NASA/TM-97- 208212

IN-27-TM

151450

12P

Reprinted from

NIM B
Beam Interactions
with Materials & Atoms

Nuclear Instruments and Methods in Physics Research B 134 (1998) 113–120

Microstructural characterization of semi-interpenetrating polymer networks by positron lifetime spectroscopy

Jag J. Singh *, Ruth H. Pater, Abe Eftekhari

NASA – Langley Research Center, Hampton, VA 23681-0001, USA

Received 6 May 1997; received in revised form 19 September 1997

ELSEVIER

BEAM INTERACTIONS WITH MATERIALS AND ATOMS
Nuclear Instruments and Methods in Physics Research – Section B

Aims and scope
Section B of Nuclear Instruments and Methods in Physics Research (NIM B) provides a special forum for the discussion of all aspects of the interaction of energetic beams with atoms, molecules and aggregate forms of matter. This includes ion beam analysis and ion beam modification of materials, as well as studies of the basic interaction mechanisms of importance for this work. The Editors invite submission of both theoretical and experimental papers of original research in this area.

Abstracted/indexed in:
Current Contents: Engineering, Technology and Applied Sciences; EI Compendex Plus; Engineering Index; INSPEC; Physics Briefs.

Subscription information 1997
Volumes 121–133 of Nuclear Instruments and Methods in Physics Research - Section B (ISSN 0168-583X) are scheduled for publication. A combined subscription to NIM A volumes 384–401 and NIM B volumes 121–133 is available at a reduced rate.
Subscriptions are accepted on a prepaid basis only and are entered on a calendar year basis. Issues are sent by SAL (Surface Air Lifted) mail wherever this service is available. Airmail rates are available upon request. For orders, claims, product enquiries (no manuscript enquiries) please contact the Customer Support Department at the Regional Sales Office nearest to you:
New York: Elsevier Science, P.O. Box 945, New York, NY 10159-0945, USA; tel +1 212 633 3730 (Toll free number for North American customers: 1-888-4ES-INFO (437-4636)), fax +1 212 633 3680, e-mail usinfo-f@elsevier.com
Amsterdam: Elsevier Science, P.O. Box 211, 1000 AE Amsterdam, The Netherlands; tel +31 20 485 3757, fax +31 20 485 3432, e-mail nlinfo-f@elsevier.nl
Tokyo: Elsevier Science, 9-15, Higashi-Azabu 1-chome, Minato-ku, Tokyo 106, Japan; tel +81 3 5561 5033, fax +81 3 5561 5047, e-mail kyf04035@niftyserve.or.jp
Singapore: Elsevier Science, No. 1 Temasek Avenue, #17-01 Millenia Tower, Singapore 039192; tel +65 434 3727, fax +65 337 2230, e-mail asiainfo@elsevier.com.sg
Claims for issues not received should be made within six months of our publication (mailing) date.

US Mailing notice: Nuclear Instruments and Methods in Physics Research – Section B (ISSN 0168-583X) is published semi-monthly (for five months of the year), monthly from August to December, three times a month in May, and four times in April, by Elsevier Science B.V., Molenwerf 1, P.O. Box 211, 1000 AE Amsterdam, The Netherlands. Annual subscription price in the USA is US$ 6396 (valid in North, Central and South America only), including air speed delivery. Periodicals postage paid at Jamaica, NY 11431.
USA Postmasters: Send address changes to Nuclear Instruments and Methods in Physics Research – Section B, Publications Expediting, Inc., 200 Meacham Avenue, Elmont, NY 11003. Airfreight and mailing in the USA by Publications Expediting Inc.

Printed in The Netherlands

North-Holland, an imprint of Elsevier Science

ELSEVIER

Nuclear Instruments and Methods in Physics Research B 134 (1998) 113–120

NIM B
Beam Interactions with Materials & Atoms

Microstructural characterization of semi-interpenetrating polymer networks by positron lifetime spectroscopy

Jag J. Singh *, Ruth H. Pater, Abe Eftekhari

NASA – Langley Research Center, Hampton, VA 23681-0001, USA

Received 6 May 1997; received in revised form 19 September 1997

Abstract

Thermoset and thermoplastic polyimides have complementary physical/mechanical properties. Whereas thermoset polyimides are brittle and generally easier to process, thermoplastic polyimides are tough but harder to process. It is expected that a combination of these two types of polyimides may help produce polymers more suitable for aerospace applications. Semi-Interpenetrating Polymer Networks (S-IPNs) of thermoset LaRC^{TM}-RP46 and thermoplastic LaRC^{TM}-IA polyimides were prepared in weight percent ratios ranging from 100:0 to 0:100. Positron lifetime measurements were made in these samples to correlate their free volume features with physical/mechanical properties. As expected, positronium atoms are not formed in these samples. The second life time component has been used to infer the positron trap dimensions. The "free volume" goes through a minimum at about 50:50 ratio, suggesting that S-IPN samples are not merely solid solutions of the two polymers. These data and related structural properties of the S-IPN samples have been discussed in this paper. Published by Elsevier Science B.V.

