

Synthesis, Characterization, and Application of the Sodium Poly(styrenesulfonate) Produced from Waste Polystyrene Cups as an Admixture in Concrete

Rosana M. N. de Assunção,¹ Betina Royer,¹ Juliana S. Oliveira,¹ Guimes Rodrigues Filho,¹ Leila A. de Castro Motta²

¹Instituto de Química da Universidade Federal de Uberlândia, Caixa Postal 593, 38400-905, Uberlândia/MG, Brazil

²Faculdade de Engenharia Civil da Universidade Federal de Uberlândia, Caixa Postal 593, 38400-905, Uberlândia/MG, Brazil

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ABSTRACT: Wasted polystyrene (PS) plastic cups were used in the synthesis of sodium poly(styrenesulfonate) (NaPSS). The produced polyelectrolyte was water-soluble. The viscosimetric molecular weight was 126,146 g mol⁻¹. The sulfonation of the polymer was estimated through FTIR spectroscopy and chemical analysis of the number of sulfonic groups. The presence of bands at 1326 and 1188 cm⁻¹ in the infrared spectra was characteristic for sulfonic groups. The polymer was obtained with 60.3% of sulfonation. An aqueous solution of NaPSS was used as an admixture in concrete of portland cement. The results showed that the slump increasing of the concrete was up to 300% with 0.3%

content of NaPSS per weight of cement. It was possible to reduce the water content of the concrete in 13.2% using NaPSS solution as an admixture. The compressive strength gain was 23.9% after 28 days of curing. The results indicated that NaPSS, produced from waste PS cups, can be satisfactorily used either as a plasticizer or as an admixture for water reduction in concrete. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1534–1538, 2005

Key words: polystyrene; recycling; sodium poly(styrenesulfonate); polyelectrolytes; concrete

INTRODUCTION

Polystyrene is a polymer that is used in several applications such as cups and trays in the food industry, wrapping for electronics devices, and foams.¹ The high consumption of this polymer increases the rate of discard of material in the landfill. One way to minimize this adverse amount of waste is using this polymer in the production of modified polymers. In this sense, the polymer can be modified to produce a derivative with new commercial applications. The polystyrene is easily sulfonated, producing a polyelectrolyte, sodium poly(styrenesulfonate). This material can be used in several processes, such as water treatment^{2,3} and dispersion of cement particles in water/cement systems.⁴

Many chemicals are used as plasticizers or superplasticizers for concrete. These concrete admixtures include sulfonated alkali salts of naphthalene or mel-

amine formaldehyde polymers, lignosulfonic acids, and hydroxycarboxylic acids, for example.^{4,5} The effectiveness of these substances is strongly influenced by their structure, their molecular weight, and their surface activity. The surface activity is related to the presence of polar groups in the structure. These groups interact with cement particles to improve dispersion and homogeneity. As a result, an increase in the workability of the concrete is observed for a given water/cement (w/c) ratio,⁶ which can be used to reduce water in concrete. The reduction of the w/c ratio improves the properties of concrete, mainly the compressive strength; however, the w/c ratio cannot be reduced too drastically because, in this procedure, the concrete becomes dry and difficult to be compacted.⁶ In this case, the workability of the concrete can be increased by adding admixtures that improve the dispersion process and allow the reduction of the w/c ratio.

With the perspective of producing a material for application in concrete, we prepared a sulfonated derivative sodium poly(styrenesulfonate) (NaPSS) from waste polystyrene cups. In this work, we have focused our attention in the characterization and evaluation of the polyelectrolyte in relation to slump, water reduction, and improvement of the compressive strength of the concrete.

Correspondence to: R. de Assunção (rosana@ufu.br).

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TABLE I
Portland Cement with High Early Strength Properties^a

Cement type	Ingredient/Parameter	CPV Ari (Brazilian Norm NBR 5733)
Chemical composition, %	SiO ₂	18.99
	Al ₂ O ₃	4.32
	Fe ₂ O ₃	3.00
	CaO _(total)	64.75
	MgO	0.68
	SO ₃ ^b	3.01
	Insoluble residue	0.26
	Loss on ignition	3.47
	CaO _(free)	1.63
Physical property	Specific surface ^b (Blaine), cm ² g ⁻¹	4672
Mechanical test	<i>a/c</i> = 0,288	
	7 days, ^b MPa	48.8
	28 days, ^b MPa	55.4

^a Data supplied by supplier [Holdercim (Brasil) S.A., São Paulo, Brazil].

^b Values obtained experimentally by authors.

