Electrically conducting ionomers

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The preparation and physical properties of conducting ionomers have been investigated. A two-step process was used to prepare a polyethylene-based film grafted with poly(styrenesulphonic acid). A pre-irradiation technique was applied to carry out the grafting of polystyrene on various polyethylene films. The grafted films were then sulphonated to yield the ionomer. Chemical polymerization of pyrrole into the ionomer was carried out in aqueous solutions and caused a four orders of magnitude increase in the conductivity of the film. Better conductivities were obtained when 1,1,2-trichloroethane was used as the chain transfer reagent during grafting of polyethylene with styrene. The conductivity, structure, composition and mechanical properties of the electrically conducting ionomers were evaluated. Films having high conductivities and improved mechanical properties were obtained.

(Keywords: conducting polymers; electrical conduction; ionomers; synthesis, characterization; polyethylene; grafting)

INTRODUCTION

'Inherently conducting polymers' are currently being investigated world-wide owing to their practical and theoretical significance[1]. They are characterized by high specific conductivity and controllable conductivity. These properties have spawned a broad spectrum of potential applications based on the conducting and insulating states of these materials and their ability to be transferred reversibly between them. Good mechanical properties and stability as well as processability are essential for practical purposes. Conducting polymers are usually brittle materials and therefore much effort is currently invested in improving their mechanical properties.

Several approaches have been applied to strengthen conducting polymers. For example, the use of a bulky dopant that also plays the role of plasticizers[2] or *in situ* electrochemical formation of plasticizer during polymerization[3] were recently reported. Implanting a conducting polymer in an insulating host matrix is another method to improve their mechanical properties[4,5]. The new composite is expected to gain both conductivity and good mechanical properties from its two components, but with some sacrifice of these qualities. This method is, however, limited by the requirement that the different species, namely neutral monomer, charged dopant and sometimes an oxidation agent, would diffuse inside the film. It is rare that a film will be permeable to species that exhibit a noticeable difference in hydrophilicity[6]. This obstacle can be partly avoided by the use of insulating films, in which the ionic dopant is already bound to the polymer backbone, viz. *ionomers*. The advantages of the ionomer–conducting polymer composite are that composite preparation is no longer dependent on the diffusion rate of dopant in the film, and that the doping–undoping kinetics are enhanced due to the movement of small counterions in the course of this process.

Chemical methods for oxidative polymerization of pyrrole have been known for many years[7]. Ferric chloride has been used extensively in the last few years to prepare polypyrrole (PPy)[8]. Although chemical polymerization usually leads to powders, conducting films can be obtained by allowing oxidation to take place in an insulating film[9] or on its surface[10].

Electrically conducting ionomers were prepared either by the use of polyelectrolyte in an electrochemical polymerization of pyrrole[11] or by the electro-polymerization of pyrrole into a Nafion-modified electrode[12]. In these cases the $-SO_3^-$ group in the film played the role of the dopant in the formed PPy.

In this paper a novel approach to prepare electrically conducting polymers, which combines a radiation-induced grafting to prepare ionomers and a chemical polymerization of pyrrole inside the ionomer, is described. Polyethylene (PE) grafted with poly(styrenesulphonic acid) (PSSA) was chosen as the ionomer. The polypyrrole was chemically bound to the host matrix on its surface and in the *bulk*, and hence the mechanical durability of the film increases because the material is less susceptible to external mechanical forces. The electrically conducting ionomers were characterized in terms of their conductivity, composition and mechanical properties.

EXPERIMENTAL

Materials

High-density polyethylene (HDPE, 20 μm, from Dow Chemicals, Belgium) was used as received. Low-density PE(LDPE), linear low-density PE(LLDPE), medium-density PE(MDPE), crosslinked PE(CL-PE) and poly(ethylene-*co*-butyl acrylate (PE-BA; 7% BA) were donated by CLP, Kibbutz Negba, Israel. Styrene, CP grade, was either distilled under reduced pressure and used immediately thereafter, or used without purification. In the latter case it contained 20 ppm of

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4-t-butylcatechol as inhibitor. Pyrrole (Aldrich Chemical Co.) was distilled under reduced pressure and kept at 4°C in the dark. Ferric and ferrous chloride hexahydrate (Fisher) and 1,1,2-trichloroethane (TCE, Aldrich Chemical Co.) were used without further purification. Triply distilled water was used in all the experiments.

Grafting procedure

Grafting of PE was carried out using a pre-irradiation method. A commercial high-voltage electron-beam accelerator, model EPS-550-IND, supplying a maximum current of 20 mA at 250–520 MeV and scan width of 43 cm, was used. The PE samples were exposed to electron-beam irradiation under an air atmosphere by means of a conveyer travelling at the rate of $10\,\mathrm{m\,min^{-1}}$. The irradiation was carried out at a dose rate of ~1 Mrad/pass. The films were then immersed in a styrene solution, presaturated with nitrogen, and held at 70°C in an inert atmosphere for a certain period of time. The films were then washed thoroughly with acetone and dried to constant weight. The grafted film is denoted PE/PS. The percentage of grafting, $\%G$, was calculated as follows:

$$\%G = \frac{(W_g - W_i)}{W_i} \times 100 \tag{1}$$

where W_i and W_g represent the weights of the initial and grafted films, respectively.