Keywords: Semi-interpenetrating polymer networks; Positron annihilation spectroscopy; Free volume; Electrostatic bonding; Dielectric constant; Density

1. Introduction

Increasing emphasis on easy processing and good fracture toughness of composite matrix resins for aerospace structural applications has provided an impetus to develop high performance Semi-Interpenetrating Polymer Networks (S-IPNs). Thermosetting polyimides are generally easy to process, but are brittle. In contrast, thermoplastic polyimides are tough, but difficult to process. Combining them would be expected [1] to lead to tough and easy to process high performance S-IPNs. Based on this concept, we have synthesized a series of S-IPNs by combining LaRC^{TM}-RP46 and LaRC^{TM}-IA in various weight ratios.

The morphology of polymeric materials strongly affects their physical and mechanical properties. However, no reliable techniques are currently available for detailed morphological studies of

---

* Corresponding author. Tel.: 757 864 4760; fax: 757 864 7607; e-mail: j.j.singh@larc.nasa.gov.

0168-583X/98/$19.00 Published by Elsevier Science B.V.
PII S0168-583X(97)00534-X

these materials, particularly at the molecular level, mainly because of the rather intractable nature of the interpenetrating polymer networks. In this investigation, Positron Annihilation Spectroscopy (PAS) was employed to directly measure free volume cell sizes (V_f) in seven S-IPN systems that contained 100:0, 75:25, 65:35, 50:50, 35:65, 25:75, 0:100 weight percent ratios of LaRC™-RP46 and LaRC™-IA polyimides. The experimental techniques, results of various measurements, and correlations between V_f and physical/mechanical properties are discussed in this paper.

2. Experimental techniques

2.1. Sample preparation

LaRC™-RP46 is a thermosetting polyimide prepared from the dimethyl ester of 3,3,4,4′-benzophenone tetracarboxylic acid (BTDE), 3,4′-oxydianiline (3,4′-ODA) and the monomethyl ester of 5-norbornene-2,3-dicarboxylic acid (NE). NE is an end-capping agent through which cross-linking reactions occur. The formulated molecular weight (FMW) of this polymer was arranged to be 1500 g/mol.

LaRC™-IA is a thermoplastic polyimide, prepared from 4,4′-oxydiphthalic anhydride (ODPA), 3,4′-ODA and 8 mol % of phthalic anhydride. Phthalic anhydride acts as a non-reactive end group to control the molecular weight of the polymer. The FMW of this polymer was controlled to be 9000 g/mol.

Both LaRC™-RP46 and LaRC™-IA polyimides were recently developed [2,3] at NASA – Langley Research Center. Their outstanding physical and mechanical properties show promise for a wide variety of aerospace and non-aerospace applications. Both polymers are now commercially available.

The S-IPNs were prepared from LaRC™-RP46 oligomer and LaRC™-IA polyamic acid. Typically, the RP-46 oligomers were dissolved in a minimum amount of N-methyl pyrrolidone (NMP) at 70°C and then added to the IA polyamic acid solution in NMP. The mixture was stirred for 1 h at room temperature and then heated for 2 h at 60°C in a vacuum oven. This was followed by heating for 2 h each, at 200°C and 250°C. This heating sequence produced B-staged molding powder. Approximately 5.0 g of the B-staged molding powder was placed in a 3.18×3.18 cm^2 stainless steel mold, which was preheated with a Frekote™ release agent. The mold was heated to 290°C at a pressure of 13.8 Mpa and then held for 1 h at 325°C. Because the LaRC™-IA material had greater resin flow than the S-IPNs and LaRC™-RP46, it was cured at 355°C for 1 h under 2.07 Mpa pressure. The thickness of the resin prepared for PAS measurements was controlled by using a 0.33 cm spacer inserted in the mold. Much thicker samples were prepared for moisture absorption and dielectric constant determinations. Fig. 1 shows the synthesis sequence of the S-IPN materials.