EXPERIMENTAL

Synthesis and characterization

The sulfonated derivative of polystyrene was produced using concentrated sulfuric acid (97%) as sulfonating agent, and silver sulfate (Ag₂SO₄) as catalyzer. The procedure performed by Holboke et al.⁷ was adapted as follows: 1.000 g of PS Zanatta[®] Plastic cups postconsumption was added to a solution containing 15.0 mL of sulfuric acid and 0.02 g of silver sulfate. The mixture was occasionally stirred and kept at 25°C for 24 h. The obtained material was rubbery and swollen, presenting a brown color. The polyelectrolyte was washed with water at 10°C and filtered. The excess sulfuric acid was removed through a difference of density method by immersing the system in an ice and NaCl bath at approximately -5°C. The resulting material was treated in an oven at 90°C for 3 h. The sulfonation of polystyrene was confirmed by FTIR. PS films and tablets of KBr, pressed with sulfonated polystyrene, were analyzed in a Perkin-Elmer Spectrum 1000 infrared apparatus (Perkin Elmer Cetus Instruments, Norwalk, CT); 24 scans were made using 4 cm⁻¹ resolution. The degree of sulfonation was calculated through volumetric titration with NaOH 0.10M, using phenolphthalein as acid-base indicator.

Aqueous solutions of NaPSS were prepared from the polyelectrolyte treated with NaOH (pH = 10). The concentration of the solution used as an admixture in the concrete was 17% (w/w).

Determination of intrinsic viscosity

The viscosimetric molecular weight was obtained from results of intrinsic viscosity for each polymer (PS and NaPSS). The measurements were performed in an Ostwald viscometer (Canadawide Scientific Ltd., Ottawa, Canada) at 25°C. For nonelectrolyte polymers as polystyrene, the reduced viscosity (η_{sp}/c) is a function of the concentration of the solutions. For systems that behave ideally, this relation is directly proportional.^{8,9} In this case, it is possible to use the Huggins equation [eq. (1)]⁸ to determine the intrinsic viscosity of the polymer. The molecular weight was determined by measuring the intrinsic viscosity using the Mark-Houwink-Sakurada equation [eq. (2)]⁸, as follows:

$$(\eta_{sp}/c) = [\eta] + K_H[\eta]^2c \quad (1)$$

$$[\eta] = k(M_v)^a \quad (2)$$

For polyelectrolytes such as NaPSS, however, the viscosity has a different behavior. The "effect of the polyelectrolyte" is observed, in which the reduced viscosity increases exponentially for low concentrations of solution.⁹ To modify this effect, the polyelectrolyte was studied in the presence of an excess of salts of low molecular weight because, in this case, the interactions among the polar groups at the carbonic chain are suppressed and the polyelectrolyte behaves as a neutral polymer. In this study, we used the solvent CH₃COOH/NaCl.¹⁰ The use of this solvent allowed us to determine the intrinsic viscosity of the polyelectrolyte through the Huggins relation.

Preparation of test specimens

For molding the test specimens, portland cement type CPV ari 32 (high early strength portland cement) was used in the mixes. The physical properties and chemical analysis of the cement are detailed in Table I. In Table II, the mix proportion of the cement and aggregates used in the preparation of the concrete are described.

Samples of concrete were prepared using 355 kg/m³ of cement content. NaPSS was added to the mixing water at 0.3% rate by weight of cement content. Con-

TABLE II
Mix Proportions of Concrete (%)

Material	(%)
Cement	14.84
Sand (fineness modulus 2.2)	28.19
Crushed stone (maximum size of the 19 mm)	49.11
Water	7.86

TABLE III
Sulfonation of Waste Polystyrene and Resulting NaPSS

Sample	SO ₃ H groups ^a (mmol)	% Sulfonation ^a	% S ^b	Number of structural units per SO ₃ H group
1	5.75	59.7	8.24	2
2	5.61	58.3	8.05	2
3	6.06	63.0	8.69	2

^a Determined by titration of NaOH aqueous solution.

^b Yield: 100% sulfonated; 9.62 mmol SO₃H groups (1 g of PS) and 12.6 and 15% S, by elementary analysis C₈H₇O₃SK.¹¹

trol specimens without NaPSS solution were also cast to make comparisons. The evaluation of the admixture in the concrete was based on results of increasing workability and compressive strength for samples after 7 and 28 days of curing. For the mechanical test of compressive strength, eight cylindrical test specimens with dimensions of 20 × 10 cm were prepared for each of the studied concrete samples. The tests of compression were performed in a Losenhausen universal testing machine. Four specimens for each mix were tested at the end of 7 and 28 days, respectively. The concrete consistency was measured by the test method for slump of portland cement concrete (ASTM C-143).

