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Functionalization of polystyrene and adhesion studies

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Abstract—The adhesion capability of novel functional polystyrenes to metals and their capability to provide corrosion resistance to metals under various conditions have been investigated. The polyfunctional polystyrenes were prepared via reaction of the polystyrene with different functional groups [2-methyl-2,3-epoxy-6-octene-4-one (**I**), 2-methyl-2,3-epoxy-5,7-nonadien-4-one (**II**), 1-chloro-2,3-epoxy-5-chloromethyl-5-hexene (**III**), 1-(Δ^3 -tetrahydrobenzaloxime)-2,3-epoxy propane (**IV**), and maleic anhydride (**V**)] in the presence of catalysts. The results show that the addition of functional groups to the polystyrene increases its adhesion capability and corrosion resistance. This increase is attributed to the quantity and nature of the functional groups bonded to polystyrene.

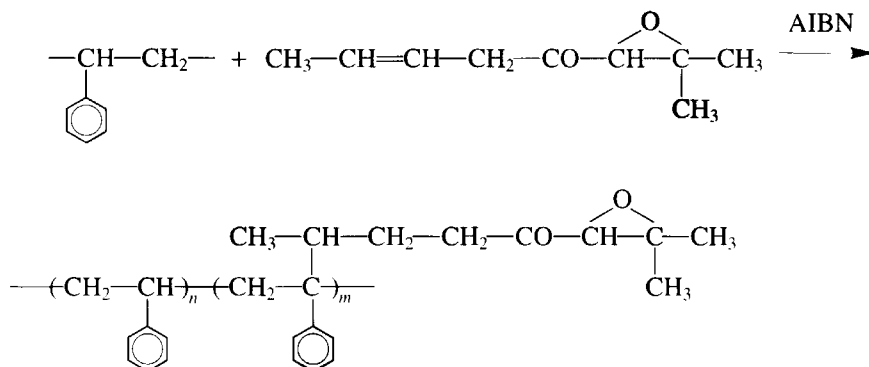
Keywords: Polystyrene; functionalization; adhesion; corrosion resistance.

1. INTRODUCTION

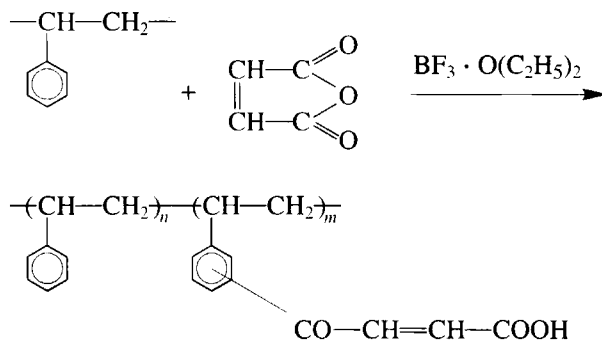
The synthesis of polymeric materials that adhere well and provide corrosion resistance to metals is an important topic in polymer chemistry and technology. Polystyrenes have limited adhesion capability without additional functional groups. Desired physical and mechanical properties of polystyrenes such as thermal stability and mechanical strength have been obtained by anchoring some functional groups [1–3]. For this reason, we have synthesized new polyfunctional polystyrenes and have examined their adhesion capability and corrosion resistance. In our earlier work [4–9], the synthesis of polyfunctional polystyrenes which have adhesion capability and corrosion resistance with different functional groups (epichlorohydrin, organic anhydrides, and unsaturated hydrocarbons) against various materials such as metal, glass and wood in the presence of cationic catalysts was carried out.

In this study, the chemical modification of polystyrenes was investigated with 2-methyl-2,3-epoxy-6-octene-4-one, 2-methyl-2,3-epoxy-5,7-nonadien-4-one, 1-chlo-

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Scheme I. Epoxylated polystyrene, $m/n = 1/11$.



Scheme II. Maleated polystyrene, $m/n = 1/(5-22)$.

ro-2,3-epoxy-5-chloromethyl-5-hexene, and 1-(Δ^3 -tetrahydrobenzaldoxime)-2,3-epoxy propane in the presence of a radical initiator [α, α' -azobisisobutyronitrile (AIBN)] (Scheme I), and also with maleic anhydride in the presence of a cationic catalyst ($\text{BF}_3 \cdot \text{OEt}_2$) [10] (Scheme II).