2.2. Positron lifetime measurements

Positron lifetime measurements were made with a standard fast–fast coincidence measurement technique. Samples were cut in the form of $2.5 \times 2.5 \times 0.25$ cm^3 coupons. A 25 microcuries positron source was prepared by depositing Na^{22}Cl solution on a 2.5 micron thick Kapton foil

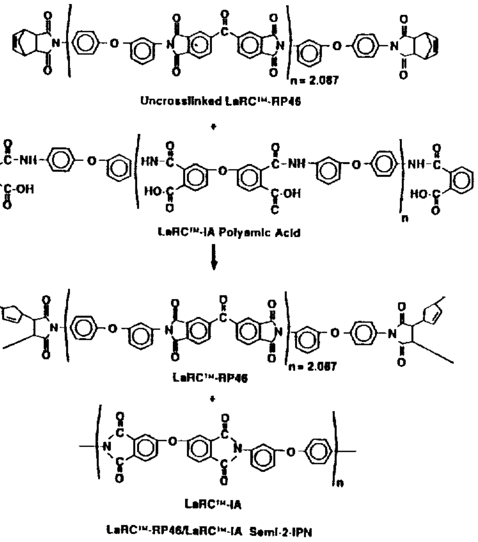

Fig. 1. Synthesis of LaRC™-RP46:LaRC™-IA Semi-Interpenetrating Polymer Network (S-IPN).

folded on itself. The positron source was sandwiched between the test coupons and the spectra were accumulated for 24 h. This counting period produced a total of over 10^6 counts in each spectrum. The time resolution of the lifetime system was about 280 ps. All measurements were made at room temperature in dry samples. The lifetime spectra were analyzed with the PATFIT [4] program.

2.3. Saturation moisture measurements

All of the cured resin specimens, having sizes of approximately 2.5 × 2.5 × 0.4 cm^3 were immersed in water at 90°C. Their weights were monitored continually, over a period of several days, until they stabilized. The samples were then desiccated in a vacuum oven at 90°C for several days for subsequent determination of saturation moisture content in each sample.

2.4. Density measurements

The density of each sample in its desiccated state was measured by a standard water displacement technique.

2.5. Dielectric constant measurements

The desiccated S-IPN samples were configured into the form of parallel plate condensers whose capacitances were measured with an impedance analyzer at 10 GHz. The dielectric constants were then computed on the basis of the measured values of the capacitances and the thicknesses of the samples.

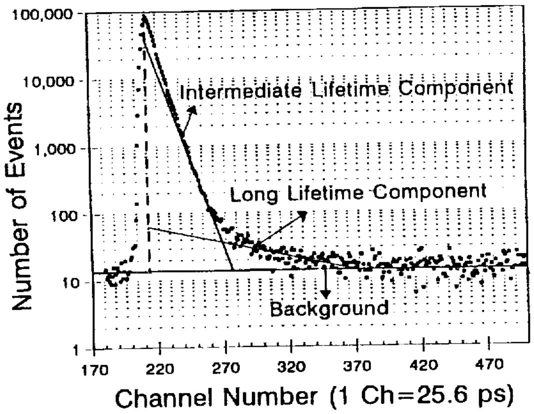

Fig. 2. Typical positron lifetime spectrum in thermoplastic polyimide-IA.

3. Experimental results

3.1. Positron lifetime measurements

All positron lifetime spectra were acquired under ambient conditions, with frequent time resolution checks with a Co^{60} gamma radiation source. Fig. 2 shows a typical lifetime spectrum observed in S-IPN samples. All spectra were analyzed into three components since it gave the best least squares fit, using PATFIT program [4]. The lifetime measurements are summarized in Table 1. It is noted that the intensity of the third component

Table 1

Summary of positron lifetime spectra in S-IPN samples

Sample composition LaRC™-RP46:LaRC™-IA	τ_1 (ps)/I_1 (%)	τ_2 (ps)/I_2(%)	τ_3 (ps)/I_3 (%) [a]
0:100	182 ± 8/19.5 ± 1.6	488 ± 3/80.0 ± 2.0	2165 ± 181/0.5 ± 0.1
25:75	204 ± 12/20.3 ± 3.0	422 ± 5/79.3 ± 3.0	2185 ± 286/0.4 ± 0.1
35:65	206 ± 12/20.8 ± 2.8	399 ± 4/78.9 ± 2.9	2533 ± 323/0.3 ± 0.1
50:50	200 ± 4/20.2 ± 2.0	394 ± 1/79.4 ± 1.0	2285 ± 216/0.4 ± 0.1
65:35	195 ± 9/23.6 ± 2.3	400 ± 2/76.3 ± 1.4	2205 ± 216/0.1 ± 0.1
75:25	198 ± 8/20.1 ± 2.0	399 ± 2/79.6 ± 1.8	2337 ± 312/0.3 ± 0.1
100:0	195 ± 9/18.2 ± 2.1	400 ± 4/81.4 ± 2.2	2215 ± 210/0.4 ± 0.1

[a] Large errors on τ_3 are due to extremely low intensity of this component. They have been included here for the completeness of the analysis.

