flocculation[9].

Vegetal tannins are widely distributed in plants and have been used as tanning agents, dyestuffs and drugs since earlier times. They can be divided into two major groups, hydrolysable tannins and condensed tannins[10]. The former are mixtures of simple phenols, such as pyrogallol and ellagic acid, and of esters of sugar, mainly glucose, with gallic and digallic acids. The lack of macromolecular structure, the low level of phenol substitution they allow, the low nucleophilicity and limited worldwide production, somewhat decrease their chemical and economical interests[11].

Condensed tannins, on the other hand, constitute more than 90% of total world production of commercial tannins. They are present at very high concentrations in the wood and bark of various trees. Consisting of flavonoid units which have undergone varying degrees of condensation, condensed tannins are invariably associated with their immediate precursors (flavan-3-ols, flavan-3,4-diols), other flavonoid analogs, carbohydrates, and traces of amino and imino acids[10-13]. The knowledge of the composition and physical properties of those natural extracts in which tannins occur, the organized structure of tannins, the differential reactivity of their nucleophilic centers, and of their phenolic substitution, has assisted in extending the scope of their industrial application to include a range of phenolic adhesives, depressants and flocculants[12].

However, despite the technological and environmental advantages offered by the tannin-based products, their use in water treatment, either industrially or for human consumption, must be carefully evaluated. Particularly in the emulsion polymerization of styrene and butadiene to produce SBR rubbers, changes in the properties of the water used in the production process can introduce undesirable variations in color and stability, which would make this rubber unsuitable.

The emulsion polymerization is a process by which an aqueous dispersion of monomers is converted, through free radical polymerization, into a stable dispersion of polymeric particles less than 1 micron in diameter[14]. In emulsion polymerization the dispersing medium is usually water, in which the various chemical components are dispersed. The most important property of an emulsion is its stability and a number of factors can affect it, such as the presence of electrolytes, degree of stirring, temperature and addition of organic solvents. The reaction is usually carried out using demineralized water, as the presence of extraneous ions can interfere with both the initiation process and the action of the emulsifier[15]. The emulsion polymerization technique is normally conducted under mild conditions. Water is the dispersing medium most used and the primary care to be taken is to ensure that oxygen is absent in the reaction medium. The method is advantageous in many respects including a better temperature and viscosity control of the reaction medium which facilitates process control[16].

This work evaluated the use of tannins in the treatment of the water used in the emulsion polymerization of styrene and butadiene to produce styrene-butadiene rubber. This is one of the most important commercial elastomers, so that any modification in the production process that results in characteristics different from the established specifications would bring serious economical drawbacks.

Experimental

The untreated water from Saracuruna River, Rio de Janeiro State, was flocculated with Tanfloc (Tanac S.A., Montenegro, Rio Grande do Sul, Brazil), a tannin-based product, and then demineralized. The physicochemical properties of the treated water and the content of residual tannin were determined in each stage of the purification process. The treated water was used in emulsion polymerizations and the latexes obtained were analyzed as for the content of reacted styrene, surface tension, mechanical stability, total solid content and coagulum weight. The obtained rubber was then submitted to ageing.

Water treatment: Untreated water was placed in 2 L flasks, equipped with mechanical stirrer. To each flask, 1 mL of a solution containing 10,000 ppm of tannin was added. After 15 minutes of stirring, the solution was let to stand for 12 minutes. The treated water passed through four treatment columns (50 × 1000 mm) filled up with 800 mm sand, active coal, Amberlite Na (H^+ form) (Rohm and Haas Química Ltda., Jacareí, São Paulo, Brazil) and Amberlite IRA 458 Cl (OH^- form) (Rohm and Haas Química Ltda., Jacareí, São Paulo, Brazil) ion exchange resins. The physicochemical characteristics of the treated water were observed on a turbidimeter (Hach Company, model 2100P, Loveland, Colorado), a conductivity meter (Micronal, model B331, São Paulo, São Paulo, Brazil) and a pH meter (Mettler-Tolledo, Inc., model MP120, Columbus, Ohio).

Content of residual tannin: To a 50 mL sample, 1 mL Folin phenol reagent (Merck S.A. Indústrias Químicas, Rio de Janeiro, Rio de Janeiro, Brazil) and 10 mL carbonate-tartarate reagent (Merck, S.A. Indústrias Químicas, Rio de Janeiro, Rio de Janeiro, Brazil) were rapidly added. The mixture was allowed to stand during 30 minutes for color development and photometric readings were made on a

photometer (Hach Company, model DR/210, Loveland, Colorado) at a wavelength of 690 nm.

