

# Adhesion and Corrosion Resistance Properties of Modified Polystyrenes

Gulnare Ahmetli, Ayse Kaya, Ayse Ozkececi

Department of Chemical Engineering, Selcuk University, Campus-Konya 42075, Turkey

Received 13 April 2007; accepted 17 July 2007

DOI 10.1002/app.27182

Published online 10 October 2007 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** In this study, chemical modification of different molecular weight polystyrenes (PS) was researched with various functional group modifiers: epichlorohydrin, maleic, and acetic anhydrides, in one stage and in the medium of  $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$  cationic catalyst. It was determined that the amounts of the functional groups, bound to the structure of the polymer, have been changed depending on the molecular weight of the PS used and more functional groups have been bonded to the lower molecular weight PS. It is stated that the adhesion properties and

corrosion resistance of the modified PS on metal surface have been changed depending on the molecular weight of PS and the amount of the functional groups bound to the aromatic ring of the polymer. Various functional groups bound to the aromatic ring of the PS and their amounts were determined by spectral and chemical analysis methods. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1373–1377, 2008

**Key words:** polystyrene; modification; adhesion

## INTRODUCTION

Coating of metal surfaces with polymeric materials is one of the actual methods to protect the metals from corrosion. In recent years, the synthesis of functionalized polymers by chemical modification and their application areas have been developed continuously.<sup>1–5</sup>

One of the important deficiencies of polystyrene (PS) was that it had a very weak adhesion property on metal surfaces. This property was prevented by the use of PS as polymeric coating material. It was determined that it was possible to gain new properties to PS and ameliorate these defective properties by bonding various functional groups to the aromatic ring of PS.

Modified PS was found to have higher mechanical, thermal, and elasticity properties than PS had and they were more durable against impact. Therefore, various functional groups were bound to the aromatic ring of PS by carrying out chemical modification of Li-PS via multistage method.<sup>1–5</sup> But this method was used very seldom, because it was a multistage method. Therefore, referring to our studies in recent years about polymeric coatings, it is possible to carry out chemical modification reactions in single stage. It is also possible to bind various functional groups (carboxyl, acyl, epoxy, chlorohydrin, and C=C double bond) to the aromatic ring of the polymer and to

obtain polymeric coatings having high adhesion property and corrosion resistance.<sup>6–8</sup> In our previous study, the reactions of high molecular weight ( $M_n = 500 \times 10^3$ ) PS with maleic anhydride (MAH), acetic anhydride (AAH), butadiene, and isoprene in the medium of cationic catalysts ( $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ ,  $\text{AlCl}_3$ ,  $\text{ZnCl}_2$ , etc.) by one stage method were researched. The activity of cationic catalysts was determined as  $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2 > \text{AlCl}_3 > \text{ZnCl}_2$ . It was shown that the modified polymer obtained properties such as adhesion, corrosion resistance, photosensitivity, thermostability, and impact resistance.<sup>9,10</sup>

In this study, to bond more functional groups to the aromatic ring, different molecular weight PS was used. Also, it is aimed to obtain more economical polymeric coatings having high adhesion and corrosion resistance properties by bonding more functional groups to the structure of polymer. The effect of the functional groups bonded to the structure of the polymer on the coating properties of modified PS was investigated.

## MATERIALS AND METHOD

Different molecular weight PS ( $M_n = 500 \times 10^3$ ,  $350 \times 10^3$ , and  $230 \times 10^3$ ), epichlorohydrin (ECH), maleic anhydride (MAH), and acetic anhydride (AAH) were purchased from Merck.

### Synthesis of functionalized PS

As the modification of PS with AAH was performed on 20°C, 30°C, and 45°C, the optimum temperature

Correspondence to: G. Ahmetli (ahmetli@selcuk.edu.tr).

TABLE I  
Effect of Temperature on the Modification Reaction of PS with AAH

Reaction temperature (°C)	PS $M_n \times 10^3$	—CO—CH <sub>3</sub> (mol %)	PS $M_n \times 10^3$	—CO—CH <sub>3</sub> (mol %)	PS $M_n \times 10^3$	—CO—CH <sub>3</sub> (mol %)
20	500	4.8	350	6.0	230	6.8
30	500	5.1	350	6.5	230	7.0
45	500	4.5	350	5.0	230	6.0

PS, 0.05 mol; PS : AAH mol ratio = 1 : 0.25; AAH : catalyst mol ratio=1 : 1.

for modification reaction was determined as 30°C, and this reaction temperature was also applied to other modifications (Table I).