Sulphonation of PE/PS films

The sulphonation was carried out in 98% sulphuric acid (AR grade). Several sheets of PE/PS, separated by spacers made of paper or polypropylene web, were placed in a wide tube and the reaction proceeded at 90°C for a certain period of time. The films were then consecutively washed in solutions of 70% and 30% sulphuric acid, and finally rinsed thoroughly with water and dried to constant weight. The loading of the films (number of meq/g) and the percentage of sulphonation, $\%S$, were calculated as follows. The practical loading of film, $\mathrm{meq^p}$, was calculated by:

$$\mathrm{meq^p} = \frac{W_s - W_g}{0.08 W_s} \tag{2}$$

where W_s is the weight of the film after sulphonation and 0.08 is the equivalent weight of the SO_3 moiety. The maximal theoretical loading, $\mathrm{meq^t}$, was calculated according to:

$$\mathrm{meq^t} = \frac{\%G}{(\%G \times 0.184) + 10.4} \tag{3}$$

where 0.184 and 0.104 are the equivalent weights of styrenesulphonic acid and styrene, respectively, $\%S$ is the ratio between the practical and theoretical loadings:

$$\%S = \frac{\mathrm{meq^p}}{\mathrm{meq^t}} \times 100 \tag{4}$$

Polymerization of pyrrole into PE/PSSA

Films of $2 \times 2\,\mathrm{cm^2}$ PE/PSSA were immersed in a solution containing a mixture of iron(III) and iron(II) chloride. The ratio between the two iron species determined the initial potential of the solution, which was measured on a Pt electrode vs. saturated calomel electrode (SCE). The polymerization was carried out in the dark at 2±1°C. The solution was stirred for 30 min before pyrrole was injected into the reaction mixture. The films darkened shortly after the addition of pyrrole and a black precipitate ('pyrrole black') immediately appeared in the solution. The PE/PSSA/PPy films were removed from the reaction vessel and rinsed thoroughly with water. Post-treatment was carried out before their conductivity was measured using the four-probe Van der Pauw technique[13]. The film thickness was measured with a Digimatic bench micrometer (Mitutoyo, Japan) having resolution of 1 μm.

Stretching of films

The tensile properties of the conducting film were tested using ASTM D638-71a. Dog-bone specimens were cut from a large sheet of the chemically prepared PPy film. Stress–strain curves were obtained using an Instron D1206-1. The experiments were carried out at room temperature. The stretching rate was $1\,\mathrm{mm\,min^{-1}}$.

SEM and surface analysis

Scanning electron microscopy (SEM) and energy dispersive analysis X-ray (EDAX) experiments were carried out using a JEOL JXA-8600 superprobe. EDS (energy dispersive spectrometry) and WDS (wavelength dispersive spectrometry) techniques with a defocused beam (20 μm) were employed for the surface analysis of the films. A conducting polymer with known composition was used as internal reference for the quantitative determination of the element content.

RESULTS AND DISCUSSION

A major part of our work was devoted to radiation processing. Therefore, the preparation of the ionomers is described in the first part of this section. In the second part of this section the results concerning the conductivity of the films are presented. Because a repetitive methodology was used, the second part is divided into subdivisions due to a modification in the preparation of the ionomer. The characterization of the conducting films is presented in the third section.

Formation of ionomers

Radiation-induced grafting has been used frequently to impart new properties, such as hydrophilicity, to given polymers[14]. Exposure of a polymer to electron-beam irradiation causes the generation of reactive radicals in the polymer, which can either react with a monomer, initiating grafting, or form internal bonds, namely crosslinking. Grafting and crosslinking are competitive processes, which depend upon the concentration of the radicals and the crystallinity of the polymer. Generally, pre-irradiation and mutual grafting are frequently used. In the pre-irradiation technique the film is irradiated and then transferred to a monomer solution, while in the mutual process the film is irradiated in the presence of a monomer. In the present work only the pre-irradiation technique was used.

In the first set of experiments several types of PE were screened while commercial and distilled styrene were used as the monomer in the grafting process. The effect of radiation dose and time on the percentage of grafting ($\%G$) and sulphonation ($\%S$) are summarized in *Table 1*. It can be seen that *%G decreased with the decrease in the density of the PE*. When high-, medium- and

Table 1 The effect of radiation dose and time on the percentage of grafting (%G) and sulphonation of PE[a]

No.	Type of PE film and monomer	Dose of radiation[b] (Mrad)	Grafting time (min)	Grafting percentage, %G	Sulphonation[c] Time (min)	%S
1	HDPE[d]	1	20	20.1	70	86.5
2		3	20	62.2	120 150	99.6 141.4
3		5	20	83.1	120	92.7
4		1	30	24.1	75	97.0
5		3	30	67.9	120	107.5
6		5	30	90.4	120	93.2
7	HDPE[e]	1	30	23.0	80	101.6
8		1	60	29.9		
9		1	90	30.1	80	110.7
10		3	30	45.2		
11		5	5	36.7	80	121.6
12		5	15	51.3	85	134.0
13		5	30	61.3	100	136.3
14	MDPE[e]	3	30	39.7	80 100	42.7 70.9
15	LDPE[e]	3	30	13.6	80	71.9
16	CL-PE[e,f]	3	30	14.2	70	7.9
17	PE-BA[e,g]	3	30	0.7		

