

Mössbauer spectroscopic study of Fe^{II}-doped sulphonated poly(ether-urethane)—styrene-acrylate copolymer

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Abstract Thermoplastic linear ionomer based on sulphonated poly(ether-urethane)—styrene-acrylate copolymer, doped with natural Fe²⁺, was studied by Mössbauer spectroscopy at $T = 78$ and 290 K to monitor the chemical state of Fe species. The Fe²⁺ added to aqueous suspension of the system was only partly oxidised in the course of polymer film preparation and drying in air. The oxidised part comprised a magnetic phase (~19 % of total Fe both at $T = 78$ and 298 K) and a quadrupole doublet (~40 %), while Fe^{II} (over 40 %) stabilised in two types of microenvironments.

Keywords Iron(II)-doped sulfonated poly(ether-urethane)—styrene-acrylate copolymer · Thermoplastic linear ionomer · Mössbauer spectroscopy

1 Introduction

A favourable combination of characteristics of many poly(ether-urethane)-based polymeric materials or blends is the reason for their wide-range industrial

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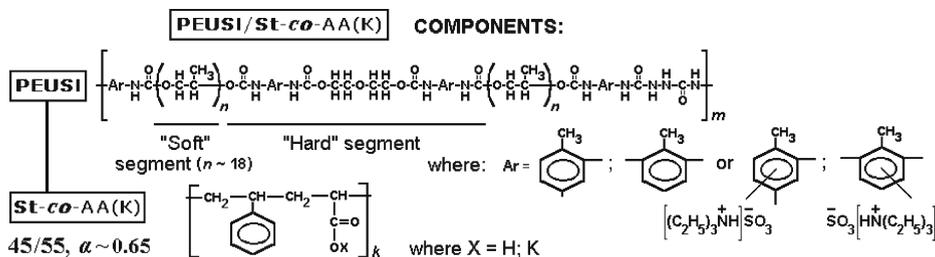


Fig. 1 Scheme of the structure of PEUSI/St-co-AA(K). PEUSI sulphonation degree ca. 3 %; 70 % PEUSI + 30 % St-co-AA(K); St/AA = 45/55 mol. %; in AA, [COOK/COOH]~0.65

applications, in particular, in medicine as biomaterials [1–3]. Earlier [4], linear poly(ether-urethane) sulphonated ionomer (PEUSI) (Fig. 1, upper part), doped with Fe^{2+} (as $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), was studied by Mössbauer spectroscopy to monitor the chemical state of Fe species.

In this work, a similar study was performed with a microheterogeneous system of linear ionomers based on PEUSI and a random copolymer of styrene (St) and acrylic acid (AA) partly neutralised with KOH [PEUSI/St-co-AA(K)].

2 Experimental

The PEUSI/St-co-AA(K) material (Fig. 1), with 70 % PEUSI and 30 % St-AA(K) copolymer, was synthesised as reported in [5]. Fe^{II} doping (with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) of its aqueous emulsion, preparation of a dry film (0.7 ± 0.1 mm thick; 4.5 mg cm^{-2} Fe), Mössbauer spectroscopic measurements and data treatment were performed as described in [4].

3 Results and discussion

Mössbauer spectra of the Fe^{2+} -doped PEUSI/St-co-AA(K) dry films ($T = 78$ and 290 K) are presented in Fig. 2; the calculated parameters are listed in Table 1.

Similarly to PEUSI [4], in PEUSI/St-co-AA(K) the added Fe^{2+} appeared to get only partly oxidised in the course of polymer film preparation and air-drying. However, in PEUSI/St-co-AA(K), the oxidised part, in addition to quadrupole doublet 3, gave a larger portion (~ 19 %) of a magnetic phase both at $T = 78$ and 298 K, implying larger sizes of its particles (most probably oxide/ FeOOH). This is ascribable to the binding effect of the acrylate moieties in St-co-AA(K) resulting in a slower formation of Fe^{3+} oxide/ FeOOH crystallization centres.

Iron(II) (over 40 % of total Fe added) stabilised in PEUSI/St-co-AA(K) also in two different forms (doublets 1 and 2), similarly to PEUSI [4], representing two types of Fe^{II} microenvironments, where Fe^{II} may be coordinated by $-\text{COO}^-$ of acrylate moieties, sulphonate groups, as well as probably by $-\text{CONH}-$ and $-\text{NHNH}-$ moieties (see Fig. 1). In our opinion, it is unlikely that Fe^{II} in such an air-dried film would stabilise as hexaquo complex, although the parameters of doublet 1 are similar to the latter (while H_2O may still be coordinated). For comparison, Fe^{II} -doped chitin