A reactor composed of mixer, cooler, and thermometer was used in the experiments. 0.0125 mol modifier (25% of the polymer amount) was added to the solution of 0.05 mol PS in 60 mL chloroform by mixing. After modifier was dissolved completely, 0.0125 mol BF<sub>3</sub>O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> was added drop-by-drop and the reaction was ended in 2 h at the temperature of 30°C. Modified PS was obtained without forming any by-product. The mixture was poured into a beaker and the modified PS was precipitated with methanol, dried in a vacuum oven at 50–60°C for 1 h, weighed, and analyzed.<sup>9</sup>

### Measurements and analyses

IR spectra of modified PS films were recorded with a Unicam SP 1025 spectrometer.

### Chemical analyses

#### Determination of acid number

The amount of functional groups bonded to the structure of the modified PS was determined by functional group analysis. To determine the number of carboxyl (—COOH) groups in the PS, the polymer sample was boiled under reflux with excessive 0.1N KOH and then the remaining KOH was titrated with 0.1N HCl solution.

$$\text{A.N. (mg KOH/g polymer)} = 56.1(V_1N_1 - V_2N_2)/m$$

where A.N. is the acid number,  $V_1$  is the volume of the added 0.1N KOH (mL),  $N_1$  is the normality of the KOH solution,  $V_2$  is the volume of wasted 0.1N HCl (mL),  $N_2$  is the normality of the HCl solution, and  $m$  is the amount of the sample (g).

#### Determination of acetyl (—CO—CH<sub>3</sub>) groups

The concentration of the acetyl group, connected to the structure of PS, was calculated by titrating of acetic acid with 0.1N KOH, which occurred after the chemical modification reaction of PS with AAH by using BF<sub>3</sub>O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> as catalyst.

$$\text{AAH, mol/L} = (\Delta V \times T_{\text{KOH}} \times 1000)/56.1 \times 2$$

where, AAH is the concentration of the reacted AAH,  $\Delta V$  is the volume of 0.1N KOH used for titration of acetic acid in 1 mL sample (mL),  $T_{\text{KOH}}$  is the amount of KOH in 1 mL 0.1N KOH solution (0.005208 g), 56.1 is the molecular weight of KOH (g).

#### Determination of epoxy groups

To determine the percentage of bonded epoxide groups to PS, 0.5 g modified PS was placed in a 250 mL flask and 25 mL solvent mixture (60 mL acetone + 1.5 mL concentrated HCl) was added to it. It was mixed for 2 h at room temperature. The epoxy groups in the sample were cleaved with excessive HCl and then the remaining HCl was titrated with 0.1N KOH. The epoxy group was calculated by the following equation:

$$\text{Epoxy groups (\%)} = (V_1 - V_2) \times 0.0043 \times F \times 100/m$$

where  $V_1$  is the 0.1N KOH used for the titration of control (mL),  $V_2$  is the 0.1N KOH used for the titration of sample (mL),  $F$  is a titration factor for 0.1N KOH solution,  $m$  is the amount of the sample analyzed (g), 0.0043 is the number of epoxy groups corresponding to 1 mL of 0.1N KOH.

### Coating properties of modified PS

The 10% polymer solution was prepared in toluene for the investigation of coating properties of different molecular weight PS synthesized with functional groups. The film with a thickness of 100–120 μm was applied to the metal (steel of moderate carbon content with dimensions 50 mm × 100 mm × 1 mm surface). The film was dried first at room temperature, and then in an oven at 70°C for 1–2 h.

#### Determination of the adhesion properties

The adhesion property of the modified polymers was determined by the "Lattice notch method." For the determination of the adhesion capability to metal (cold rolled carbon steel with content C, 0.2%; Mn,

TABLE II  
The Effect of Functional Groups on the Adhesion Property of Modified PS

PS, $M_n$ ( $\times 10^3$ )	—COOH mg KOH/g <sup>a</sup>	Adhesion (%)	—CO—CH <sub>3</sub> (mol %)	Adhesion (%)	CH—CH <sub>2</sub> O (mol %)	Adhesion (%)
500	30	65	5.1	55	3.4	51
350	35	72	6.5	64	6.1	60
230	56	80	7.3	70	7.0	70
Unmodified PS	—	2	—	—	—	—

<sup>a</sup> The higher this value, the higher the amount of —COOH groups.