[a] The grafting was carried out under nitrogen atmosphere at 70°C

[b] The radiation was carried out using 520 kV and current of 4 mA. Under this condition a pass is equivalent to 1 Mrad

[c] The sulphonation was carried out at 90°C in 97% sulphuric acid

[d] The monomer was distilled styrene with 1% divinylbenzene as crosslinking agent

[e] The monomer was commercial (undistilled) styrene containing 20 ppm of 4-t-butylcatechol as inhibitor

[f] Crossedlinked PE was used

[g] Poly(ethylene-*co*-butylacrylate) with 7% BA was used

low-density PE were grafted with commercial styrene, %G values of 45%, 39.7% and 13.6% were obtained, respectively (entries 10, 13 and 14). Crosslinked PE (entry 16) yielded low %G similar to the LDPE (entry 15), whereas PE containing 7% of butyl acrylate gave almost no grafting (entry 17).

The density of PE, which reflects its crystallinity, has a large impact on grafting. The more rigid structure reduces the probability of two radicals forming an interior bond, and therefore grafting of the monomer is preferable and higher %G values are obtained. The small content of plasticizing butyl acrylate in PE films increased the flexibility of the polymeric chains. Consequently, the likelihood for internal crosslinking increased and extremely low %G values were obtained. The low %G obtained when crosslinked PE film was grafted is attributed to the slow diffusion of the monomer in the film.

The radiation dose had a remarkable effect on the %G. Higher radiation dose brought about higher %G. For example, %G of 24%, 68% and 90% were obtained when HDPE was exposed to radiation doses of 1, 3 and 5 Mrad, respectively. It will be shown below that this phenomenon is limited. The grafting time had a small effect on the %G, especially at low radiation doses, as is seen by comparing entries 1–4 and 7–9.

The monomer composition was important in determination of %G. Distilled monomer, containing divinylbenzene (DVB) as a crosslinking agent, gave higher %G in comparison to commercial undistilled monomer, which contained 4-t-butylcatechol as inhibitor. For example, HDPE yielded %G of 90.4% and 61.3% when distilled and commercial styrene were used, respectively (entries 6 and 12). It is our experience that DVB has a negligible effect on grafting. Thus, it is concluded that the *inhibitor* can account for the small %G when commercial monomer was used. Control experiments, which were carried out using distilled styrene containing 4-t-butylcatechol, also gave a lower level of grafting. The inhibitor slows the polymerization of styrene inside the film, as it inhibits the formation of homopolymer in the solution.

Sulphonation of PE films was carried out in concentrated sulphuric acid. It was found that only grafted films could be sulphonated throughout the film. No weight increase nor changes in the colour of the films were observed when ungrafted HDPE or LDPE were sulphonated. The hydrophobicity of PE prevents the diffusion of sulphuric acid into the film. The presence of grafted polystyrene in the PE provides active sites, which are more susceptible to reaction with sulphuric acid. Moreover, the insertion of polystyrene in PE modified its structure, as is evident from the change in the film dimensions in the course of the grafting process. The change in the film structure might enhance its permeability towards sulphuric acid. Time and temperature played an important role in the determination of %S (entries 2 and 13).

An increase in the three dimensions of the films was obtained in the course of the grafting and sulphonation processes. In *Figure 1* the increase in the film area is plotted vs. %G. The results shown in *Figure 1* indicate that the effect of grafting on the structure was larger than that of sulphonation. The changes in the three dimensions of the films were similar. Large films of PE/PS and PE/PSSA were cut into equal small pieces, which were weighed. A small standard deviation for the weight was obtained. These results indicate a uniform macroscopic distribution of the graft in the film. Dyed cross-sections of the PE/PSSA film (slices of 5 μm) were inspected under a microscope. The result implies penetration of the styrenesulphonic acid through the whole thickness of the PE film.

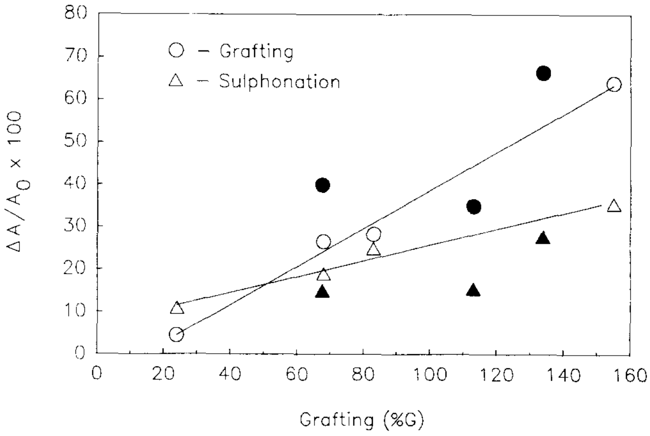

Figure 1 Variation of the increase of the PE film area (ΔA) with the grafting percentage. ΔA is normalized with respect to the film area before the grafting or sulphonation (A_0). In all the experiments %S was 110±5%. The filled symbols represent grafting in the presence of 0.5% TCE

