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The Influence of the Chemical Additives in Polystyrene on the Features of Flocculants Obtained During Sulphonation of the Polystyrene

Wiesłw W. Sułkowski,[*1] *Agnieszka Wolińska,*[1] *Danuta Pentak,*[1]
Sławomir Maślanka,[1] *Anna Sułkowska*[2]

Sumary: One of the ways of polymer waste management is its chemical modification. Waste polystyrene foam (EPS) and virgin polystyrene (VPS) as reference material were converted into polymeric flocculants by chemical reactions. One of the most popular and widely used procedures to follow the flocculation kinetics is the monitoring of the turbidity as a function of the polyelectrolyte dosage. The application of the obtained products caused a significant decrease of turbidity of the studied solutions. The products were successfully used as flocculants in the treatment of waste water. A colloid system composed of ferrum(III) hydroxide formed the discharge model.

Keywords: flocculation; polyelectrolyte; polystyrene waste; sulphonation; sulphonic derivatives

Introduction

Management of reusing polymer materials and polymer wastes is of crucial importance to the environment. Generally polymer materials after usage still retain some valuable properties. They are relatively cheap and may be used after mechanical or chemical recycling. We attempted to convert expanded polystyrene (EPS) waste into polymeric flocculants by transformation into its water soluble derivatives.[1–3] The results of the performed experiments showed that the process of sulphonation was complicated and probably led to the occurrence of some undesirable reactions.[3] Flocculation is a ffundamental stage in many solid/liquid separation processes, especially during waste water treatment or sludge conditioning when the solid particles are too small to be effectively removed. Polyelectrolyte can be used to speed up flocculation and make it more efficient. Flocculation is a complicated proccess which strongly depends on the type of the flocculants used since they determine the properties of the obtained polyelectrolytes.[4,5] Therefore different types of virgin polystyrene (VPS) which are the substrate for the obtaining the expanded products were used in the experiments of chemical modification. A virgin polystyrene (VPS), different from the one usually used to obtaining expanded products, was converted to check the influence of the type of the used polystyrene on the features of the products of the chemically modified products.[6–8]

Experimental

Materials and Methods

Samples of expanded polystyrene wastes (EPS) $M_{\eta EPS} = 230000$ and virgin polystyrene $M_{\eta VPS} = 200000$ were used. Sulphuric acid, calcium carbonate and sodium carbonate produced by Chemical Company POCh in Gliwice Poland were used for the

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[1] Department of Environmental Chemistry and Technology, Institute of Chemistry, University of Silesia, Szkolna 9, 40-006 Katowice, Poland
Tel/Fax: ++ 48 32 3591371
E-mail: wsulkows@uranos.cto.us.edu.pl

[2] Department of Physical Pharmacy, Medical University of Silesia, Jagiellońska 4,41-200 Sosnowiec, Poland

synthesis of chemical modification. The samples of each polystyrene were pulverised in a mill and fractions of the size 0.40–1.04 mm were separated. They were sulphonated by mixing them with concentrated sulphuric acid (the molar ratio of the EPS to H_2SO_4 was 1:5) and silver sulphate (1% of EPS weight) as a catalyst. In a glass flask equipped with a mechanical agitator, vertical condenser and thermometer, the amount of Ag_2SO_4 was dissolved in H_2SO_4 (95–97%), polystyrene (EPS) was added at 80 °C and the reaction mixture was stirred in the temperature range 80–90 °C. To find the dependence between the sulphonation conditions and the properties of the obtained derivatives the temperature and time of the reaction were changed. The duration of the process of sulphonation with H_2SO_4 was carried out for period from 15 min. to 2 hours. After several minutes, the reaction mixture became highly viscous and apparently homogeneous. The products of the completed reaction, were separated by filtration and were dissolved in deionised water. The products were precipitated in the form of sodium salt in the reaction with Na_2CO_3. Sodium salt of poly(styrenesulphonic acid) NaEPSS and NaVPSS were obtained as products. The features of the products depended on the condition of the process.