RESULTS AND DISCUSSION

The polyelectrolyte that was produced through the PS sulfonation presented dark brown coloration in acid condition, which changed to a clear brown solution in alkaline medium when the solution was treated with NaOH. The NaPSS was reasonably soluble in water, unlike the original PS, indicating the presence of polar groups in the structure. In high concentration, NaPSS formed a suspension in water. The polyelectrolyte obtained is described in Table III.

The number of sulfonic groups in the produced NaPSS was between 5.61 and 6.06 mmol. These values indicate that the sulfonation reached from 58 to 63% of the 9.62 mmol (100%) possible for 1 g of PS used. The comparison of these data by elementary analysis of the

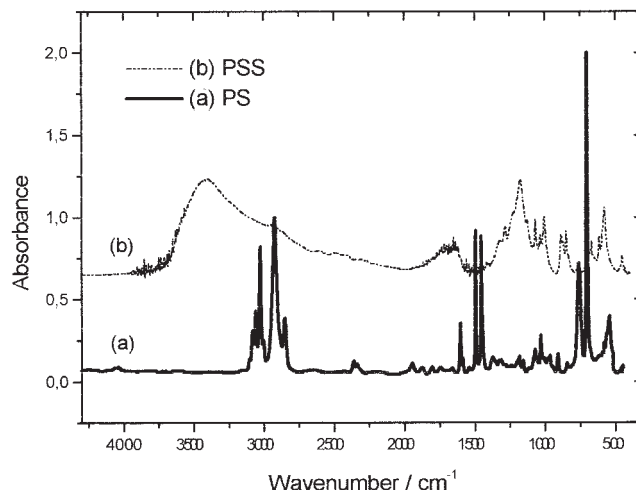


Figure 2 FTIR spectra of waste plastic cups of polystyrene (a) and sulfonated derivatives (b).

100% sulfonated polymer¹¹ indicates one sulfonic group for two monomeric units of PS, as shown in Figure 1.

The infrared spectra of PS and PSS are shown in Figure 2. The PSS spectrum exhibits characteristic bands for the presence of sulfonic groups: in the region from 1460 to 1330 cm⁻¹, attributed to asymmetric stretching of the SO₂ group and 1200 to 1150 cm⁻¹, attributed to symmetrical stretching of the SO₂ group.¹² Another important region in the infrared spectrum of the sulfonated polymer is between 3500 and 2900 cm⁻¹.¹² In this region, an intense band related to the sulfonic group and water absorption can be observed. The drastic changes in the spectrum of PSS indicate an effective sulfonation of the PS. A medium-intense band in 1720 cm⁻¹ in the PSS spectrum was observed, which can be attributed to the presence of carbonyl groups that indicate the occurrence of degradation during the PSS synthesis.

The measurement of the intrinsic viscosity was used as a parameter for the control of the synthesis in relation to quality and degradation. Through these data, it was possible to determine the viscosimetric molecular weight of PS and NaPSS. The results are presented in Table IV.

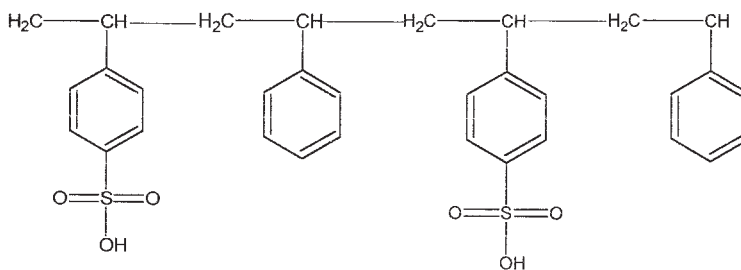


Figure 1 Fragment of the structure of PSS.