(I_3) is very low ($\leqslant 0.5\%$) in all cases. It has, therefore, been attributed to the source and background. The second lifetime component (τ_2) dominates in all cases. The thermosetting constituent (LaRC™-RP46) has BTDA as its acid anhydride moiety, while ODPA is the acid moiety of the thermoplastic component (LaRC™-IA). Both these moietites inhibit positronium (Ps) formation [5]. Hence, the strong τ_2 component cannot arise from fast quenching of orthopositronium atoms. Besides, the absence of appropriate para positronium signal at about 125 ps precludes positronium contribution to the τ_2 component. It has therefore been concluded that this component corresponds exclusively to the positrons localized in potential defects (microvoids). These microvoids result from packing inhomogeneities of the molecular chains.

Deng et al. [6] have addressed the problem of positron localization in free volume holes in polymers. They investigated the pressure dependence of free-volume hole properties in amine-cured epoxies and concluded that the data of τ_2 (in nanoseconds) can be fitted well to the R-values (in nm) obtained from the τ_3 data at the same pressure, by the following equation:

$$\tau_2 = 0.22\left[1 - \frac{R}{R+0.166} + \frac{1}{2\pi}\sin 2\pi\frac{R}{R+0.166}\right]^{-1}, \tag{1a}$$

$\tau_2 = 0.22$ ns in this equation represents the trapped positron lifetime in free volume holes at very high pressure. This equation can be generalized by replacing 0.22 ns by bulk lifetime. Bulk lifetime in most polymers ranges from 0.20 to 0.25 ns. Accepting 0.222 ns as the ultimate bulk lifetime in the non-Ps-forming polyimides investigated here, leads to the following generalized expression for the free volume hole size in these materials:

$$\frac{1}{4.5\tau_2} = \left[1 - \frac{R}{R+0.166} + \frac{1}{2\pi}\sin\left(2\pi\frac{R}{R+0.166}\right)\right]. \tag{1b}$$

This equation differs from positronium localization model [7] in having $1/(4.5\tau_2)$, instead of $1/(2\tau_3)$, as its left-hand side term. It can be used to obtain free volume properties in polyimides. The values of microvoid volume (V_{f2}) for various samples, calculated from this equation are summarized in Table 2.

Table 2
Summary of free volume fractions in S-IPN samples

Sample composition LaRC™-RP46:LaRC™-IA	V_{f2} (Å^3)	f (%) (= CI_2V_{f2})
0:100	25.00 ± 0.42	2.81 ± 0.09
25:75	16.30 ± 0.61	1.81 ± 0.19
35:65	13.57 ± 0.49	1.50 ± 0.15
50:50	13.00 ± 0.11	1.45 ± 0.08
65:35	13.68 ± 0.24	1.46 ± 0.10
75:25	13.56 ± 0.23	1.51 ± 0.11
100:0	13.68 ± 0.46	1.56 ± 0.14

The free volume fractions (f) in the test samples were calculated as follows:

$$f = CI_2V_{f2}, \tag{2}$$

where C is a structural constant which can be determined by calibrating with other known physical parameters of the test samples [8]. Its value in the test samples has been calculated by equating the saturation moisture fraction (by volume) in LaRC™-IA sample with its free volume fraction. This procedure is justifiable since hydration of LaRC™-IA molecule is minuscule. The entry of water in this polymer is entirely physical, filling up all the available free volume in it. The value of C has been calculated to be 0.0014 ± 0.0001 (it should be noted that the value of C ranges from 0.001 to 0.002 in common polymers without Ps quenching functional groups in their molecular structure. It has been reported [9] at 0.0014 for polystyrene and 0.0018 ± 0.0002 for amine-cured epoxies). It has been assumed that the structural constant C will have the same value for all of the S-IPN samples since the chemical structures of the constituent polyimides are similar. The values of free volume fractions are summarized in Table 2. These values are consistent with the generally tighter molecular structure of the polyimides that do not permit positronium formation. Such polyimides are reported [10] to have relatively smaller-sized microvoids and, consequently, are expected to have smaller free volume fractions than other polymers.