Preparation of conducting ionomers

Preparation of PE/PSSA/PPy. The polymerization of pyrrole in the PE/PSSA film was usually carried out in aqueous solution containing 1 M ferric chloride, 0.4 M pyrrole and a small amount of ferrous chloride at ~0°C. The reaction mixture was stirred while the films were immersed in the solution. The ratio of iron(III)/iron(II) reflected the initial oxidation potential of the system, which was measured before the addition of pyrrole. In some experiments the procedure was slightly modified as the films were separately tangled on a mechanically stirred frame. As soon as PE/PSSA films were placed in the reaction solution the colour of the films changed to red. Ion exchange occurred between iron(III) ions in the solution and protons of the sulphonic acid of the ionomer. The oxidation agent prompted the polymerization of pyrrole inside the film, yielding a conducting ionomer. The high take-in tendency of iron(III) ions maintained a high concentration of this oxidation agent in the film during the reaction with pyrrole, and thus a high conductivity might be expected. The surface resistivity of the PE/PSSA/PPy, prepared from distilled styrene, varied in the range of 400–3800 Ω/□. Homogeneous appearances were observed when cross-sections of PE/PSSA/PPy were enlarged under a microscope.

Several conclusions could be drawn from the dependence of the film surface resistivity on the ionomer composition and the reaction conditions: (1) Pyrrole did not polymerize in ungrafted PE films, but thin coatings of PPy were obtained on the surface of the PE/PS. The PPy did not adhere well to this material and could be peeled off by a gentle scraping of the film. (2) The surface resistivity of the films decreased with reaction time. A constant minimal resistivity was achieved after a certain period of time, depending on the concentration of the reactants and the stirring of the reaction mixture. (3) The degree of grafting and the extent of sulphonation affected the surface resistivity of the films. For example, when %*G* was below ~100% high surface resistivity was obtained when %*S* was greater than ~120%. High values of %*S*, namely high degree of sulphonation per benzene ring, might have brought about localization of the charge carrier in the resulting PPy chain, which caused an increase in its resistivity[15]. (4) The lowest surface resistivity was obtained when the initial potential at the solution was ~540 mV (vs. SCE). For example, surface resistivities of 2500, 370 and 800 Ω/□ were achieved when the initial potentials were 517, 538 and 630 mV, respectively (%$G = 80\%$, %$S = 93\%$). The potential decreases during the course of the reaction and after 2 h of reaction the potential was 360 mV. It was recently reported that high-conductivity PPy powder was obtained when a constant potential of 500 mV (vs. SCE) was kept during the polymerization of pyrrole[16]. (5) The use of high concentration of reactants (1 M and 0.4 M of iron(III) and pyrrole, respectively) caused instantaneous formation of pyrrole black powder in the solution upon mixing of the reactants. An order of magnitude decrease in the concentration of these reactants eliminated the formation of PPy powder in the solution and the colour of the reaction solution remained unchanged after 7 h. Under these conditions the surface resistivity of HDPE/PSSA/PPy (%$G = 26.6\%$; %$S = 89.7\%$; 1.56 meq/g) was 2430 Ω/□ after 7 h of reaction. For comparison a similar film (%$G = 19.3\%$; %$S = 86.5$; 1.2 meq/g) exhibited similar surface resistivity of 2098 Ω/□ after 2 h when a high concentration of the reactants was used. (6) Post-polymerization treatment of the films improved their conductivity; soaking the films in monovalent electrolyte followed by extraction with water improved the conductivity of the films in the order HCl > KCl > NaCl.

When various PE films were grafted using commercial *undistilled* styrene, a small content of PS was obtained owing to the existence of inhibitor at a 20 ppm level (see above). Nevertheless, *improved conductivities* were achieved; the surface resistivity was ≈270 Ω/□.

In spite of the low %*G*, and thus low loading level of films that had been grafted with undistilled styrene, low surface resistivity of the ionomers was obtained. It was suggested that the inhibitor in the monomer solution should account for the low %*G* and low surface resistivity of the film. The inhibitor not only suppressed polymerization of styrene inside the film, but caused the formation of *short polystyrene chains which were homogeneously imparted in the film*. It was assumed that the improved conductivity ensued from the difference in the length of the grafted chains.

Preparation of improved *conducting ionomers.* In order to establish the importance of short polystyrene chains in the films and to gain some control on the process, a known *chain transfer reagent*, 1,1,2-trichloroethane (TCE), was added to the freshly distilled styrene in the grafting step. Owing to the absence of inhibitor in the reaction mixture high %*G* could be obtained, while the TCE caused the formation of short chains. The surface resistivity as well as the characteristic parameters of the modified process are summarized in *Table 2*. The effect of radiation dose and grafting time on %*G* in the absence of TCE is shown in entries 1–4. At higher radiation dose, short times were required to obtain similar %*G* (e.g. when 1 and 5 Mrad were used the time decreased by a factor of 18; see entries 2 and 3). At the same radiation dose, longer grafting times yielded higher %*G*, but the increase of %*G* was not proportional to the increase in time (see entries 3 and 4).

The effect of TCE and inhibitor (4-t-butylcatechol) is seen in entries 4–6. When the inhibitor was removed by distillation of the styrene, %*G* increased from 62% to 80% in spite of the shorter reaction time. Upon addition of TCE, without changing the time, an increase of %*G* was obtained (108%). The increase in %*G* when TCE was used resulted in a larger area increase in the grafting process, whereas a small effect was observed in the sulphonation (*Figure 1*, filled symbols).

