

Some factors affecting the sulphonation of polystyrene

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Abstract:

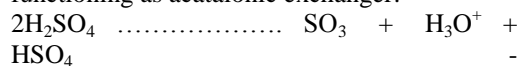
A commercial packing polystyrene had been modified via sulphonation process yielding an efficient ion-exchanger for softening of water . Some factors that have to do with such transformation had been followed up . It had been found that sulphonation conditions, molecular weight, residence time and additives have roles to play.

Introduction:

Due to high consumption of the plastic materials in every day's life ⁽¹⁾ as a consequence huge wastages of these products could be expected. Generally the majority of the plastics are not expensive to be recycled nevertheless for environmental causes some of them are recycled . Since materials of this nature, which polystyrene is one of them are highly stable towards biodegradation for instance it takes (500) years to decompose , especially if deprived of moisture and oxygen ⁽²⁾. Other ways to get rid of them are via chemical reactions

which aim at transforming them to other useful products. Polystyrene can be transformed by sulphonation to another useful material which have many industrial applications, one of which is being a good ion-exchanger for water softening, though it is well known that the best ion-exchanger ever prepared is that of cross-linked copolymer of styrene with divinylbenzene ⁽³⁾ which acts as a cationic exchanger

In reality the sulphonated polystyrene was found to be as good as it is. Sulphonated polystyrene actually is an anion but once it meets water becomes protonated , hence functioning as a cationic exchanger.



The sulphonation of benzene ring which is the basic unit of polystyrene done at temperature of (70-110 C⁰) using concentrated sulphuric acid, this process yields

water as a by-product causing the dilution of the acid which is considered to be a disadvantage of this process. A problem that can be tackled via the fact benzene with water can be distilled azeotropically . Sulphonation can be done using oleum (SO₃.H₂SO₄) at 80 C⁰ . Un recommended the sulphonation by sulphur trioxide because of its multi side products

, especially diphenyl sulphone ⁽⁴⁾. Other sulphonations processes had been reported by other authors using a variety of sulphonating agents ^(5,6). This study aims at getting use of the large amounts of polystyrene flakes which are used for the protection of domestic goods during storage and transportation by sulphonation to produce an ionic-exchanger (I.E) for both potable and industrial water , besides this main target many factors that expected to have a role to play at the process had been investigated

Experimental:

A. Materials:

Commercial polystyrene was used as it is, toluene (fluka) and methanol (99%) GCC were used as received, sulphuric acid (99%) BDH , Methylmethacrylate (MMA) (99%) Aldrich, thio glycolic acid (fluka). Benzoyl peroxide was recrystallised from methanol. It was of 103 C⁰ as melting point.

B: Molecular weights: ⁽⁷⁾

Were determined by using Ostwald-fenske viscometer (USA) (0.54) mm diameter according to Howunick-Sakarada equation:

$$\eta = k M^a \quad \text{at } 20 \text{ C}^0 \text{ using toluene as solvent}$$

C: Sulphonation of polystyrene ⁽⁸⁾: was done as described in the reference.

D: Titrations ⁽⁹⁾:

Were executed by taking a constant volume of ten milliliters for all samples . Ethylene diamine tetra acetic acid as disodium salt was used as a titrant. Eriochrome black-T was the indicator, a buffer solution of PH = 10 was inserted to all samples

E. Preparation of an additive ⁽¹⁰⁻¹¹⁾ :

MMA after the removal of the inhibitor was distilled under vacuum and the central part distillate was used for radically initiated polymerization using benzoylperoxide (1.5 × 10⁻² mol/ L) as initiator.

And thioglycolic acid as a chain transfer agent (0.04-0.05g/10 ml MMA) for the purpose of getting a carboxylic-terminated Prepolymers of precontrolled molecular weights ($1.7 - 4 \times 10^6$) g/mol of different chemical nature of the sulphonated polystyrene. Bearing in mind that the relation {conc. of the transfer agent / conc. of the monomer} should be less than 0.4 mol./L to avoid the high reduction at the values of the molecular weights.

Results and discussions:
Having determined the molecular weight of the commercial polystyrene sample which is used at this study, it was found of the order 5.62×10^6 g/mol. Different concentrations of the concentrated sulphuric acid, firstly a 30% (w/v) was used, then a 50% and finally a 75%. Knowing that the 98% conc. led to total charring of the polymer. The obtained results were tabulated in table (1).

Table (1) Effect of sulphonating agent conc. And time

Exp.No.	Capacity (PPM) retended in I.E			Time (hr.)
	30%	50%	75%	
1	20	44	156	1
2	21	45	156	2
3	24	47	158	24

It is very clear that the time has a little role to play after half an hour of treatment as table (1) reveals. These results are in good accordance with the literature which suggests that if the half time of any I.E is less than five minutes is considered to be good⁽³⁾. Undoubtedly the sulphonation conditions are the governing factor of the prepared I.E. As the conc. of the sulphonating agent was raised from 30% to 50

% and finally to 75% the efficiency increased from 12.2% to 26.8% and finally to 95% as table (2) indicated bearing in mind that the calculated Ca^{+2} conc. of the tap water was of 164 PPM. % efficiency was taken as the conc. of Ca^{+2} retended by the ion-exchanger divided by its original conc. In the sample

Table (2): Effect of sulphonating agent conc. On % efficiency of I.E.

H ₂ SO ₄ conc.	[Ca ⁺²] ppm after treatment	% efficiency
30%	144	12.2
50%	120	26.8
75%	8	95

To follow the effect of the residence time right from the beginning after the insertion of a constant amount of the carboxylated

prepolymer (0.5 g) of different molecular weights { $1.7 - 4$ } * 10^6 g/mol. , to a fixed quantity (1 g) of the sulphonated polystyrene.

Table (3) Effect of M.wt. of the additive and residence time on I.E efficiency at 75 % conc.

Time (Min.)	H ₂ SO ₄ % efficiency		
	{ 4×10^6 }	2×10^6	1.7×10^6 } gmol ⁻¹
15	92	87.6	84
30	84	79.6	79
45	80	74	72
60	74	70	68

Table (3) figures out these results. It is clear that the residence time has a job to play till the half hour of treatment which confirms with the

definition of a good I.E, but beyond that it has a slight effect as table (1) showed. Regarding the molecular weights, one could notice that an

increment in the molecular weight leads to an increase at the percentage of the efficiency which proves the viability of the added additive, though a small change had been noticed, this may be attributed to the low activity of the carboxylic group in comparison with that of the sulphone group, besides the different chemical nature of the additive used. It could be implied that the high increase in the efficiency may be due to the high porosity of I.E, besides the higher exchanging centers in addition to pre-mentioned other factors

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بعض العوامل المؤثرة على سلفنة البولي ستايرين

ضاري محمد عبد الله

الخلاصة

متعدد الستايرين التجارى المستخدم لاغراض التعبئة تم تحويله بعملية السلفنة منتجا مبادلا ايونيا لتحلية المياه. بعض العوامل المؤثرة على هذه العملية تمت متابعتها حيث تبين انه ظروف السلفنة,الوزن الجزيئى,زمن التماس والمضافات المستخدمة كلها عوامل لها تأثير على كفاءة المبادل الناتج .