Table 3
Summary of density and saturation moisture contents in S-IPN samples

Sample composition LaRC™-RP46:LaRC™-IA	Density (ρ) (g/cm^3)	Saturation moisture content	
		% by weight (W/O)	% by volume (V/O) [a]
0:100	1.3402 ± 0.0029	2.15 ± 0.07	2.81 ± 0.09
25:75	1.3815 ± 0.0028	1.69 ± 0.05	2.28 ± 0.07
35:65	1.3668 ± 0.0020	2.00 ± 0.06	2.66 ± 0.09
50:50	1.3713 ± 0.0041	2.39 ± 0.07	3.17 ± 0.10
65:35	1.3629 ± 0.0032	1.93 ± 0.06	2.56 ± 0.08
75:25	1.3546 ± 0.0036	2.18 ± 0.07	2.87 ± 0.09
100:0	1.3572 ± 0.0020	2.75 ± 0.09	3.60 ± 0.12

[a] $(V/O) = [\rho(W/O)\,100/\{100+\rho(W/O)\}]$ (Ref. [11]).

3.2. Density and saturation moisture measurements

The results of density and saturation moisture content measurements in various samples are summarized in Table 3. The saturation moisture contents have been expressed both as percentages by weight and by volume.

A quick reference to Tables 2 and 3 shows that the saturation moisture contents of the S-IPN samples bear no direct correlations with their free volume fractions except in the case of 0:100 sample. This is not surprising because water can enter the LaRC™-RP46 polymer chemically as well as physically. This hydration of the thermosetting component makes it difficult to equate the saturation moisture contents of the RP-46 bearing S-IPN samples with their free volume fractions. However, the hydration of 0:100 sample (LaRC™-IA) is very low and can be neglected. Thus, the free volume fraction in it is equal to its saturation moisture content by volume.

3.3. Dielectric constant measurements

The dielectric constants of the desiccated S-IPN samples were determined by comparing the capacitances of the parallel plate condensers configured with air and the test samples, respectively, as the dielectric media between the condenser plates. The results are summarized in Table 4.

4. Discussion

As shown in Fig. 1, the cured thermosetting and thermoplastic components have nearly the

Table 4
Comparison between the experimental and the computed values of the densities and the dielectric constants of the S-IPN samples

Sample composition LaRC™-RP46:LaRC™-IA		Density (g/cm^3) [a]		Dielectric constant at 10 GHz	
(% by weight)	(% by volume)	ρ (Experimental)	ρ (Computed)	ε (Experimental)	ε (Computed) [b]
0:100	0:100	1.3402 ± 0.0029	1.3402 ± 0.0029	2.82 ± 0.06	3.05 ± 0.05
25:75	24.0:75.2	1.3815 ± 0.0028	1.3557 ± 0.0031	3.01 ± 0.06	3.11 ± 0.05
35:65	34.7:65.3	1.3668 ± 0.0020	1.3618 ± 0.0036	3.11 ± 0.06	3.13 ± 0.06
50:50	49.7:50.3	1.3713 ± 0.0041	1.3712 ± 0.0045	3.14 ± 0.06	3.14 ± 0.05
65:35	64.7:35.3	1.3629 ± 0.0032	1.3672 ± 0.0034	3.14 ± 0.06	3.14 ± 0.05
75:25	74.8:25.2	1.3546 ± 0.0036	1.3643 ± 0.0026	3.13 ± 0.06	3.13 ± 0.05
100:0	100:0	1.3572 ± 0.0020	1.3572 ± 0.0020	3.13 ± 0.06	3.13 ± 0.06

[a] ρ (Computed) $= v_1\rho_1 + v_2\rho_2 + (0.0168 \pm 0.0031)\beta\,\{(\rho_1 + \rho_2)/2\}$.

[b] ε (Computed) $= [\{(1 - f)/\varepsilon_R\} + (f/\varepsilon_{Air})]^{-1}$; $\varepsilon_R = 3.24 \pm 0.06$.

same molecular weights in their repeating units (486 vs. 458). Thus their weight rates are essentially equal to their molar ratios. The mutual interpenetration of the constituent polymers in the S-IPNs would progressively increase until they reach a 50:50 composition where a maximum overlapping of the molar chains would occur. It would, therefore, be expected that the S-IPNs would become gradually stronger until they reach a 50:50 composition. However, this linear concept does not take into account the interatomic electrostatic forces that would also maximize under the same conditions. The dipolar charge distribution in RP-46 molecules would induce opposing charge distributions in the overlapping IA molecules, resulting in a strong electrostatic bonding between them.

In the presence of both mechanical and the electrostatic interactions between the constituent polymers, the density (ρ) of an S-IPN sample can be written as follows:

$$\rho = v_1\rho_1 + v_2\rho_2 + (1/2)\alpha\beta(\rho_1 + \rho_2), \qquad (3a)$$

where v_i is the volume fraction of the ith component ($v_1 + v_2 = 1$), α the intermolecular chain interaction constant, β is the molar chain overlap parameter.