1.5%; Si, 0.1%; P, 0.01%; S, 0.008% and with dimensions 50 mm  $\times$  100 mm  $\times$  1 mm), the tested side was blasted and cleaned to apply the coated materials. The solution of each polymer was prepared in 10% toluene and deposited as a layer (120–140  $\mu$ m) over the metal. This material was first dried in open air and then in an oven at 50°C. According to the "Lattice notch method" a thin polymer layer (120–140  $\mu$ m) is formed on the metal surface and the polymer layer is divided into small squares (1 mm  $\times$  1 mm) by a razor blade. Insulating tape (10–100 mm) is over these squares and the tape is suddenly pulled. In this process, a portion of small squares is separated from the surface of the metal and another portion remains on the surface. Therefore, the percent adhesion is calculated from the number of small squares still remaining on the metal surface. The percent adhesion was calculated as:

$$\text{Adhesion (\%)} = [(a - b)/a] \times 100$$

where  $a$  is the total number of squares,  $b$  is the number of squares removed from the substrate.<sup>11</sup>

#### Determination of the corrosion resistance

Polymer coatings (100–120  $\mu$ m thick) were formed on the metal surfaces from the prepared polymer solutions and were exposed to 3% NaCl, 10% NaOH, 10% HCl, pure water, and air for 8 days. After removal of the coated metals from the treating solutions, the amount of decomposition observed by the naked eye was taken as a measure of the corrosion resistance.

## RESULTS AND DISCUSSION

The IR results for PS modified with MAH (Fig. 1), AAH (Fig. 2), and ECH (Fig. 3) using cationic catalyst  $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$  are given below.

The 1598  $\text{cm}^{-1}$ , 1539  $\text{cm}^{-1}$ , 1488  $\text{cm}^{-1}$  (alkene C=C), 1733  $\text{cm}^{-1}$  (acid CO), 1800  $\text{cm}^{-1}$  (CO-alkyl), 3034–2900  $\text{cm}^{-1}$  (acid OH) peaks in the IR spectrum of PS modified with MAH show the bonding of the —CO—CH=CH—COOH group to the structure of the PS at the end of the modification.

The 1373  $\text{cm}^{-1}$  and 1453  $\text{cm}^{-1}$  ( $\text{CH}_3$ ), 1803  $\text{cm}^{-1}$  (CO-alkyl) peaks in the IR spectrum of PS modified with AAH show the bonding of the acetyl (—COCH<sub>3</sub>) group to the structure of the PS at the end of the modification.

The 908  $\text{cm}^{-1}$ , 1261  $\text{cm}^{-1}$  peaks in the IR spectrum of PS modified with ECH show the bonding of the epoxy group to the structure of the polymer at the end of the modification.

PS have been modified with various functional group modifiers in order to develop their application areas and improve their certain deficient properties. The properties of modified polymers depend on the amount and the structure of the functional groups bound to the polymer.

The optimum conditions for chemical modification of PS were found within the mole ratios of PS : modifier as 1 : 0.25 and modifier : catalyst as 1 : 1 mol proportions, 2 h reaction period at 30°C.

The experimental results obtained were given in Table II. As seen in Table II, the amount of functional groups bound to the aromatic ring of the polymer as a result of chemical modification of different molecular weight PS depends on the molecular weight of the polymer, and more functional groups are bound to the lower molecular weight PS.

It was determined that the amount of functional CO—CH=CH—COOH groups, bound to the structure of the polymer by modification with MAH under the same reaction conditions, increased with decreasing molecular weight of PS ( $M_n$  from 500  $\times 10^3$  to 230  $\times 10^3$ ), i.e. it was determined that the acid number of modified polymer increased from 30 mg KOH/g to 56 mg KOH/g.

The same results were also obtained for the chemical modification of different molecular weight PS with AAH and ECH using  $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$  catalyst. It was determined that acetyl group mol percent of modified polymer increased from 5.1 to 7.3% and epoxy group mol percent increased from 3.4 to 7.0%. The bonding of functional groups to the aromatic ring of polymer using  $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$  catalyst is shown in Figure 4.

