Sulfonation of (Glycidyl Methacrylate) Chains Grafted Onto Nonwoven Polypropylene Fabric

Yuliya V. Bondar,[1,4] Hong Je Kim,[2] Yong Jin Lim[3]

[1]*Institute of Environmental Geochemistry, 03142 Kiev, Ukraine*
[2]*Korea Dyeing Technology Center, 404-7, Pyongri-6Dong, Seo-Gu, Daegu 703-834, Korea*
[3]*Department of Dyeing and Finishing, Kyungpook National University, Daegu, Korea*
[4]*School of Display and Chemical Engineering, Yeungnam University, 214-1 Dae-Dong, Kyoungsan, 712-749, South Korea*

ABSTRACT: Sulfonation of polyglycidyl methacrylate (PGMA) chains grafted onto nonwoven polypropylene fabric is investigated in detail. Sulfonation reaction consists in implantation of sulfonate groups via epoxy ring-opening of PGMA chains grafted onto nonwoven polypropylene fabric by reaction between the GMA-grafted sample and sodium hydrogensulfite in water–dimethylformamide solution. On the basis of analyses of IR spectra of the appropriate samples and data of backward titration, two simultaneous processes are demonstrated to take place during the sulfonation reaction. These processes are the implantation of sulfonate groups via opening of the GMA epoxy rings and hydrolysis of the GMA epoxy rings with α-glycol groups formation. The main peculiarities of the sulfonation reaction in depending on the GMA grafting degree are reported. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 3256–3260, 2007

Key words: polypropylene (PP); fibers; synthesis; electron beam irradiation; functionalization of polymers

INTRODUCTION

Radiation-induced graft polymerization is one the effective ways for imparting desirable properties to inert polymer substrate. Two approaches, including direct grafting of vinyl monomers already containing desirable functional groups and graft polymerization of precursor-monomer and its subsequent chemical modification to form required functional groups, are developed.

Owing to limited number of vinyl monomers with functional groups, the second approach turned out to be the most prospective one. Radiation-induced graft polymerization of epoxy-group containing monomer glycidyl methacrylate, as a precursor, and subsequent polymer-analogous reactions of epoxy groups allowed to obtain functionalized polymeric materials of a broad range of industrial and biomedical application.[1–7]

Significant progress of the second approach has been reached principally owing to comprehensive investigations of Japanese scientists.[8–16] However, despite numerous publications on this theme, mainly the same synthetic routes have been employed by the authors: a procedure of GMA graft polymerization, consisting in the electron beam irradiation with a total dose of 200 kGy and subsequent grafting in 10% (v/v) GMA–methanol solution at 313 K, and further functionalization of the GMA-grafted polymers by different reactants. Conversion efficiency of such reactions varied from 20 to 80% and the remaining epoxy groups have been converted (or not) to diol groups by reaction with $0.5M$ H_2SO_4.

The same three-stage approach has been employed for synthesis of the polymer adsorbents with strong-acid sulfonate groups: radiation-induced graft polymerization of GMA (1st stage), subsequent epoxy ring-opening with sodium sulfite in isopropyl alcohol–water solution(2nd stage),[3,16–18] and hydrolysis of the remaining epoxy rings in $0.5M$ H_2SO_4 (3rd stage). According to the obtained data[3] the conversion efficiency of GMA epoxy groups to sulfonate groups deceased from 60% to 40% with increasing GMA grafting degree from 20% to 250%.[3] However, no rational explanations of this phenomenon have been done by the authors.

This study is of special interest to study of some peculiarities of sulfonation reaction, namely the influence of the reaction time and the degree of GMA grafting onto epoxy group conversion efficiency. To gain a better understanding, the backfill titration method as well as IR spectroscopic analysis were employed.