Fractional precipitation process of the VPS and EPS were performed with the use of toluene as the solvent for EPS and VPS; a n-butanol was used as the precipitant.

The fractions were precipitated from a 0.5 M NaOH solution of the polymers with the use of the 2-propanol as a precipitant.

Techniques and Instruments

The IR spectra were obtained on the Perkin-Elmer Spectrum One FTIR spectrometer. The spectra obtained for the derivatives NaEPSS and NaVPSS confirmed the presence of sulphonic groups in the polyelectrolyte structure.

The content of sulphur and carbon in products of PS sulphonation was determined with the use of Perkin Elmer CHNS/O elementary analyser. The contents of sulphur and carbon were then used for calculations of the number of sulphonic groups per one monomer unit (n.sulph). The quotient of sulphur and carbon contents were linearly dependent on n.sulph for the theoretical structures of NaPSS.[8] The data obtained from the elementary analysis were taken for the calculations of the theoretical molecular weight values M_{cal}.

The NaEPSS and NaVPSS samples were characterised by determining their intrinsic viscosities [η] in 0.5 M NaCl solution at 25 °C. The measurements were carried out with an Ubbelohde type of viscometer. Parameters $\boldsymbol{K} = 1.86 \cdot 10^{-4}$ and $\boldsymbol{a} = 0.64$ (from Mark-Houwink equation), determined from light-scattering measurements for these conditions, were used to obtain the molecular weight of the samples.[9]

Study of the Flocculation Process

Studies of the flocculation process was conducted according to PN-71/C-04583 standard on TURB 550 IR. The initial value of turbidity of the investigated water was measured and then the optimal dose of polymeric flocculants was determined. The waste water discharge model was prepared by acid hydrolysis of $1{,}8 \cdot 10^{-2}$ M $FeCl_3$ solution containing 10^{-3} M HCl at room temperature for a duration of 3 weeks.[1] The initial turbidity of the waste water discharge model was 360 [NTU].

Results and Discussion

During the fractionation process of VPS and EPS, 7 and 10 fractions were obtained, respectively (Table 1). The results of the fractionation process confirmed that VPS has a narrow molecular weight distribution. Fractions with M_η equal to 217 000 and 207 000 constituted 86.5% of the polymer sample. The participation of fractions with the M_η value higher than 217 000 was only 1.0% of the polymer sample, and of fractions with the M_η value smaller than 207 000 was equal to 13.5% of the polymer sample. The lowest value of the molecular weight of VPS fractions was 170 000 and the

Table 1.
Results of the fractionation process of the VPS and EPS: mass of the fraction, volume of the fraction [%] (percentage part of the sample), intrinsic viscosity ([η]) and molecular weight (M_η).

	No	mass [g]	Volume of the fraction [%]	[η]	M_η
VPS	1.	0.003	0.5	0.93	277 000
	2.	0.003	0.5	0.88	257 000
	3.	0.175	35.0	0.77	217 000
	4.	0.255	51.5	0.88	207 000
	5.	0.025	5.0	0.74	197 000
	6.	0.023	4.5	0.69	187 000
	7.	0.015	3.0	0.66	170 000
EPS	1.	0.006	1.2	0.88	258 000
	2.	0.019	3.8	0.85	247 000
	3.	0.230	4.5	0.86	248 700
	4.	0.490	9.8	0.84	242 000
	5.	0.123	24.6	0.83	237 000
	6.	0.248	50.1	0.82	236 000
	7.	0.011	2.1	0.80	226 000
	8.	0.009	1.8	0.77	218 000
	9.	0.006	1.2	0.72	199 000
	10.	0.005	0.9	0.69	187 000

highest 277 000. However participation of the low and high molecular weight fractions in the mass of the whole sample was much more higher for the EPS fractions than for the VPS fractions. Moreover a bigger amount of fractions with high molecular weight value (242 000–258 000) was obtained for EPS (19.3%) than for VPS. The mass of the two basic biggest fractions is equal to 74.7% of the total mass of the polymer used for the fractionation process. It can assumed that the technological process applied to obtain EPS products caused the decrease of the molecular weight of polystyrene used as the substrate. Besides the values of the molecular weight (236 000–258 000) of 93% of the EPS are very similar (Table 1).