The least squares fit of the experimental density values with the parameters of Eq. (3a) gives $\alpha = 0.0168 \pm 0.0031$. Such a strong interaction constant between LaRC^{TM}-RP46 and LaRC^{TM}-IA molecular chains is consistent with the dipolar charge distribution at the carbonyl site in LaRC^{TM}-RP46 inducing an opposing dipole in LaRC^{TM}-IA chain overlapping it. A comparison between the experimental and the computed values of the densities of the various S-IPN samples is summarized in Table 4. The agreement is reasonably good, except for the 25:75 S-IPN samples where the experimental value is about 1.9% too high, probably due to processing anomalies. The variation of density as a function of the sample composition is illustrated in Fig. 3. It appears to go through a maximum at 50:50 composition.

The same mechanical and electrostatic forces which produce changes in the sample densities as a function of their composition, are also expected to affect their free volume fractions and dielectric constants. Fig. 4 shows variation in the free volume fraction as a function of the sample composition. The free volume goes through a minimum at 50:50 composition in agreement with the density model. Fig. 5 shows variation in the dielectric constant (at 10 GHz) as a function of the sample composition. The dielectric constant appears to go through a maximum at 50:50 composition as would be expected on the basis of the density model. Density as a function of the free volume in various S-IPN sample is shown in Fig. 6. It is evident that the denser samples have smaller free volume fractions, as would be expected.

Re-writing Eq. (3a), we get

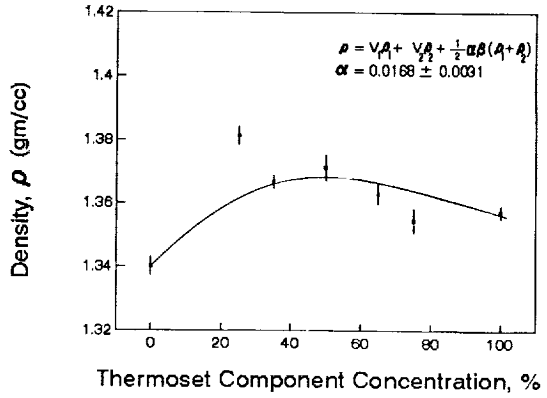

Fig. 3. Density as a function of the thermoset component concentration in S-IPN samples.

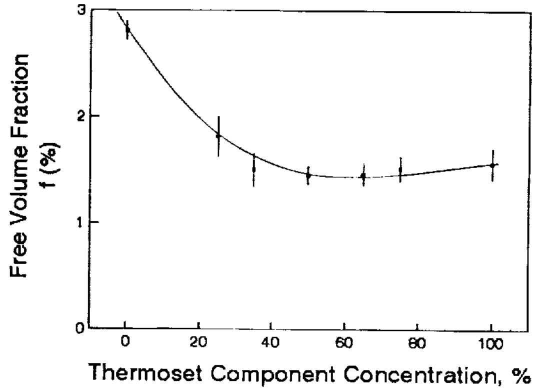

Fig. 4. Free volume fraction as a function of the thermoset component concentration in S-IPN samples.

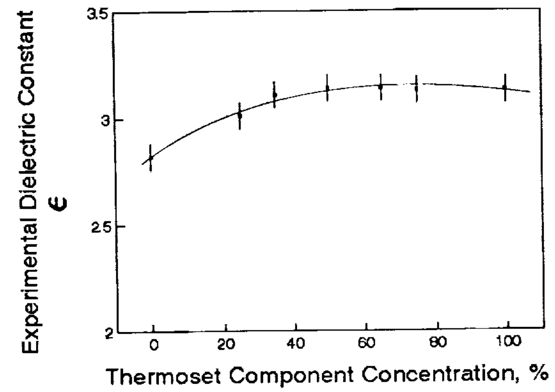

Fig. 5. Dielectric constant as a function of the thermoset component concentration in S-IPN samples.

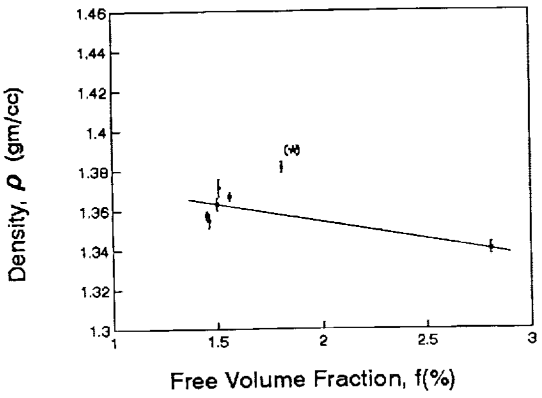

Fig. 6. Density as a function of the free volume in S-IPN samples. (The solid line merely illustrates the trend.) (*) This datum is most likely the result of processing anomaly in the (25:75) sample ($\rho = 1.3815 \pm 0.0028$; $f = 1.81 \pm 0.19$).