MATERIALS AND METHODS

Materials

Commercial nonwoven polypropylene fabric (2 mm in thickness and 46 g/m² of density) obtained from
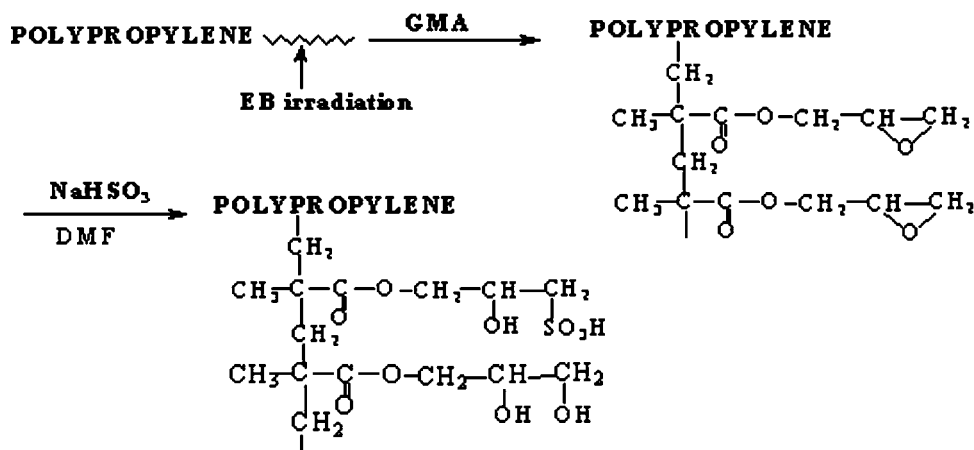
Figure 1 Principal scheme of sulfonation reaction of poly-GMA chains grafted onto PP fabric.

Saehan Industries Inc. (Korea), was used as the trunk polymer for grafting of poly-GMA chains. Reagent-grade sodium hydrogensulfite (NaHSO$_3$, Aldrich, Korea), and other chemicals of reagent grade or higher were used as received.

Modification of Poly-GMA graft chains

The implantation of the sulfonate groups was fulfilled by reacting the GMA-grafted samples with sodium hydrogensulfite in water–dimethylformamide solution (NaHSO$_3$/water/DMF = 1/7/3 (weight ratio)) at 70°C. Upon depletion of the prescribed time the modified sample was taken from the solution, washed down, and dried.

The principal scheme of the sulfonation reaction is shown in Figure 1.

The sulfonate group density ($S_{R\text{-SO3Na}}$, mmol/g) was determined by a titration experiment and gravimetrically, by weight gain:

$$S_{R-SO3Na} = \frac{W_2 - W_1}{W_2 \times M_{NaHSO3}} \times 1000 \qquad (1)$$

where, W_1 is the weight of GMA-grafted sample. W_2 is the weight of sulfonated sample in the Na-form. M_{NaHSO3} is the molecular weight of the NaHSO$_3$ group (taken as 104).

Conversion efficiency (C_E, %) of GMA epoxy groups to the sulfonate ones was determined as follows:

$$C_E = \frac{S_{R-SO3Na}}{S_{GMA}} \times 100 \qquad (2)$$

where, S_{GMA} is the GMA group density, mmol/g

FTIR analysis

To confirm the introduction of functional groups onto the PP backbone the IR spectra of modified samples were obtained from FTIR spectrometer (Perkin–Elmer, 1725).

RESULTS AND DISCUSSION

Modification of PGMA graft chains

A set of GMA-grafted polypropylene samples with a wide range of GMA- chain density, exhibited in Figure 2, have been preliminary synthesized with the purpose to investigate the sulfonation reaction peculiarities.[19]