The effect of TCE on the surface resistivity of the films is shown in entries 9 and 10. Although similar films were used, a large difference in the surface resistivity was obtained. Surface resistivity of 56 Ω/□ was obtained when TCE was used. A two-fold increase in the surface conductivity was observed when TCE was not used in the grafting step. The lower resistivity was attributed to the role of TCE as a chain transfer reagent.

An increase of the TCE concentration in the styrene had practically no effect on %*G* and the surface resistivity of the films (entries 6–8). Therefore a concentration of 0.5% was used as standard.

The effect of the radiation dose on the properties and performance of the films was investigated. When %*G* was plotted vs. the radiation dose, a curve that went through a maximum was obtained (*Figure 2*). The highest %*G* was obtained between 10 and 15 Mrad. In the grafting

Table 2 The effect of experimental conditions on the composition and surface resistivity of the films[a]

No.	Radiation dose (Mrad)	TCE[b] (%)	%G	Grafting time (min)	%S	Film loading (meq/g)	Surface resistivity[c] (Ω/□)	Remarks
1	1	–	30.8	90	67.5	1.29	281	d
2	1	–	29.4	90	110.7	2.06	242	d,e
3	5	–	36.5	5	121.6	2.61	250	d
4	5	–	61.8	30	136.3	3.87	–	d,f
5	5	–	80.4	20	92.3	2.96	320	g
6	5	0.5	107.7	20	74.1	2.61	146	g
7	5	1.0	112.9	20	76.9	2.79	165	g
8	5	2.0	99.8	20	76.9	2.68	162	g
9	10	–	155.2	20	113.2	4.51	138	g
10	10	0.5	144.4	20	118.6	4.63	56	g
11	15	0.5	145.7	20	116.4	4.56	96	g
12	20	0.5	106.7	20	71.5	2.53	190	g
13	30	0.5	89.9	20	99.3	3.36	162	g
14	50	0.5	72.8	20	115.3	3.53	150	g
15	50	–	50.1	20	137.2	3.50	227	g
16	10	0.5	191.5	60	119.0	5.0	27	g
17	10	0.5	214.3	120	121.8	5.24	24	g
18	10	0.5	191.5	60	119.0	5.0	58	h
19	10	0.5	214.3	120	121.8	5.24	51	h

[a] The polymerization of pyrrole was carried out in mechanically stirred unbuffered aqueous solution containing 1.0 M $FeCl_3$, 0.014 M $FeCl_2$ and 0.4 M pyrrole. The initial potential was 540 mV vs. SCE. Reaction temperature was 2±2°C. Post-polymerization treatment included 5 h soaking in 1 M HCl and then drying under a stream of air

[b] Percentage by volume

[c] The surface resistivity was measured on a round piece of film ($d=1.1$ cm) using the four-probe Van der Pauw method

[d] Commercial styrene was used in the grafting reaction. It included 20 ppm of 4-t-butylcatechol as inhibitor

[e] Longer sulphonation duration was used

[f] Polymerization of pyrrole was not carried out on this film

[g] Distilled styrene was used

[h] The polymerization of pyrrole was carried out in methanol

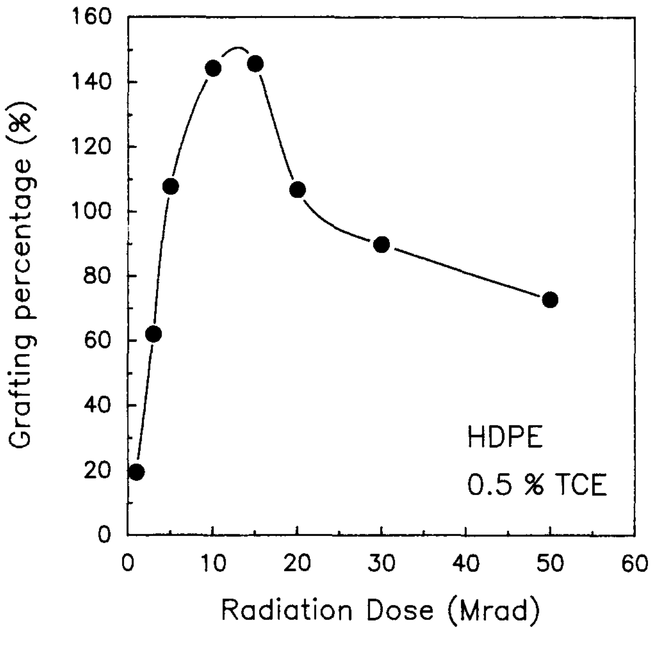

Figure 2 Grafting percentage vs. radiation dose. TCE (0.5%) was used in the grafting of HDPE. The grafting was carried out for 20 min

process the reaction of the radiatively formed radicals with the monomer competes with the recombination of two free radicals in the film (crosslinking). The latter is a second-order reaction with respect to the concentration of the radicals. Therefore, at high radiation doses, when high concentration of free radicals is formed, the relative rate of the recombination route increases at the expense of grafting, causing a decrease of %G. In addition, the crosslinking of the film lowers its permeability towards dissolved species. This decrease in the film permeability affected every step thereafter. For example, the surface resistivity of a film prepared using 5 Mrad was lower than that of a film prepared using 20 Mrad, although similar films were used (entries 6 and 12).