The adhesion capability and the corrosion resistance of the products obtained were examined according to the functional groups under various conditions. A relationship was found between the adhesion capability and the corrosion resistance of polystyrenes containing different functional groups (carboxyl, keto, epoxy, chloroepoxy, epoxy aldoxime) (Table 2). When a cationic catalyst (Lewis acid) was used [4–9], the functional groups were attached to the aromatic rings of polystyrenes, whereas the functional group was attached to the aliphatic chain of polystyrenes [11] if a radical initiator (AIBN) was used. The functional groups bonded to the aromatic rings of polystyrenes are different from those bonded to the aliphatic chain and the former increase the adhesion capability and offer high resistance against corrosion.

2. MATERIALS AND METHODS

2.1. Synthesis of functional compounds used in the chemical modification of polystyrenes

2.1.1. Synthesis of 2-methyl-2,3-epoxy-6-octene-4-one (I) and 2-methyl-2,3-epoxy-5,7-nonadien-4-one (II). These compounds were obtained from the condensation of acetaldehyde and crotonaldehyde with 4-methyl-3,4-epoxy-2-pentanone in the presence of a base [12].

2.1.2. Synthesis of 1-chloro-2,3-epoxy-5-chloromethyl-5-hexene (III). This compound was synthesized from the condensation of 2-methyl-3-chloro-1-propane and 2,3-dichloro-propanal in the presence of AlCl_3 catalyst [13].

2.1.3. Synthesis of 1-(Δ^3 -tetrahydrobenzaldoxime)-2,3-epoxy propane (IV). This compound was prepared using epichlorohydrin with Δ^3 -tetrahydrobenzaldoxime under basic conditions.

2.1.4. Maleic anhydride (V) was purchased and used as received.

2.1.5. Polystyrene (PS) (MW \sim 250 000) was dissolved in benzene, followed by precipitation in methanol, and was used after drying under vacuum at 50°C .

Some of the properties of these compounds are given in Table 1.

Table 1.

Some of the properties of the compounds used for modification of polystyrenes

Compound No.	Formula	MW	B.p. (C)	Refractive index	Density (g/ml)
I	$\text{CH}_3\text{CH}=\text{CH}-\text{CH}_2-\text{CO}-\text{CH}-\text{C}(\text{CH}_3)_2$ 	140	67-68 (5 mm Hg)	1.460	0.9920
II	$\text{CH}_3\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CO}-\text{CH}-\text{C}(\text{CH}_3)_2$ 	154	71-72 (5 mm Hg)	1.459	0.9856
III	$\text{CH}_2=\text{C}(\text{CH}_2\text{Cl})-\text{CH}_2-\text{CH}-\text{CH}-\text{CH}_2\text{Cl}$ 	146.5	64-66 (4 mm Hg)	1.461	1.0360
IV		181	112-114 (2 mm Hg)	1.498	1.0520
V		98	— 54 (m.p.)	—	0.9340

2.2. Synthesis of functional polystyrenes

2.2.1. Polyfunctionalization of polystyrene in the presence of a radical initiator. 5.2 g (0.05 mol) of polystyrene was dissolved by stirring in 40 ml of toluene in a three-necked flask at 20°C. 1.04 g (0.0068 mol) of 2-methyl-2,3-epoxy-6-octene-4-one (**I**) was added and the mixture was stirred for 30 min; then 0.15 g of AIBN was added and the mixture was again stirred for 3 h at 60°C. After completion of the reaction, the solvent was evaporated using a Rotavapor. The product was dried under vacuum at 1 mm Hg at 20°C for 5 h.

Chemical modification of the polystyrene with the other functional compounds (**II**, **III**, and **IV**) (Table 1) was carried out under the same reaction conditions.

2.2.2. Chemical modification of polystyrene with maleic anhydride in the presence of a cationic catalyst. 5.2 g (0.05 mol) of polystyrene was dissolved in 40 ml of chloroform by stirring in a three-necked flask at 20°C, then 0.98 g (0.01 mol) of maleic anhydride was added. 1.26 ml (0.01 mol) of the catalyst $\text{BF}_3 \cdot \text{OEt}_2$ was added drop by drop to the mixture at 20°C for 30 min and the mixture was stirred for 2 h. After completion of the reaction, the product was precipitated with methanol and dried under vacuum at 50°C for 5 h.