To incorporate sulfonate groups onto the PP backbone through GMA epoxy ring-opening, the authors[17,18] used sodium sulfite in isopropyl alcohol–water solution (Na$_2$SO$_3$/isopropyl alcohol/water = 10/15/75 (weight ratio)). Once the reaction at 80°C for 24 h has been completed, the conversion of epoxy groups to sulfonate ones reached 60–80% and the remaining epoxy groups were converted to diol groups by reacting with 0.5M H$_2$SO$_4$ for 2 h at 80°C.
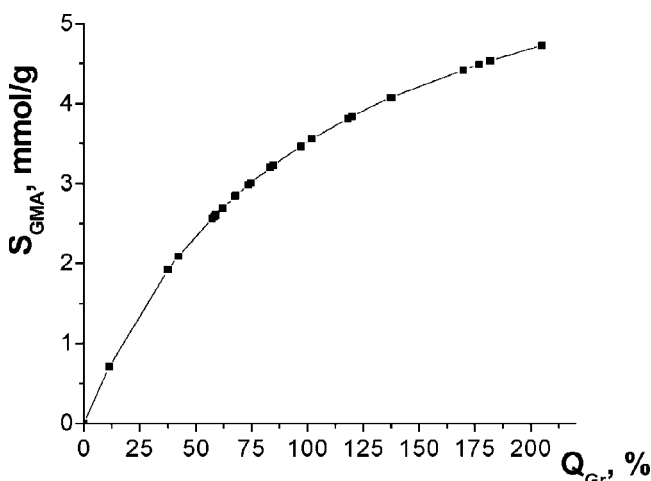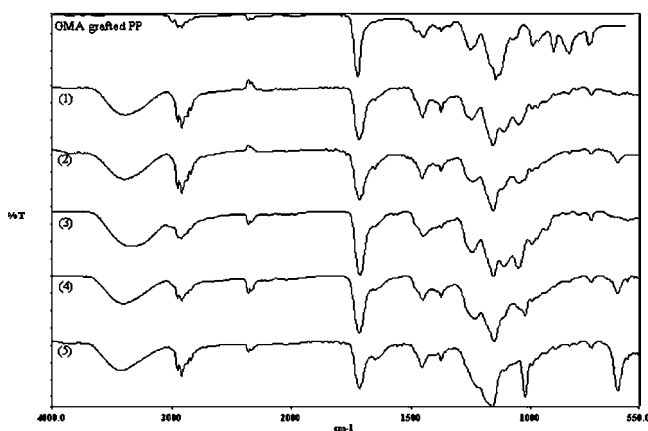

Figure 2 Properties of the GMA-grafted PP nonwoven fabric used for sulfonation experiments. S_{GMA}—GMA group density; C_{Gr}—GMA grafting degree.
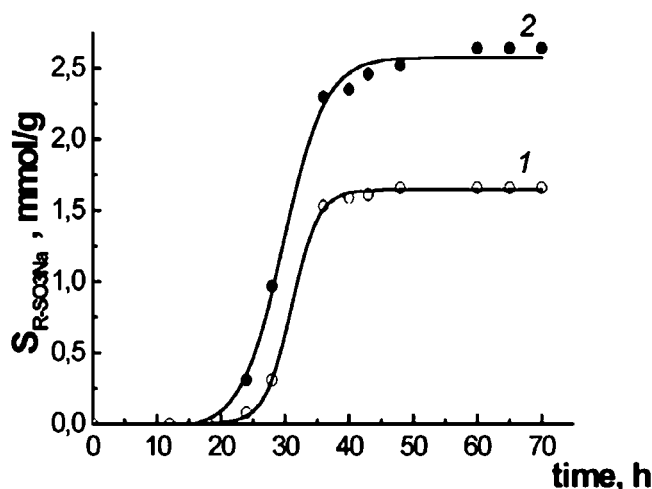
Figure 3 IR spectrum of GMA-grafted PP fabric and spectra of GMA-grafted PP samples modified in different NaHSO$_3$/organic solvent/water (10/30/70) solutions at 70°C during 70 h. Solvent (1) Ethanol, (2) Propanol, (3) N,N-Dimethylacetamide, (4) Dimethyl sulfoxide, (5) N,N-Dimethylformamide.

Figure 4 Curves of sulfonation reaction of GMA-grafted PP fabric at 70°C. 1: GMA grafting degree of 40%; 2: GMA grafting degree of 180%;

The first step of our study lay in a comprehensive investigation of the sulfonation process in different water–organic solutions. We used a rather concentrated (almost saturated) solution of NaHSO$_3$/organic solvent/water (10/30/70).