A radiation dose of 10 Mrad and distilled styrene containing 0.5% TCE were found to be the best conditions in terms of the resulting surface resistivity. Film loading was also a parameter that affected the surface resistivity. Using these conditions %G could be increased by a change in the grafting duration. Entries 10, 16 and 17 in *Table 2* show the increase in %G when the grafting was carried out for 20, 60 and 120 min, respectively. The corresponding %G were 144%, 192% and 214%, and the corresponding surface resistivities were 56, 27 and 24 Ω/□. Grafting percentage of 160–170% yielded similar surface resistivity (see below). In summary the optimal parameters for the preparation of these conducting ionomers in terms of their surface resistivity were: $\%G \approx 160$–170%, $\%S \approx 120\%$ (loading of ≈ 5 meq/g). The specific conductivity obtained using these parameters was $\approx 5\,\mathrm{S\,cm^{-1}}$.

It was interesting to examine the dependence of the surface resistivity on the loading of the films (*Figure 3*). The data were taken regardless of the relative contribution of %G and %S. The filled circles and the unfilled squares in *Figure 3* represent experiments that were carried out with and without TCE, respectively. An increase in the film loading caused a decrease in their surface resistivity. Higher loading resulted in higher concentration of iron(III) ions in the film, and therefore longer defect-free PPy chains could be obtained. In all the cases the use of TCE improved the conductivity of the films, but the effect of TCE was larger at low loadings of the film.

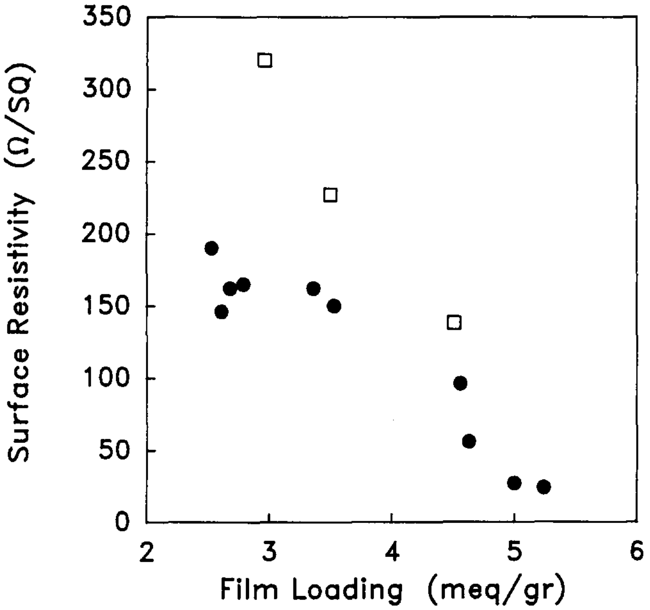

Figure 3 The dependence of the surface resistivity on the loading of the films. The filled circles and the unfilled squares represent experiments that were carried out with and without TCE, respectively

Methanol was also tested as a solvent for the polymerization of pyrrole. The results are shown in entries 18 and 19. The surface resistivity of the ionomers increased by a factor of 2 in comparison with films that were produced in aqueous solution. The appearance of the films was, however, better than those prepared in aqueous solution: the films were smoother and more flexible.

Ionomers are essentially polyelectrolytes, and as such they are ionically conducting polymers. It was of interest, therefore, to compare the conductivity of a film before and after the insertion of PPy. Two-probe measurements of the film resistivity ($\%G = 146\%$, $\%S = 102\%$, 4 meq/g) before and after polymerization of pyrrole showed resistivities of 3 MΩ and 133 Ω, respectively. Thus, the resistivity of the film decreased by four orders of magnitude owing to the take-in of the electrically conducting PPy.

Characterization of the conducting films

Composition and morphology of the conducting ionomers. WDS provided information concerning the atomic percentage of carbon, nitrogen, chlorine, sulphur, iron and oxygen atoms in the films, which enabled the evaluation of its empirical formula. Knowing the number of nitrogen and sulphur atoms made it possible to estimate the carbon atom fraction due to the pyrrole and styrene moieties in the film. The difference between this carbon atom fraction and the total number of carbon atoms give the contribution of polyethylene carbon atoms. The calculation was completed by the evaluation of the hydrogen and oxygen content and recalculation of the weight percentage of the sample.

Two films, which had the same $\%G$ and the similar $\%S$, were examined. They were prepared during 0.5 and 120 min and their conductivity was 0.82 and 5.7 S cm^{-1}, respectively. Surface analysis of these two films *did not show any iron*, and thus $[FeCl_4]^{2-}$ can be excluded as the dopant. The less conducting film exhibited a negligible content of chlorine. The best fitted composition for this film was $(Py)_{12}(SS)_7(SO_3)_{0.8}(CH_2)_{17}(O^{ex})$, where Py is the pyrrole, SS is the sulphonated styrene, SO_3 is the fraction of over-sulphonated film, (CH_2) is the polyethylene and O^{ex} is the oxygen excess in the film. The oxygen excess could have resulted from the additives in the PE film, water content and/or over-oxidation of the PPy film, especially when prepared in aqueous solutions[3,17]. Surface analysis of the more conducting film showed a large content of chlorine, only traces of sulphur and the amount of carbon was very small. It is concluded that the film was covered with a layer of PPy/Cl, which was formed in the solution and adhered strongly to the film. Hence, the polyethylene contribution to the carbon content was absent and only the carbon from the pyrrole moiety was detected.