It was also found that the synthesis of sodium salts of the poly(styrenesulphonic acid) with the use of different polystyrene waste as substrates was complicated. The experiments showed that the use of some kinds of polystyrene wastes led to the unexpected products. The obtained data suggests that the fractions exhibit different types of structures. These results confirmed the presence of intramolecular cross-links in the structures of polyelectrolytes. Probably the presence of the additives (organometalic compounds, mineral compounds) in the VPS influences the results described in Table 2, Figs. 1, 2.[8]

The decrease of the n.sulph value points to the lack of cross linking between the molecules of products which are still solved in water (Table 2).

The decrease of the values of n.sulph suggest that the sulphonic groups are removed from the modified molecules and probably give rise to the intramolecular bonds in products with postulated sulphone-type cross-linked structures (Fig. 2).[8]

The results of the fractionation process of the NaEPSS and NaVPSS also suggest that the sulphonation process is probably influenced by the additional substances present in the polystyrene structures. Data obtained from the elementary analysis showed that the numbers of sulphonic groups per one monomer unit (n.sulph) calculated in the same way as in[8] are of the range 0.59 to 2.00 for fractions. However no dependence between the obtained results and the other properties of the fractions was found.

Molecular weight values of NaEPSS are lower than those of NaVPSS (Table 2). This phenomenon may be the results of the presence of some contaminants in the EPS waste. We assume that additional substances (metals, metalorganics) were added during

Table 2.
Properties of the obtained NaEPSS and NaVPSS (number of sulphonic group per one monomer unit (n.sulph), intrinsic viscosity ([η]) and molecular weights (M_η, M_{cal}) of selected NaEPSS, NaVPSS, obtained at 80–90 °C, after fractionation.

Time [h]	NaEPSS				NaVPSS			
	n.sulph	[η]	M_η	M_{cal}	n.sulph	[η]	M_η^{a}	M_{cal}
0.25	0.86	0.75	427 000	424 000	0.91	0.80	480 000	379 000
0.50	0.89	0.75	430 000	431 000	0.97	0.88	550 000	390 000
0.75	0.95	0.77	450 000	444 000	0.97	0.91	580 000	390 000
1.00	0.97	0.79	470 000	449 000	0.98	0.92	590 000	392 000
1.50	0.96	0.88	515 000	447 000	1.01	0.93	600 000	398 000
2.00	0.96	0.84	495 000	447 000	1.00	0.92	590 000	396 000
3.00	0.85	0.82	475 000	422 000	0.95	0.91	580 000	386 000
4.00	0.85	0.80	452 000	422 000	0.89	0.89	560 000	375 000
5.00	0.82	0.74	420 000	415 000	0.88	0.86	530 000	373 000
8.00	0.85	0.68	370 000	422 000	0.88	0.83	500 000	373 000
12.00	0.57	0,68	368 000	359 000	0.70	0.80	480 000	337 000

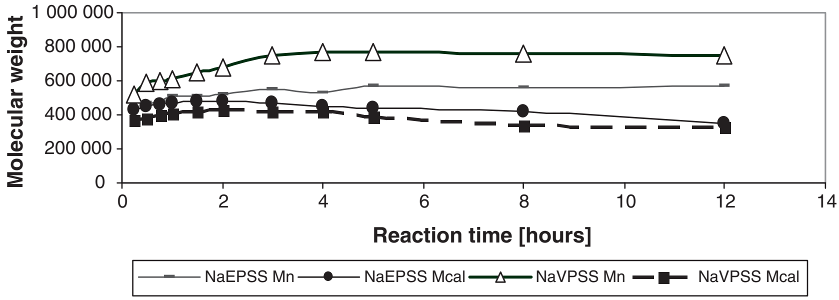

Figure 1.
Molecular weight M_η and M_{cal} of the NaEPSS and NaVPSS obtained with the use of sulphuric acid (VI) in different time duration.