The Figure 3 shows five FTIR spectra of the PGMA-grafted samples (120%) after 70-h sulfonation reaction in different organic solvent–water solutions at 70°C. As is evident, we failed to introduce sulfonate groups in water–ethanol (1), water–N,N-dimethylacetamide (3) as well as water–methanol solutions, while spectra of the samples modified in water–prophanol (2), water–dimethyl sulfoxide (4), and N,N-dimethylformamide (5) solutions showed the presence of characteristic absorbent bands of the sulfonate groups (at 1150 cm^{-1}, 1030 cm^{-1}, 670 cm^{-1}). Water–dimethylformamide solution was chosen for the experimental work discussed herein as the most effective one for the sulfonation process.

The second step of our work comprehended detailed investigation of the sulfonation reaction kinetics. The kinetic curves of two samples with different GMA grafting degrees (40% (Curve 1) and 180% (Curve 2)) are shown in Figure 4. It illustrates the similar behavior of these curves as to presence of a long induction period before the implantation of sulfonate groups (about 20 h) and then their sharp rising till the "plateau" level. As is seen, the "plateau" level corresponds to maximum density of implanted sulfonate groups. Reaction time required for reaching the "plateau" level depends on the GMA grafting degree, for example, being 48 h for the sample with lower grafting degree and 60 h for the other one.

The next step of our investigation consisted in study of the relation between GMA grafting degree and value of sulfonate group density, as well as the conversion efficiency at the "plateau" level. To obtain the results exhibited in Figure 5 the reaction duration of 70 h was chosen, which allows all studied samples to reach "plateau" level. All calculations have been made according to the weight gain using formulas 1 and 2.

This figure shows that the sulfonate group density value at the "plateau" level (maximum possible value) rises proportionally to GMA grafting degree for the samples with a low value of GMA grafting, while for the samples in which the grafting degree exceeds 50%, appreciable reduction of growth rate is observed. Since the conversion efficiency reflects the part of epoxy groups transformed to sulfonate groups, the similar course might be expected also for
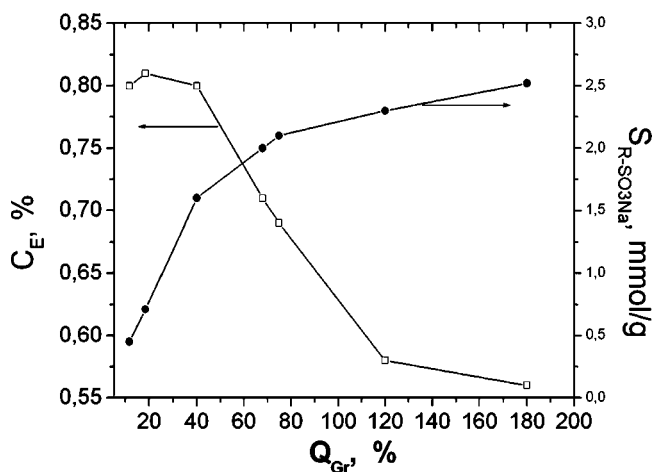
Figure 5 Relation between GMA grafting degree (Q_{Gr}) and both sulfonate group density (S_{RSO3Na}) and efficiency of "epoxy group–sulfonate group conversion" (C_E) at the "plateau" level of the corresponding sulfonation curves.
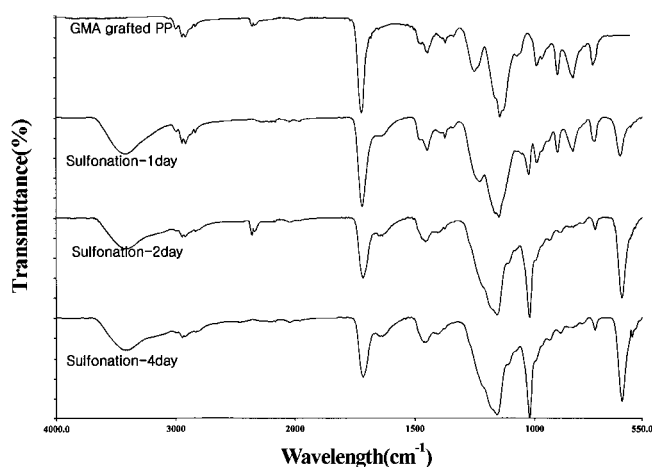
Figure 6 IR-spectra of the GMA-grafted PP fabric and modified GMA-grafted PP fabric (Q_{Gr} = 100%) after 24-h, 48-h, and 96-h sulfonation reaction.