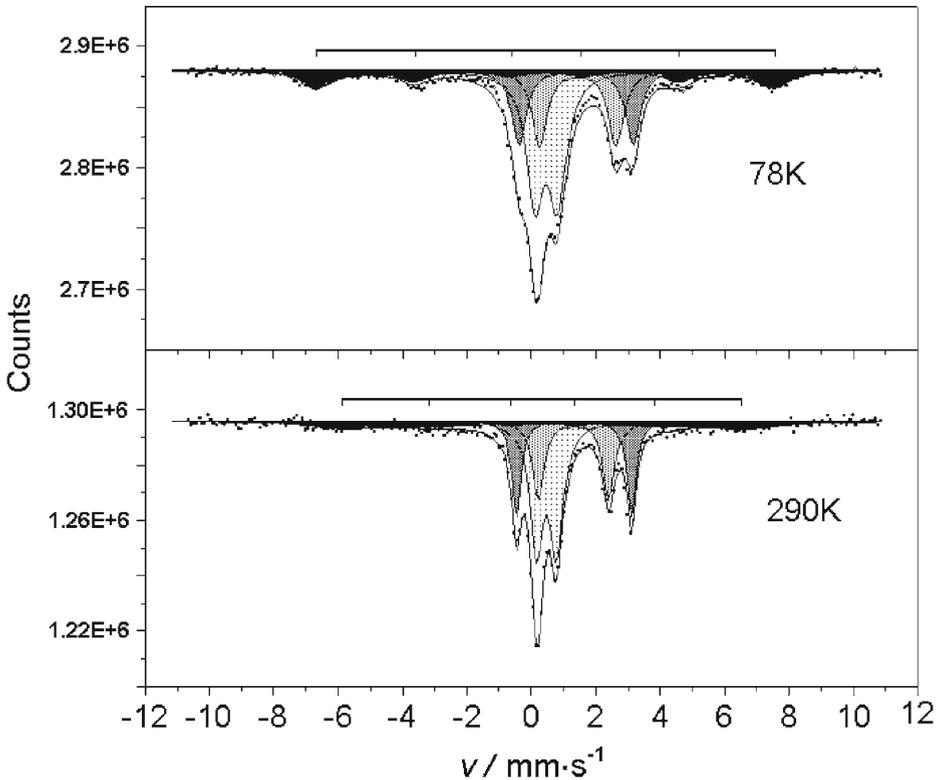


Fig. 2 Mössbauer spectra of Fe²⁺-doped PEUSI/St-co-AA(K) dry films measured at $T = 78$ and 290 K. The positions of the weak magnetically split sextets (depicted in *black*) are shown above each spectrum. For both spectra, doublets 1 and 2 (see also Table 1), representing two different Fe^{II} forms, are depicted as more and less *dark shaded* areas, respectively; the narrower doublet 3 (representing Fe^{III}) is shown by *light shading* (velocity scale calibrated relative to α -Fe at room temperature; the same for the δ values in Table 1)

Table 1 Mössbauer parameters^{a,b} for Fe²⁺-doped partly sulphonated PEUSI/St-co-AA(K) dry films measured at $T = 78$ and 290 K (see also Fig. 2)

T , K	Multiplet	Fe oxidation state	Magnetic field, T	δ , mm/s	Δ , mm/s	Γ_{exp} , mm/s	S_r , %
78	Sextet	+3	44.0(1)	0.45(2)	–	1.10(7)	18.8
	Doublet 1	+2	–	1.38(1)	3.54(2)	0.53(2)	20.0
	Doublet 2	+2	–	1.45(1)	2.37(2)	0.55(2)	20.9
	Doublet 3	+3	–	0.47(1)	0.71(1)	0.64(1)	40.3
290	Sextet	+3	38.6(9)	0.45(12)	–	2.3(4)	19.7
	Doublet 1	+2	–	1.32(1)	3.57(1)	0.34(2)	20.3
	Doublet 2	+2	–	1.32(1)	2.19(2)	0.44(2)	21.6
	Doublet 3	+3	–	0.48(1)	0.63(2)	0.48(2)	38.4

^a δ , isomer shift (vs. α -Fe at room temperature); Δ , quadrupole splitting; Γ_{exp} , experimentally observed line width at half maximum; S_r , the relative area of a relevant spectral component (relative error ± 5 %) representing the relative content of the related form, assuming a common recoilless fraction for all forms in a sample contributing to the spectrum

^bErrors (in the last digits) are indicated in parentheses

and chitosan showed full oxidation of Fe^{II} to two Fe^{III} forms both in air and under N_2 [6], indicating involvement of the polymers in oxidation.

Note that the parameters for all the Fe forms in PEUSI/St-*co*-AA(K) noticeably differ from those in PEUSI [4]. Thus, introducing 30 % St-AA(K) copolymer to PEUSI significantly alters the Fe microenvironments.

4 Conclusions

Fe^{II} -doping of the PEUSI/St-*co*-AA(K) system showed significant differences in the appearance and Mössbauer parameters of iron species, including stabilised Fe^{II} (over 40 % of the total Fe added) and a magnetic phase, from those in PEUSI studied earlier [4]. Thus, Fe^{II} -doping of such PEUSI-based materials may be used for probing their structural characteristics by Mössbauer spectroscopy.

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