the EPS production to improve its quality. These additives influenced the sulphonation process of EPS, however, their identification proved difficult. It should be stressed that the presence of such substances could also be the reason for the possible inter and intra molecular cross-linking (Fig 2).[8] To confirm our assumptions the sulphonation process of pure PS (without additional substances) was performed. The comparison of

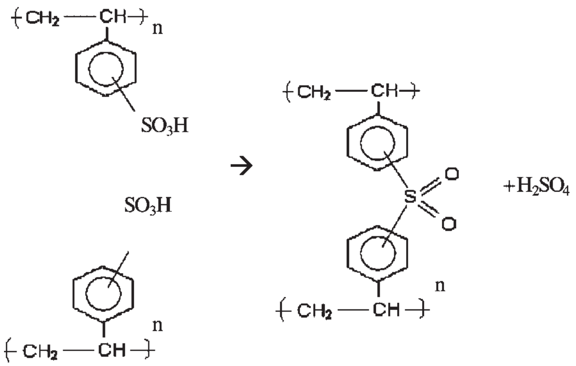

Figure 2.
The intermolecular sulphone-type cross-linking.

Table 3.
The dependence of turbidity of the waste water discharge model after flocculation on the dosage of the polyelectrolyte NaEPSS obtained in the temperature range 80–90 °C (for a duration of 15 minutes).

*properties of	0.86[a]	1.02[b]	0.84[b]	1.20[b]	0.99[b]	0.62[b]	0.59[b]	0.73[b]	1.01[b]
the NaEPSS	427 000	480 000	478 000	460 000	429 000	410 000	398 000	380 000	291 000
dosage [mg/dm^3]	turbidity [NTU]/change of the turbidity [%]								
0.000	360/0	360/0	360/0	360/0	360/0	360/0	360//0	360/0	345/4
0.005	290/19	350/3	310/14	350/3	345/4	356/1	240/33	332/8	300/17
0.006	189/48	176/51	200/44	200/44	300/17	265/26	210/42	299/17	258/28
0.007	110/69	169/53	170/53	184/49	258/28	256/29	210/42	254/29	200/44
0.008	87/75	158/56	158/56	145/60	200/44	198/45	200/44	212/41	188/47
0.009	50/86	71/80	115/68	139/61	121/66	195/46	205/43	210/42	170/53
0.010	42/88	80/78	85/76	133/63	115/68	161/55	189/48	200/44	170/53
0.011	75/79	85/76	95/74	90/75	90/75	121/66	184/49	189/48	171/53
0.012	–	–	95/74	91/75	91/75	121/66	145/40	172/46	165/54
0.013	–	–	–	129/64	98/73	121/66	156/57	161/55	161/55
0.014	–	–	–	–	–	–	156/57	161/55	161/55
0.015	–	–	–	–	–		–	–	–

* n.sulph/M_η.
[a] before flocculation.
[b] after flocculation.

the products obtained during the reactions of the sulphonation of EPS, VPS and pure PS may serve to explain the influence of the additional metalorganic compounds on this process (Table 2).

The flocculation processes with the use of fractions of the polyelectrolytes were most effective with the use of the NaEPSS before fractionation and then with the use of fractions with the M_η value higher than 400 000 (Table 3).