The amounts of the functional groups ($-\text{COOH}$, $-\text{CH}-\text{CH}_2$, $-\text{Cl}$) in the polystyrene were determined by titration methods [14–16].

2.2.2.1. Determination of carboxyl numbers. To determine the number of carboxyl groups in the polymer, the polymer sample was boiled under reflux with excessive KOH and then the remaining KOH was titrated with HCl solution [14].

$$\text{A.N.} = \frac{56.1(V_1N_1 - V_2N_2)}{w},$$

where N_1 is the normality of KOH, V_1 is the volume of KOH added, N_2 is the normality of HCl, V_2 is the volume of HCl used, and w is the weight of the sample (g).

The number of carboxyl groups was calculated as above and the acid number (A.N.) was found to be 7.36% (20.0 mol%).

2.2.2.2. Determination of epoxy groups. To determine the percentage of bonded epoxy groups to polystyrene, the epoxy group in the sample was cleaved with excessive HCl and then the remaining HCl was titrated with KOH [14]. The epoxy group was calculated by the following equation:

$$\text{Epoxy groups \%} = \frac{(V_1 - V_2)f \times 0.0043}{w} \times 100,$$

where V_1 is the volume of KOH that equals the blank sample (for blank titration of excess HCl), V_2 is the volume of KOH that equals the free acid (HCl) remaining at the end of the reaction, w is the amount of the sample (g), f is a titration factor

for 0.1 N KOH, and 0.0043 is the number of epoxy groups corresponding to 1 ml of 0.1 N KOH.

The percentage of epoxy groups and their mol% were found to be:

- (I) 3.33% (8.7 mol%);
- (II) 5.55% (16.0 mol%);
- (III) 1.80% (4.4 mol%).

2.2.2.3. *Determination of chlorine groups.* To determine the amount of chlorine, the polymer sample was burned and the free chlorine generated was converted to KCl with H_2O_2 and KOH. Then this solution was titrated, using diphenylcarbazone indicator in $Hg(NO_3)_2$ solution, until the appearance of a pink colour [15, 16].

The percentage of chlorine was calculated as follows:

$$Cl \% = \frac{(V_2 - V_1) f \times 0.35457}{w} \times 100,$$

where V_1 and V_2 are the volumes (ml) of 0.01 N $Hg(NO_3)_2$ in the titration procedures for the blank and sample, respectively; f is a titration factor for $Hg(NO_3)_2$ solution; 0.35457 is the equivalent amount of chlorine corresponding to 1 ml of 0.01 N $Hg(NO_3)_2$; and w is the amount of polymer (mg).

The chlorine percentage in polymer III was found to be 3.1%, which corresponds to 10.2 mol%.

The results of analyses of the functional groups (I–V) in the polystyrene are given in Table 2.

Table 2.

The results of chemical analyses of the functional groups

Compound		Bonded group	
No.	Effective part of functional group	mol%	m/n
I	$-\text{CO}-\overset{\text{O}}{\text{CH}}-\text{C}(\text{CH}_3)_2$	8.7	1:11
II	$-\text{CH}=\text{CH}-\text{CO}-\overset{\text{O}}{\text{CH}}-\text{C}(\text{CH}_3)_2$	14.8	1:7
III	$-\text{CH}_2-\overset{\text{O}}{\text{CH}}-\text{CH}-\text{CH}_2\text{Cl}$	10.8	1:9
IV	$-\text{CH}=\text{N}-\text{O}-\text{CH}_2-\overset{\text{O}}{\text{CH}}-\text{CH}_2$	4.5	1:22
V	$-\text{CO}-\text{CH}=\text{CH}-\text{COOH}$	20.0	1:5

m/n = the ratio of modified polystyrene to unmodified polystyrene.

2.3. Determination of adhesion capability and corrosion resistance

2.3.1. Percentage of coating failure. For the determination of the adhesion capability of the polyfunctional polystyrene to metal (steel of moderate carbon content with dimensions $70 \times 100 \times 1$ mm), a solution of each polymer was prepared in 10% toluene and deposited as a layer (120–140 μm) over the metal. This material was first dried in open air and then in an oven at 50°C . The percentage of adhesion capability was determined by the 'lattice notch' method [17].