Reinforcement of the surface analysis results was obtained from the scanning electron micrograph of these two films (*Figure 4*). The less conducting ionomer (0.82 S cm^{-1}) showed ordered aligned sinewy structure (*Figure 4a*). Some sediments can be seen in the upper left corner of the micrograph, which were shown to be PPy/Cl by WDS. A completely different structure was obtained in the more conducting ionomer (5.7 S cm^{-1}, *Figures 4b* and *4c*). A granular vesicle structure with a narrow size distribution of the particles (0.3–0.5 μm) can be seen (*Figure 4c*). The analysis showed that it was a layer of PPy/Cl, the thickness of which was a few micrometres.

Mechanical properties of the conducting ionomers. The experimental set-up was slightly modified to enable the preparation of 10 × 10 cm^2 conducting ionomers. The basic system was similar to the one used for the formation of the small films, except one big film (10 × 13 cm^2) was taped to the rotating holder. The conductivities of the films were similar to those obtained in the small-scale reactions. When the optimal conditions were used (see above) the specific conductivities of the large films were 2–5 S cm^{-1}. Moreover, uniform films, with respect to their conductivity, were obtained and similar results were obtained from the two faces of the film.

Tensile properties of HDPE raw material, grafted films (PE/PS), grafted and sulphonated films (PE/PSSA) and conducting films are tabulated in *Table 3*. The grafting and sulphonation percentages of all the investigated films were similar ($\%G = 151$–157% and $\%S = 113$–123%) but films with different conductivities were used. This was done to focus on the effect of the PPy content (viz. the conductivity of the film) on the mechanical properties of the composite. The polymerization of pyrrole was always carried out under the same conditions. The different conductivities were obtained by a change in the time of polymerization.

The first three entries show the effect of treatment prior to the polymerization of pyrrole on the mechanical properties of the films. The elongation and tensile strength decreased gradually in every stage of the process. Thus, the films became weaker and less flexible. The elongation at yield, on the other hand, was very similar. Hence, the decrease in the ductility of the films occurred in their non-elastic state. The insertion of polystyrene—a more rigid polymer than PE—caused an increase in the modulus of elasticity, but the transfer of styrene to an ionic species (styrenesulphonic acid) brought about a decrease in the mechanical strength of the films.

When PPy was imparted into the ionomer, the yield point in the stress-strain curve disappeared, implying that