TABLE IV
Molecular Weight of Waste PS and NaPSS Derivative by Viscosimetric Measurement

Sample	Solvent	Constants K (g L^{-1}) and a	Temperature ($^{\circ}\text{C}$)	Intrinsic viscosity $[\eta]$ (L g^{-1})	M_v average (g mol^{-1})
PS	Tolueno	$K = 3.80 \times 10^{-5}$ $a = 0.630^8$	25	0.05245	96,398
NaPSS	$\text{CH}_3\text{COOH}/\text{NaCl}$	$K = 3.29 \times 10^{-6}$ $a = 0.788^{10}$	25	0.03441	126,146

The results in Table IV show that the viscosimetric molecular weight of NaPSS is higher than that of waste PS. This result was expected because of the chemical modification with sulfonic groups. This can be easily verified because the monomeric unit weight is 104 g/mol for PS and 184 g/mol for NaPSS. The ratio between the monomeric unit weight of NaPSS and PS is approximately 1.76. In this case, the expected result for 100%-sulfonated PS is about 169,660 g/mol. The value shown in Table IV was 126,146 g/mol. An explanation for this observation is that the degree of sulfonation of the PS is <100% (Table III). The average degree of sulfonation obtained from Table III data was around 60.3%. The estimated viscosimetric molecular weight for 60.3% of sulfonation of the polymer was around 146,756 g/mol. This result suggests that PS could be degraded during chemical modification because the result observed is less than the estimated value. This observation corroborates the indication observed in the infrared analysis of NaPSS in relation to degradation during the reaction.

An aqueous solution of NaPSS was used as an admixture in portland cement concrete. For this purpose, we evaluated the workability of the concrete in relation to the reference without NaPSS solutions, the reduction of water in the preparation of concrete with NaPSS solutions, and the compressive strength of the prepared concrete. The results obtained are shown in Table V.

In experiment A, NaPSS solution was used to improve the workability of concrete without loss in the concrete strength. In the preparation of concrete with NaPSS, we maintained the water/cement (w/c) ratio for the control concrete. An increase in the slump for

concrete A was observed, which is related to the increase in workability. The workability increase of the concrete can be attributed to NaPSS adsorbed on cement particles in the concrete. One hypothesis for this increase is the presence of the polar group ($-\text{SO}_3^-$) in NaPSS. In the adsorption of NaPSS, these groups can convey a negative net electric charge to the surface of the cement particles, inducing repulsive forces between neighboring cement particles, thereby increasing dispersion. This mechanism is observed for several commercial admixtures such as sulfonated alkali salts of naphthalene or melamine formaldehyde polymers and lignosulfonic acids.⁴ As observed in this experiment, we can say that NaPSS is a plasticizer admixture because an increase of slump up to 300% was verified. It is important to point out that the NaPSS solution does not cause negative effects in relation to the compressive strength of the concrete in experiment A (cf. the increase in fluidity with the maintenance of the same w/c ratio of the control concrete). Therefore, approximately the same value of compressive strength for the control and the NaPSS concrete was observed after 7 days of cure, and a small elevation on the value of the NaPSS concrete after 28 days.

We were able to use the NaPSS as a water reducer admixture because it was possible to increase the workability of the concrete by using it in the mix. The production of a stronger concrete at a low w/c ratio requires the use of water-reducing admixtures. In experiment B, we used the NaPSS solution to decrease the w/c ratio. The concrete with NaPSS was prepared so that it had a slump closer to the control concrete. In this case, the addition of NaPSS allowed a reduction in the amount of water necessary for the production of the concrete in about 13.2%. According to this procedure, it was verified that the produced concrete improved its mechanical resistance in relation to the control concrete. An increase in compressive strength was observed: the results reached 18.6% at the end of 7 days and 23.9% at the end of 28 days of curing. According to the classification of commercial admixtures,⁶ these results can be used to classify NaPSS solutions as plasticizers and/or water-reducing admixtures of medium performance.

TABLE V
Compressive Strength Results for Concrete with NaPSS Solutions

Sample	Water/cement ratio (w/c)	Slump (mm)	Compressive strength (MPa)	
			7 days	28 days
Control	0.53	53	29.22	35.17
NaPSS 0.3% (A)	0.53	210	29.37	37.26
NaPSS 0.3% (B)	0.46	49	34.66	43.57

The results shown in this work demonstrated that NaPSS produced from waste PS cups can be used with efficiency as an admixture in production of concrete.

CONCLUSIONS

The chemical modification of PS plastic cups, by a sulfonation reaction, yields a water-soluble polymer that can be satisfactorily used as an admixture in portland cement concrete. The NaPSS was produced with 60.3% of sulfonation and viscosimetric molecular weight of 126,146 g/mol. An aqueous solution can be directly used in the hydration process of cement in the mixture. A significant increase in the concrete slump was observed when the concrete was prepared using a NaPSS solution. The results demonstrated that the workability and the homogeneity of the concrete increased. By using a NaPSS solution, it was possible to reduce the w/c ratio for obtaining a more resistant concrete. The resistance gain was of 23.9% after 28 days of curing.

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