Polymerization reaction: The emulsion polymerizations of styrene and butadiene were conducted in 20L vessels containing the necessary ingredients, according to the standard formulation. The reaction took place at 8 °C until the latex presented a total solids content around 25.8% w/w. Four polymerizations were carried out with water of different characteristics. In the first reaction, water was treated with aluminum sulfate (this treatment was taken as the reference). In the second reaction (Tann0) the water was treated with tannin. In the last two reactions the water was also treated with tannin but additional amounts of tannin were added to the pre-treated water, 1 ppm (Tann1) and 3 ppm (Tann3), in the third and the fourth reactions respectively.

Total solid content: In previously weighed aluminum pan, approximately 1.000 g of latex was weighed. The material was dried in an oven, at 170 °C during 15 minutes, then weighed again.

Content of chemically bound styrene: A small amount of latex was transferred to an aluminum pan where it was coagulated and washed twice with acetone. The coagulated material was then spread on an aluminum foil so as to form a film. The material was dried in an oven at 100 °C, during 20 minutes, then pressed for 8 minutes at 100 °C and 15,000 psi (Dan-Presse Indústria e Comércio de Prensas e Equipamentos Ltda., model DCV.L.10, Duque de Caxias, Rio de Janeiro, Brazil). After cooling**,** the laminate was cut into 0.5 cm strips for determinations of refractive index at 25 °C on an ABBE refractometer (Carl Zeiss, Inc., model 33040, Thornwood, New York). **Surface tension:** Approximately 25 mL of filtered latex was transferred to a Petri dish, dry and clean, and with the platinum ring (# 03/98) of a Cenco DuNoüy (Cenco Instruments, model 70535, Chicago, Illinois) tensiometer, the surface tension of the sample was determined, according to ASTM D 1417-96.

Mechanical stability: After filtration through an 80 mesh sieve, 50 g of latex were placed in the test jar where it was stirred for 30 minutes at 14,000 rpm. The latex was filtered again in the 80 mesh sieve and the retained material was dried and weighed.

Latex coagulation: Filtered latex, demineralized water, antioxidant and 20% w/v brine solution were placed in a heated flask. To this, 3.5% w/v H_2SO_4 was added until pH 4.5. After coagulation of the rubber, the heating was interrupted and demineralized water was added for washing until pH 6.5-7.0. The solid material was dried in an oven, at 70 °C during 24 hours.

Analysis of rubber after ageing: Ageing was estimated by visual observation of the changes in rubber color. Small amounts of the material were kept in an oven at 70 °C for 4 weeks. The samples were collected weekly and analyzed as for color development.

Results and Discussion

The criteria adopted to select the optimum concentration of tannin were based on the following parameters: the least amount of flocculent necessary to produce the largest flakes, the shortest decantation time, the lowest water turbidity and coloration and low residual tannin. Tannin is brown colored and thus, as its concentration in the polymerization water increases, the color becomes more intense and brownish rubber may be produced, which is undesirable. Thus, the presence of tannin must be kept as low as possible.

According to Table 1, acceptable results for turbidity and residual tannin were obtained at pH 6.5, the original pH of the untreated water, and 5 $mg \cdot L^{-1}$ of tannin. It can also be seen that small differences in tannin concentration deeply affect the turbidity level of the treated water. The higher the tannin concentrations, the smaller are the formed flakes and more intense the turbidity of the treated water. Such behavior has not been observed when using aluminum sulfate.

From the results shown in Table 1, it can be seen that both $Al_2(SO_4)_3$ and tannin are efficient flocculating agents. Nevertheless, Table 2 shows that, for a given variation in turbidity, tannin can be used in lower concentration. Other advantages are that by using tannin, both the conductivity and pH are less affected. Thus, there is no need for pH adjustment for flocculation to occur and this together with the lower detrimental effect on the ion exchange resin, since no salt is used in the process, allows for reduced costs when tannins are used as flocculants in water treatment.

The treatment with 5 $mg \cdot L^{-1}$ of tannin was then the procedure adopted to clarify the water for the polymerizations.

As described in the experimental part, in two of the water samples used, an additional amount of tannin was added to evaluate the effect of residual tannin on the polymerization reaction. Table 3 presents the characteristics of the water samples used. As can be seen, by increasing the concentration of tannin, the turbidity

Table 1. Control parameters for flocculation.