According to the 'lattice notch method', a thin polymer layer (120–140 μm) is formed on the metal surface and the polymer layer is divided into small squares (2×2 mm) by a razor blade. Insulating tape (10–100 mm) is stuck 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 % adhesion is calculated from the number of small squares still remaining on the metal surface.

2.3.2. Corrosion resistance. Thin polymer films (120–140 μm) were formed over metal (plates of steel of moderate carbon content with dimensions $70 \times 150 \times 1$ mm) from the prepared polymer solution and were subjected to 10% NaOH, 10% HCl, 3% NaCl, pure water, and open air for 7 days. Then the plates (metals covered with polymer) were removed from these environments and the amount of decomposition observed by the naked eye was taken as a measure of the corrosion resistance.

2.3.3. Percentage of absorbed water. In addition, the percentage of water absorption was determined by exposing samples of the polymer to water at 20°C for 24 h and then removing the sample from the water and weighing the polymer. The sample was then dried over a desiccant in vacuum at 50°C and weighed. The difference between the wet and dry weights gives the amount of water absorption [14].

The adhesion and corrosion resistance results are given in Table 3.

Table 3.

Effects of the functional groups on the adhesion capability and corrosion resistance of functional polystyrenes

Functional group	Adhesion capability (%)	Corrosion resistance					Water absorption (%)
		3% NaCl	10% NaOH	10% HCl	Pure water	Air	
I	63	–	+	+	+	+	1.5
II	84	++	++	++	++	++	0.7
III	74	±	+	+	+	+	1.0
IV	50	+	+	+	+	+	1.3
V	98	++	++	++	++	++	0.2
Polystyrene	2	+	++	++	++	++	0.01

– = No resistance; ± = little resistance; + = medium resistance; ++ = high resistance.

3. RESULTS AND DISCUSSION

In our earlier work [4–9], the synthesis of polystyrenes with functional groups such as epoxy, carboxyl, and olefinic hydrocarbons was carried out and it was shown that these groups were responsible for polymer adhesion and corrosion resistance. In this study, the relationship between the structure, the nature, and the quantity of synthesized functional polystyrenes (I–V) (Table 2) and the polymer adhesion capability and corrosion resistance of these polymers were investigated. The bonding of functional compounds (I–V) to polystyrene are shown in Schemes I and II. The bonding of compounds I–IV was obtained in the presence of a radical initiator, while compound V was obtained in presence of a cationic catalyst. The results of analysis of the bonded functional groups to polystyrene are given in Table 2. The quantity of bonded functional groups (I, II, III, and IV) to the aliphatic ring of polystyrenes in the presence of a radical initiator is about 4.4–16.0 mol%, the m/n ratios are 1 : 7 (II), 1 : 9 (III), 1 : 11 (I), and 1 : 22 (IV) (Table 2). It can be seen from Table 2 that a more bonded group was obtained with compound II (14.8 mol%) and a less bonded group was observed with compound IV (4.5 mol%). The most bonding, 20 mol%, was found in the chemical modification with maleic anhydride of polystyrenes in the presence of a cationic catalyst ($\text{BF}_3 \cdot \text{OEt}_2$). In this reaction, the quantity of carboxyl group bonded to the aromatic rings of polystyrenes is 20 mol%. In other words, the ratio of the contents of unmaleated PS (n) and maleated PS (m) units (n/m) was found to be 5 : 1 (Scheme II).

IR spectra of the synthesized functional polystyrenes were obtained on a Py-Unicam SP-1025 spectrophotometer. The characteristic peaks of the functional groups were observed: $-\text{COOH}$ group at 1720 cm^{-1} , epoxy group at 940 and 1250 cm^{-1} , and an ethylenic double bond at 1630 cm^{-1} . These characteristic peaks clearly show which functional group was bonded to the polystyrenes.