Adhesion and other coating properties of modified PS varied depending on the structure and the amount of the functional groups bound to the struc-

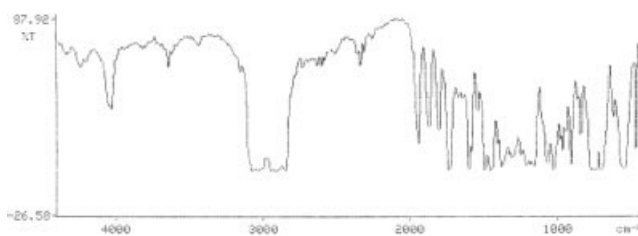


Figure 1 IR spectrum of PS with MAH.

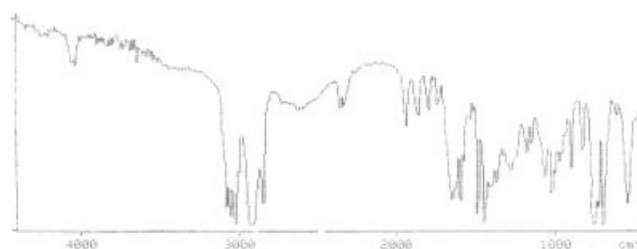


Figure 3 IR spectrum of PS with ECH.

ture of polymer. It was found that it was better to study the chemical modification reactions of lower molecular weight PS in order to understand the functionality effect of polymer on the adhesion and corrosion resistance properties of coatings.

Coating properties of modified different molecular weight PS were investigated in laboratory conditions. The effect of functional groups bound to the aromatic ring of the PS on the adhesion and corrosion resistance properties of functionalized polymers coated on the surface of the metals was investigated, and it was found that these properties varied depending on the molecular weight of PS and the amount of the functional groups bound to the structure of the polymer.

It was observed that adhesion percent to the metal surface increased from 65 to 80% by increasing the amount of carboxyl groups bound to the modified PS with MAH. It was found that at the end of the modification with ECH, adhesion percent varied between 51 and 70% depending on the amount of epoxy groups bound to the modified PS. Adhesion percent of modified PS with AAH to the metal surface reached up to 55–70%. The unmodified PS shows less adhesion property. The results obtained are given in Table II.

As shown in Table II, the adhesion properties of modified PS improve with increasing of functional groups bonding to PS and decreasing of molecular weight of PS. In addition, the best adhesion results were obtained for PS with molecular weight  $230 \times 10^3$  modified with MAH. Therefore, the corrosion resistance properties of coatings were examined by

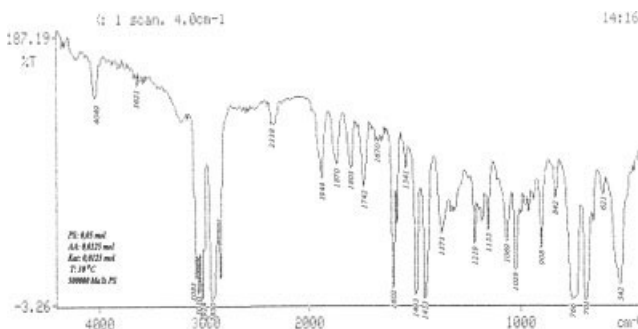


Figure 2 IR spectrum of PS with AAH.

microscopic analysis method for modified PS with molecular weight  $230 \times 10^3$  in 3% NaCl, 10% NaOH, 10% HCl solutions, deionized water, and air. The effect of functional groups bound to lower molecular weight PS on corrosion resistance was investigated and the functionalized PS showed a higher corrosion resistance, too. It was seen that there was no corrosion on the metal surface in the solution of 5% NaCl which is the aggressive sea condition in a period of 11 days. But, it was obtained that the resistance against the solution of 10% NaOH decreased by increasing the amount of carboxyl groups in the structure of polymer. The main reason for this is considered as the interaction of bound carboxyl group with NaOH (Table III).

Advantage of unmodified PS is the high resistance to NaOH medium because it has no carboxyl groups. But unmodified PS does not have an adhesion property to metal surface and this prevents using it for coating. The aim of this study is to give adhesion property to metal surfaces for modified PS by bonding various active functional groups to PS aromatic ring by chemical modification methods.