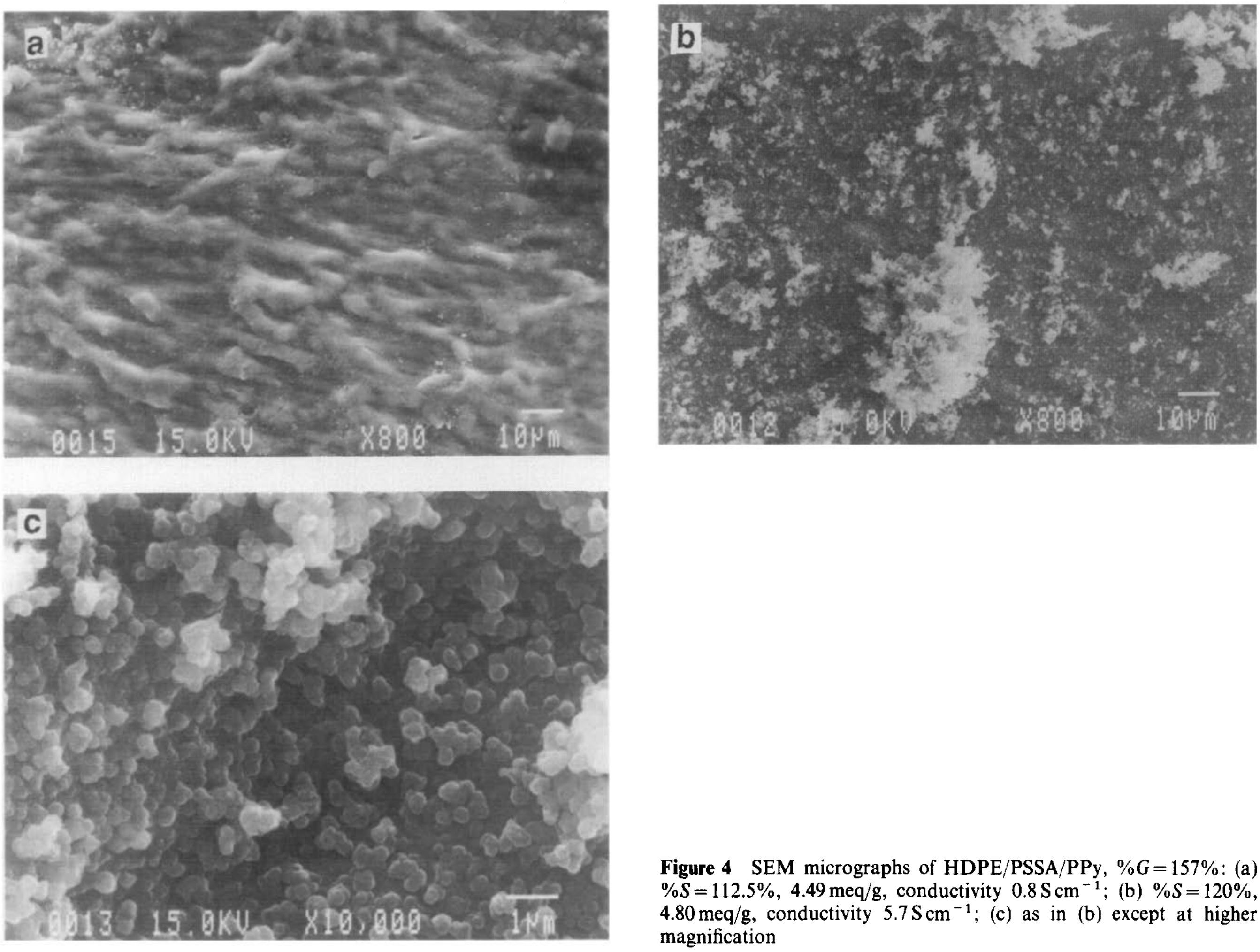

Figure 4 SEM micrographs of HDPE/PSSA/PPy, $\%G = 157\%$: (a) $\%S = 112.5\%$, 4.49 meq/g, conductivity $0.8\,\mathrm{S\,cm^{-1}}$; (b) $\%S = 120\%$, 4.80 meq/g, conductivity $5.7\,\mathrm{S\,cm^{-1}}$; (c) as in (b) except at higher magnification

Table 3 Mechanical properties of films used during the formation of HDPE/PSSA/PPy[a]

No.	%*G*	%*S*	Film loading (meq/g)	Film conductivity ($\mathrm{S\,cm^{-1}}$)	Elongation at break (%)	Elongation at yield (%)	Tensile strength at break ($\mathrm{kg\,cm^{-2}}$)	Modulus of elasticity ($\mathrm{kg\,cm^{-2}}$)
1	–	–	–	–	515.43	11.65	510.50	4869.6
2	151.6	–	–	–	198.58	8.15	415.44	6433.3
3	155.7	118.9	4.8	–	125.83	11.02	256.96	2961.1
4	157.0	112.5	4.5	0.82[b]	45.67	–[c]	246.55	2461.4
5	156.3	122.7	4.9	2.64[d]	47.24	–[c]	200.00	1757.0
6	157.4	120.1	4.8	5.70[e]	23.92	–[c]	209.49	2487.1

[a] The stretching rate in the first three entries was $50\,\mathrm{mm\,min^{-1}}$ and in all the other entries $5\,\mathrm{mm\,min^{-1}}$. The data are averages of at least five runs

[b] The polymerization was carried out for 0.5 min

[c] No yield point was obtained in the stress–strain curves

[d] The polymerization was carried out for 30 min

[e] The polymerization was carried out for 120 min

the ionomers became relatively brittle. The elongation at break declined upon polymerization of pyrrole in the films (entries 3–6), and the extent of the decrease was dependent on the conductivity of the films. Films that exhibited high conductivity were less flexible. Nevertheless, elongations of 47% and 24% were obtained for films, the conductivities of which were 3 and $6\,\mathrm{S\,cm^{-1}}$, respectively, and the *films were prepared in a non-toxic aqueous solution*. These films are more stretchable than PPy/tosylate electrochemically prepared in acetonitrile (elongation of ≈4% was reported for PPy/tosylate)[18]. The tensile strength at break and the modulus of elasticity decreased with increase of the conductivity, but these changes were relatively small. The tensile strength and the modulus of elasticity of the PE/PSSA/PPy are similar to those of PE/PSSA (compare entries 3–6). One should keep in mind that PPy films, prepared electrochemically in perchlorate aqueous electrolyte containing no additives, were too brittle to be handled.

It is reported that stretching of conducting polymers improves their conductivity[19]. Therefore the stretching–conductivity relation of the conducting ionomers was investigated. Dog-bone specimens were cut from the large films and stretched uniformly on the Instron. The experiments were carried out at room temperature and at 40°C. The conductivity was measured before and after stretching at different points along the narrow part of the dog-bone specimen. The film conductivity remained unchanged when the experiments were carried out at room temperature, but a small decrease in their conductivity (≈8%) was observed when the experiments were performed at 40°C. Since the conducting ionomers were composed of a ductile matrix into which brittle PPy had been polymerized, the stretching affected mostly the elastic matrix, leaving the brittle conducting filler, and thus the conductivity of the composite, unchanged.

SUMMARY

The preparation and physical properties of conducting ionomers were investigated. A two-step process was used to prepare PE-based film grafted with poly(styrenesulphonic acid). Chemical polymerization of pyrrole in the ionomer imported conductivity to the film. The conductivity of the films increased when 1,1,2-trichloroethane was used as a chain transfer reagent during the grafting of PE with styrene.

Unambiguous improvement of the mechanical properties of the conducting film, in comparison to PPy film prepared in aqueous solution, was achieved. A deterioration of the mechanical properties of the films during their preparation was observed. The grafting and sulphonation of PE *prior* to the insertion of the conducting phase were responsible, to a large extent, for the decline in their mechanical properties. Other polymerization techniques[20] and other materials are currently utilized to improve the physical properties of organic conducting films.

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