The results of the adhesion capabilities of the functional polystyrenes (I–V) are given in Table 3. It is clearly seen from Table 3 that the adhesion capability of polystyrene was greatly increased from 2% to 50–98% by the anchoring of functional compounds (I–IV). When the adhesion capabilities of the functional polystyrenes are compared, the highest adhesion capability (98% and 84%) is obtained with compounds V and II, and the lowest adhesion capability (50%) is observed with compound IV. The higher adhesion capability of compounds V and II can be explained by the presence of olefinic ($-\text{CH}=\text{CH}-$) and carboxyl ($-\text{COOH}$) groups. The interaction of these groups with steel is very strong.

The corrosion resistance properties of the functional polystyrenes (I–V) were examined with NaCl, NaOH, and HCl solutions in deionized water, and air, and the results are also shown in Table 3. It is seen from Table 3 that functionalized polystyrenes II and V show a higher corrosion resistance as well as having higher adhesion properties. The unfunctionalized polystyrene shows less adhesion in spite of having a higher corrosion resistance. This disadvantage was solved by the functionalization process.

The water absorption capability of these polymers was determined at 20°C for 24 h and the data are given in Table 3. The lowest water absorption capability of the functionalized polystyrenes was observed with V (0.2%) and II (0.7%). The water

absorption capability of unfunctionalized polystyrene is 0.01%. The higher water absorption capability of functional polystyrenes may be explained in terms of the interaction of functional groups with water molecules.

It can be seen from Tables 2 and 3 that both the adhesion capability and the corrosion resistance depend on the nature and quantity of functional groups.

4. CONCLUSION

In conclusion, the present work has demonstrated that the addition of functional groups to polystyrene increases its adhesion capability and corrosion resistance. Also polystyrenes with desired properties can be obtained by varying the nature and quantity of functional groups in the synthesis of polystyrenes.

REFERENCES

1. R. T. Swiger, *Polym. Preprints (Am. Chem. Soc.)* **17**, 504 (1976).
2. W. O. Kenyon and G. P. Wough, *J. Polym. Sci.* **32**, 83 (1958).
3. R. T. Swiger, *J. Polym. Sci.* **13**, 1554 (1975).
4. R. A. Kurbanova, A. V. Ragimov and K. A. Aslanov, *Lakokras. Mater.* No. 6, 19 (1979).
5. R. A. Kurbanova, D. N. Aliyev and A. V. Ragimov, *Lakokras. Mater.* No. 1, 51 (1980).
6. R. A. Kurbanova, A. A. Mehraliyev and T. M. Oruchova, *Lakokras. Mater.* No. 3, 34 (1981).
7. R. A. Kurbanova, T. M. Oruchova and A. A. Mehraliyev, *Lakokras. Mater.* No. 3, 53 (1985).
8. R. A. Kurbanova, A. V. Ragimov, S. F. Sadikov and M. M. Gurbanov, *Lakokras. Mater.* No. 1, 103 (1990).
9. A. M. Krohmalniy, I. I. Zin, J. M. Nagiyeva and R. A. Kurbanova, *Fiz.-Khim. Mekh. Polim. Mater.* No. 5, 114 (1990).
10. R. A. Kurbanova, R. Mirzaoglu, G. Akovalı, Z. M. O. Rzaev, I. Karatas and A. Okudan. *J. Appl. Polym. Sci.* **59**, 235 (1996).
11. N. Mitsuaki and A. Masyasu, *J. Chem. Soc. Jpn* **70**, 1432 (1970).
12. S. T. Ahmedov, S. B. Kurbanov, L. M. Gulahmedov and G. S. Kurbanova, *J. Org. Khim., USSR* **27**, 2479 (1986).
13. M. A. Ahmedov, S. I. Sadikzade and R. A. Kurbanova, *Dokl. Akad. Nauk Azerb. SSR* **37**, 46 (1981).
14. M. F. Sorokin and K. A. Lyalushka, *Praktikum po Khimii i Tekhnologii Plyonkoobrazuyushchikh Veshchestv*, pp. 178–202. Moscow (1971).
15. W. Schöniger, *Microchim. Acta* **5**, 869 (1956).
16. S. Yıldız, U. S. Vural and R. Kurbanova, *Macromol. Rep.* **A32**, 347 (1995).
17. *Lakokras. Mater., GOST 15140-78 Metod opredeleniya adhezii*. Moscow (1978).