the dependence of "the conversion efficiency–GMA grafting degree." However, it can be clearly seen from the same figure, that the C_E curve shows the highest value of 80% for the samples with low values of GMA grafting degree and it then decreases up to 55% with increasing of GMA grafting degree to 180%. The similar reverse correlation of C_E–GMA grafting degree has been shown in Figure 4 of the article,[3] however no explanation has been given by the authors.

The observed results can be explained from the several standpoints.

Firstly, it is possible to suppose that at a low degree of GMA grafting, the main part graft chains are formed on the surface of polymer matrix, whereas at a high degree of grafting the number of the graft chains in the depth increases. The epoxy groups of the surface PGMA chains are most accessible for the modification; however they may create some difficulties for the further modification of the inner epoxy groups. Thus, the sulfonation reaction should occur more easily when samples with a low degree of grafting are taken. In this case, the inner epoxy groups have to remain unopened and the adsorption bands of epoxy groups have to remain in the IR spectra of the sulfonated samples

Secondly, it is possible to suppose that the densely located PGMA-chains may create electrostatic (steric) hindrances for the sulfonate groups implanted into the neighbor PGMA chains. Thus the C_E value has to decrease with the rising of GMA grafting degree at the case of the samples with a high value of GMA grafting.

To understand the sulfonation process more deeply, the FTIR spectra of the GMA-grafted sample as well as some sulfonated samples picked at different stages of the sulfonation reaction have been investigated.

FTIR analysis

Figure 6 illustrates FTIR spectra of the GMA-grafted PP fabric (grafting degree = 100%) after 24 h, 48 h, and 96 h of sulfonation reaction. The first IR spectrum relates to GMA-grafted fabric, where the absorption bands can be seen at 1730, 1300–1100 cm^{-1}, arising from —C=O stretching, C—O—C stretching as well as three bands at 1260 cm^{-1}, 950–815 cm^{-1}, and 760 cm^{-1} attributed to epoxy ring. The second spectrum belongs to the sample, which has not reached the "plateau" level (after 24-h sulfonation reaction). One can see the adsorption bands of epoxy rings, which have decreased in intensity compared with the above spectrum, and absorption bands of sulfonate groups at 1150 cm^{-1}, 1030 cm^{-1}, 670 cm^{-1} of rather small intensity, as well as absorption band at 3400 due to the —OH stretching. The third IR spectrum belongs to the sample that has reached the "plateau" level (after 48-h sulfonation reaction). It can be seen that adsorption bands of epoxy rings at 1260 cm^{-1} and 950–815 cm^{-1} have disappeared, while the band at 760 cm^{-1} of small intensity was kept. (We can explain this by the fact that some GMA monomers in negligible quantity may take part in crosslinking structure formation at grafting reaction[20]). The intensity of absorption bands of sulfonate groups at 1150 cm^{-1}, 1030 cm^{-1}, 670 cm^{-1} has increased as compared with the second spectrum. No further alterations were observed in the last spectrum (after 96-h sulfonation reaction).