Parameter	Tannin content ($mg \cdot L^{-1}$)				$Al_2(SO_4)_3$ ($mg \cdot L^{-1}$)			
	4	5	6	7	5	6	7	8
Original pH	6.46	6.46	6.46	6.46	6.73	6.73	6.73	6.73
Original turbidity (FTU)	1.2	1.2	1.2	1.2	1.5	1.5	1.5	1.5
pH after flocculating agent addition	6.35	6.34	6.37	6.35	6.38	6.07	6.12	6.03
Time for flake formation (min)	3	2	3	5	3	3	3	3
Flake size (mm)	0.5-0.75	0.5-0.75	0.1-0.5	0.1-0.5	0.1-0.5	0.5-0.75	0.5-0.75	0.5-0.75
Time for total decantation (min)	>12	>12	>12	>12	12	12	12	12
Final turbidity (FTU)	0.8	0.7	1.0	1.4	1.5	0.9	0.8	1.0

also increased, due to the natural color of tannin, pH decreased and conductivity increased.

From the latexes of SBR obtained it was found that the presence of tannin in the polymerization water did not affect their characteristics significantly and did not act as polymerization inhibitor, since the reaction yields were those expected. These results are presented in Table 4.

The analysis for bound styrene measures the actual styrene/butadiene ratio in the polymer and the tendency of the polymer to be either more plastic (high styrene content) or more elastic (high butadiene content). The amount of bound styrene, which can be estimated by refractive index values, is also a measure of the polymerization conversion, and is strongly influenced by monomers purity and reaction temperature. From Table 4, the results show that this parameter is not affected by the use of tannins.

The tendency of synthetic latexes to form crumbs when submitted to high speed mechanical stirring can be determined through the analysis of mechanical stability. As seen in Table 4, the values obtained show that the use of tannin as the flocculating agent led to a latex more stable than that produced when aluminum sulfate was the flocculent. From the aging test it was found that the color modification in the produced rubber is within the allowed limits, when compared to the reference sample.

Table 2. Comparison between tannin and $Al_2(SO_4)_3$ as flocculating agents.

Parameter	Tannin 5 mg·L^{-1}	$Al_2(SO_4)_3$ 7 mg·L^{-1}
pH variation*	–0.02	–0.36
Turbidity variation (NTU)*	–14.56	–14.02
Conductivity variation (μS)*	1.55	2.25
Time of flake formation (min)	2	3
Flake size (mm)	0.5-0.75	0.5-0.75
Time for complete decantation (min)	>12	12

*Considering the property of the water before and after treatment.

Conclusion

In order to be used in the industrial SBR polymerization process, any additive directly or indirectly involved in the polymerization reaction must be carefully adjusted as to avoid interferences on the process itself or on the product properties. In the particular case of SBR emulsion polymerization, a rigorous evaluation of the water used as the polymerization medium must assure that the adopted treatment (demineralization and flocculation) will keep the control parameters within acceptable ranges.

Due to the large amounts of water involved in the polymerization, large amounts of flocculating agent are consequently used. Among them inorganic coagulants are frequently chosen, which accumulate, thus contributing for the increasing environmental pollution. Thus, the replacement of these matters by naturally occurring biodegradable ones is very welcomed.

Tannin was compared to aluminum sulfate regarding the performance as flocculant. It was observed that water suitable for use in the emulsion polymerization of SBR could be obtained in both cases and that the amount of tannin required was less than that of the sulfate.

The SBR rubbers obtained in this work did not have their properties modified, regarding discoloration and stability, and no inhibiting effect was detected in the polymerization, when the polymerization water was treated with tannin. Thus, by replacing aluminum sulfate with tannin it is possible to polymerize butadiene and styrene in order to obtain SBR with characteristics comparable to those obtained when the water was submitted to the standard treatment. However, the most relevant aspect is related to the biodegradability of tannin which, even when used in large amounts will not become a source of pollution.

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Table 3. Characteristics of the water used in the polymerizations.

Reaction	Residual tannin (mg·L^{-1})	pH	Turbidity (NTU)	Conductvity (μS)
Reference	0.036	7.63	1.72	3.23
Tann0	0.036	8.89	0.33	4.06
Tann1	1.059	6.55	0.60	2.98
Tann3	3.255	5.70	0.78	4.79

Table 4. Control parameters for the polymerization reactions.

Parameter	Reference	Tann0	Tann1	Tann3
pH	10.40	9.90	10.17	10.66
Amount of coagulum (g)	<1	<1	<1	<1
Total solid (%)	25.80	25.64	25.79	25.09
Combined styrene (%)	21.76	21.28	21.27	22.07
Surface tension (dyn·cm^{-1})	62.0	63.9	64.9	61.8
Mechanical stability (% coagulum)	0.21	0.10	0.16	0.27

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