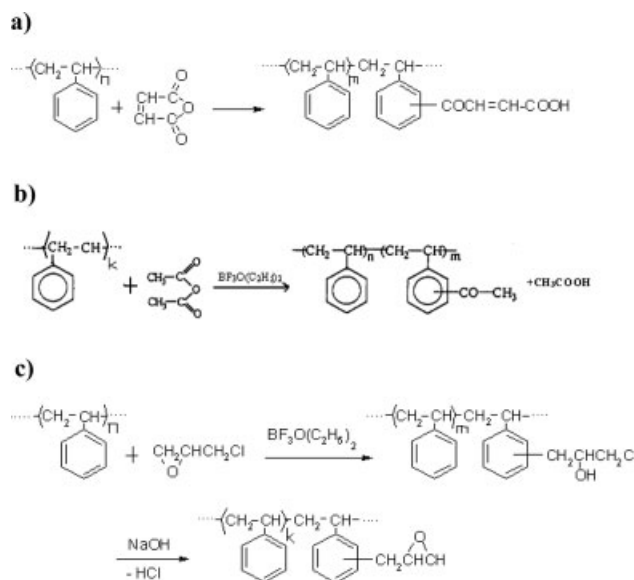


Figure 4 Modification reactions of PS with (a) MAH, (b) AAH, and (c) ECH.

**TABLE III**  
**The Effect of the Functional Groups on the Corrosion Resistance of the Modified PS ( $M_n = 230 \times 10^3$ )**

Functional group	Corrosion resistance				Water absorption (%)
	3% NaCl	10% NaOH	10% H <sub>2</sub> SO <sub>4</sub>	Air	
–COOH	++	– +	++	++	0.07
–CO–CH <sub>3</sub>	++	+	+	+	0.04
CH–CH <sub>2</sub> O	++	– +	+	+	0.06
Unmodified PS	+	++	+	+	–

–, no resistance; – +, little; +, medium resistance; ++, high resistance.

The water absorption capability of modified PS in 24 h varied between 0.04% and 0.07%. Water absorption ability decreased whereas resistance to atmosphere increased by increasing the amount of functional groups in the structure of the polymer (Table III).

### CONCLUSION

The optimum reaction conditions for chemical modification reaction of different molecular weight PS with various functional group modifiers (MAH, AAH, and ECH) using BF<sub>3</sub>O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> catalyst were ascertained based on bonding maximum amount of functional groups to the aromatic ring of PS. It was observed that more functional groups bound to the PS with lower molecular weight.

Adhesion and corrosion resistance properties of coatings of modified PS depended on the molecular weight of PS and the amount of the functional groups bound to the polymer. The adhesion properties of modified PS improve with increasing of functional groups bonding to PS and decreasing of molecular weight of PS. The best adhesion results were obtained for PS with molecular weight 230,000 modified with MAH. Modified with AAH lower molecular weight PS shows a higher corrosion resistance. It

was determined that the PS modified with MAH also was stable against thermal destruction at high temperatures.

### References

- Gaylord, N. G.; Mishira, M. K. *J Polym Sci* 1983, 21, 23.
- Gaylord, N. G.; Mehta, R.; Kumar, V.; Tazi, M. *J Appl Polym Sci* 1989, 38, 359.
- Gaylord, N. G.; Mehta, R.; Mohan, D. R.; Kumar, V. *J Appl Polym Sci* 1992, 44, 1941.
- Lee, S. S.; Ahn, T. O. *J Appl Polym Sci* 1999, 71, 1187.
- Wu, C. J.; Chen, C. Y.; Woo, E.; Kuo, J. F. *J Polym Sci* 1993, 31, 3405.
- Mirzaoglu, R.; Kurbanli, R.; Ersoz, M. *Handbook of Engineering Polymeric Materials*; Cheremisimoff, Marcer Dekker: New York, 1997; p 259.
- Kurbanli, R.; Mirzaoglu, R.; Akovali, G.; Rzayev, Z.; Karatas, I.; Okudan, A. *J Appl Polym Sci* 1996, 59, 235.
- Kurbanli, R.; Mirzaoglu, R.; Kurbanov, S.; Karatas, I.; Ozcan, E.; Okudan, A.; Guler, E. *J Adhes Sci Technol* 1997, 11, 105.
- Kurbanli, R.; Okudan, A.; Mirzaoglu, R.; Kurbanov, S.; Karatas, I.; Ersoz, M.; Ozcan, E.; Ahmedova, G.; Pamuk, V. *J Adhes Sci Technol* 1998, 12, 947.
- Ahmetli, G.; Yazicigil, Z.; Kocak, A.; Kurbanli, R. *J Appl Polym Sci* 2005, 96, 253.
- Government Standard (GOST) 1540-78. *Adhesion Determination Method*, Moscow, 1978.