Thus, the analysis of the IR spectra of the samples of different stages of sulfonation reaction allow us to conclude that during the sulfonation reaction two processes occur—one of them is implantation of the
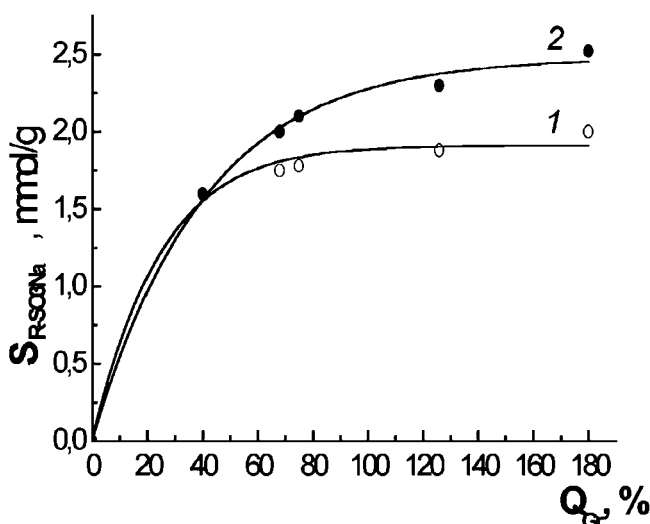
Figure 7 Comparison between results of backward titration experiments (Curve 1) and gravimetrical calculations (Curve 2).

sulfonate groups via ring-opening of the GMA epoxy groups, and the other one is hydrolysis of the epoxy-rings with the formation of the α-glycol groups. The sulfonation process is completed at the ''plateau'' level by the whole conversion of the epoxy-rings. Samples that have not reached ''plateau'' level (spectrum after 1-day sulfonation) contain both sulfonate and hydroxyl groups as well as unopened epoxy-rings, and so they exhibit hydrophobic properties. Samples that are completely sulfonated at the ''plateau'' level (spectra after 2-days and 4-days sulfonation) contain only sulfonate and hydroxyl groups, and they gain excellent hydrophilic properties.

The results of backward titration experiment gave us the additional evidence in the favor of such schema. It is generally admitted that the results of a backward titration experiment reflect the actual number of incorporated sulfonate groups. We may suppose that the number of sulfonate groups, determined by the backward titration, should coincide with the number calculated by the weight gain; however, in the case of epoxy group hydrolysis, the latter value has to be lower than the former one. As it follows from Figure 7, the actual number of the incorporated sulfonate groups (Curve 1) is rather close to that, calculated by the weight gain (Curve 2), for the samples with a low degree of GMA grafting, but it is systematically lower for the samples with a high degree of GMA grafting. This difference rises with the increase of the GMA grafting degree. Such situation is possible just in the case of GMA epoxy rings hydrolysis. According to the experimental calculations, the value of C_E reaches 48–52% for the samples with high GMA grafting degree. The reverse correlation between C_E and GMA grafting degree, as well as some peculiarities of sulfonation process intrinsic to the samples with high values of GMA grafting degree (two simultaneous processes) testify that main features of the sulfonation reaction are determined by the influence of electrostatic (steric) factors.

CONCLUSIONS

Sulfonation of poly-GMA chains grafted onto nonwoven polypropylene fabric has been investigated in detail. Sulfonation reaction consisted in the implantation of sulfonate groups by reacting the epoxy rings of GMA graft chains with sodium hydrogen-sulfite at 70°C in water–dimethylformamide solution, which was chosen as the most effective solution for the sulfonation process.

On the basis of comparing the kinetic curves of sulfonation reaction with the IR spectra of the appropriate samples, as well as data of backward titration, it was shown that during the sulfonation reaction via epoxy ring-opening of PGMA graft chains, two simultaneous processes, namely incorporation of sulfonate groups and hydrolysis of the epoxy rings with formation of α-glycol groups, take place. The sulfonation process is completed at the ''plateau'' level by the whole conversion of the epoxy ring with formation of hydrophilic fabric containing both sulfonate and hydroxyl groups. Samples, which have not rich ''plateau'' level contain both sulfonate and hydroxyl groups, as well as unopened epoxy rings and they exhibit hydrophobic properties. Obtained results testify that the main features of sulfonation reaction are determined by electrostatic (steric) factor.

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