$$[\rho - (v_1\rho_1 + v_2\rho_2)] = (1/2)\alpha\beta(\rho_1 + \rho_2). \tag{3b}$$

The left-hand side of this Eq. (3b) equals the density changes, $\Delta\rho$, while the right-hand side represents the interactions responsible for free volume changes, Δf, i.e.

$$\Delta\rho \propto \Delta f. \tag{4}$$

The values of $\Delta\rho$ and Δf for various samples are summarized in Table 5. Despite rather large errors in the data, it does appear that there is a direct correlation between $\Delta\rho$ and the corresponding Δf values for the various samples.

Dielectric constant (ε) of a sample is a function of its free volume fraction, and can be written as follows [11]:

$$\frac{1}{\varepsilon} = \frac{1-f}{\varepsilon_{\mathrm{R}}} + \frac{f}{\varepsilon_{\mathrm{Air}}}, \tag{5}$$

where ε_{R} is the dielectric constant of the sample with zero free volume in it and $\varepsilon_{\mathrm{Air}}$ the dielectric constant of air.

A least squares fit of the experimental data with Eq. (5) gives $\varepsilon_{\mathrm{R}} = 3.24 \pm 0.06$.

A comparison between the experimental and the computed values of the dielectric constant of various S-IPN samples is summarized in Table 4. The agreement is reasonably good except for the pure thermoplastic sample where the predicted value is about 8% too high. Fig. 7 illustrates the correlation between the dielectric constant and the free volume fractions of the S-IPN samples.

Table 5
Summary of changes in the densities and free volume fractions in the various S-IPN samples

Sample composition LaRC™-RP46:LaRC™-IA		$\Delta\rho$ (g/cm³) $[\rho_{\mathrm{Expt}} - (v_1\rho_1 + v_2\rho_2)]$	Δf (%) $[(v_1f_1 + v_2f_2) - f_{\mathrm{Expt}}]$
(% by weight)	(% by volume)		
0:100	0:100	0	0
25:75	24.8:75.2	0.0371 ± 0.0039 [a]	0.69 ± 0.21
35:65	34.7:65.3	0.0207 ± 0.0032	0.88 ± 0.19
50:50	49.7:50.3	0.0227 ± 0.0047	0.74 ± 0.14
65:35	64.7:35.3	0.0117 ± 0.0039	0.54 ± 0.19
75:25	74.8:25.2	0.0053 ± 0.0042	0.37 ± 0.15
100:0	100:0	0	0

[a] As indicated elsewhere, this larger change in density is due to processing anomaly in the (25 : 75) S-IPN samples.

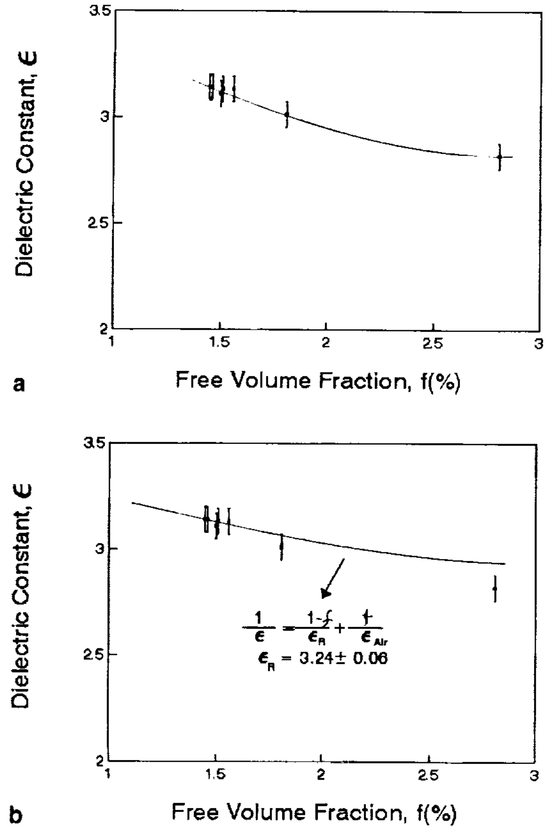

Fig. 7. (a) Dielectric constant as a function of the free volume in S-IPN samples. (b) Comparison between the experimental and computed values of dielectric constant in S-IPN samples as a function of their free volume fractions.