Some dependences between the molecular mass values and the effectiveness of the flocculation process were found together with the dependences between the changes of the molecular mass values of the polyelectrolytes (Table 3). The results suggest that the effect of all fractions yielded better flocculation due to the reinforcement effect caused by different types of structures and size distribution. With the use of other polyelectrolyte reinforcement of the flocculation processes were found and described.[10,11] Elementary analysis of the waste water discharge system did now reveal the presence of the metalorganic compounds or of other substances when the NaEPSS was used as a flocculant. It can be concluded that the presence of the additional substances influences the process of EPS modification but does not effect the flocculation process. The low molecular compounds are probably removed from the products (NaEPSS) in the second stage of the modification process.

The results confirmed that the flocculation process is complicated and the course of the flocculation process depends both on the molecular mass and the number of sulphonic groups of the used fractions. It is probable that all the found characteristics of the obtained polyelectrolyte influence the course of the flocculation strongly. The most probable cours of the flocculation phenomenon is following: charge neutralisation aggregate for the molecules with the lowest molecular mass which dissolved earlier as can suppose and the particle bridging for the molecules with higher molecular mass which dissolved next, since course of that processes strongly depend on the dimensions of the flocculants molecules and their charge and mutual do not exclude but can complete (Fig. 3).

Conclusions

It can be concluded that the presence of additional substances influence the sulpho-

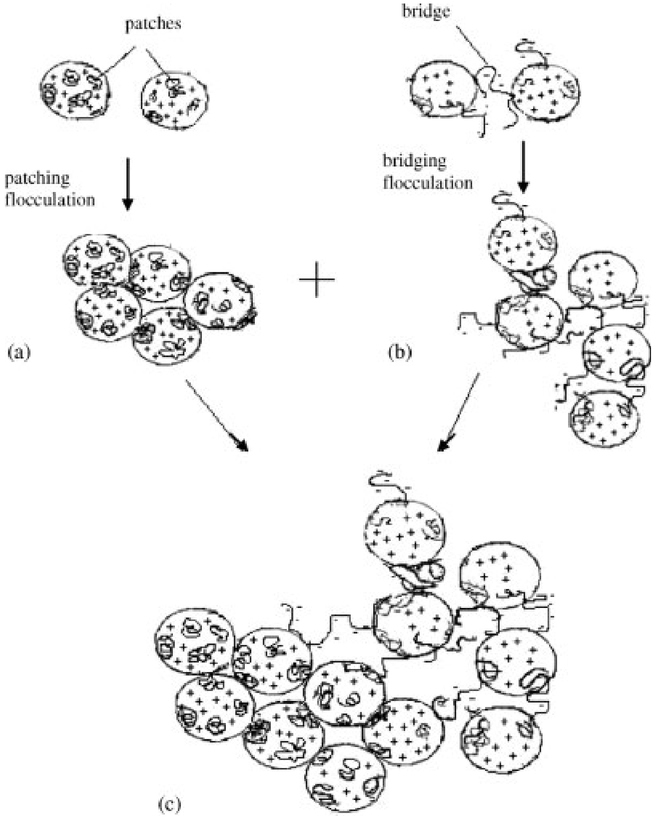

Figure 3.
The most probable course of the flocculation process in the waste water discharge system with the use of the NaEPSS 15 as a flocculant: (a) floccules obtained during patching flocculation (b) floccules obtained during bridging flocculation (c) big floccules obtained during patching and bridging flocculation.

nation processes and cause the differences in the content of n.sulph in the obtained fractions.

The differences between the properties of the macromolecules of the obtained polyelectrolytes i.e. with different n.sulph values and the possibility of the presence of sulphone type cross-linking in some of them affect the fractionation process.

The results of the fractionation process show that a smaller number of fractions was obtained for NaVPSS than for NaEPSS. VPS as an industrial product has a narrow molecular mass distribution.

It was found that characteristicts of the obtained polyelectrolytes influence the cours of the flocculation. The most probable cours of the flocculation phenomenon is the charge neutralisation aggregate and/or the particle bridging since the course of these processes strongly depend on the dimensions of molecules of the flocculants and its charge.

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