5. Concluding remarks

We have investigated free volume characteristics of S-IPN samples synthesized from LaRC™-RP46 and LaRC™-IA polyimides. The experimental data indicate that these materials are not merely solid solutions of the constituent polymers. Their non-linear characteristics dictate that both steric and electrostatic forces are needed to explain the observed relations between the density and chemical composition and between the dielectric constant and the free volume fractions of the samples. These results suggest that S-IPN materials with desired physical properties may be synthesized by selecting one member of the network to have pronounced non-spherical charge distributions along its chains.

References

[1] R.H. Pater, in: S.M. Lee (Ed.), International Encyclopedia of Composites, vol. 2, VCH Publishers, New York, 1990, pp. 377 401.
[2] R.H. Pater, US Patent No. 5171822, Low Toxicity High Temperature PMR Polyimide, 1992.
[3] T.L. St. Clair, US Patent No. 5147966, LaRC™-IA Polyimide, 1992.
[4] P. Kirkegaard, N.J. Pedersen, M. Eldrup, Report of Riso National Physical Laboratory, Denmark, vol. M-2740, 1989.
[5] Y. Ito, K.I. Okamoto, K. Tanaka, Journal de Physique IV C4 (1993) 241.
[6] Q. Deng, C.S. Sunder, Y.C. Jean, J. Phys. Chem. 96 (1992) 492.
[7] H. Nakanishi, Y.C. Jean, in: D.M. Schrader, Y.C. Jean (Eds.), Positron and Positronium Chemistry, Elsevier, Amsterdam, 1989, p. 159.
[8] Y.Y. Wang, H. Nakanishi, Y.C. Jean, T.C. Sandseczki, J. Polym. Sc. B 28 (1990) 1431.
[9] J. Liu, Q. Deng, Y.C. Jean, Macromolecules 26 (1993) 7149.
[10] K. Kamoto, K. Tanaka, N. Katsube, O. Sueka, Y. Ito, Mater. Sci. Forum 105–110 (1992) 1675.
[11] A. Eftekhari, A.K. St. Clair, D.M. Stoakley, D.R. Sprinkle, J.J. Singh, Polymers for Microelectronics, in: L.F. Thompson, C.G. Wilson, S. Tagawa (Eds.), ACS Symposium Series No. 537, Ch. 38, American Chemical Society, Washington, DC, 1994, pp. 535 545.

BEAM INTERACTIONS WITH MATERIALS AND ATOMS
Nuclear Instruments and Methods in Physics Research – Section B

Instructions to Authors

Submission of papers

Contributions should be submitted to one of the Editors (see inside front cover). It is suggested that manuscripts originating from Europe, India, The Middle East and Africa be sent to Prof. H.H. Andersen, and from The Americas, The Far East and Australasia, to Dr. L.E. Rehn.

Manuscript and figures should be submitted in duplicate, with one set of good quality figure material for production of the printed figures. If possible, please submit also an electronic version of your contribution on diskette.

Short contributions of less than 1500 words and not subdivided into sections may be published as Letters to the Editor in a shorter time than regular articles as the proofs will normally be corrected by the Publisher.

Submission of a manuscript implies that it is not being considered for publication elsewhere and that the authors have obtained the necessary authority for publication.

Manuscript preparation

Manuscripts should be written in good English. They should be typed throughout with double line spacing and wide margins on numbered, single column pages. See notes opposite on electronic manuscripts.

Structure. Please adhere to the following order of presentation: article title, author(s), affiliations, abstract, PACS codes and keywords, main text, acknowledgements, appendices, references, figure captions, tables.

Corresponding author. The name, full postal address, telephone and fax numbers and e-mail address of the corresponding author should be given on the first page.

Classification codes/keywords. Please supply one to four classification codes (PACS and/or MSC), and up to six keywords of your own choice that describe the content of your article in more detail.

References to other publications should be numbered consecutively within square brackets and listed together at the end of the text. In the case of multiple authorship all authors should be listed in the references; only in case of more than ten authors is the first author et al. acceptable.

Illustrations

The Publisher requires a set of good quality drawings and original photographs to produce the printed figures.

Line drawings should be 1.5–3 times larger than the printed size; the height of letters and numbers should, after reduction, fall within the range 1.2–2.4 mm. Do not use too narrow pen widths for machine-plotted graphs. Shaded areas should be shown by means of cross-hatching or a matrix of dots, rather than a continuous grey wash.

Photographs should not already be screened (overprinted with the point matrix used by printers). The top side of a photograph should be marked if necessary.

Colour figures can be printed in colour when this is essential to the presentation. Authors will be charged for colour reproduction. Further information can be obtained from the Publisher.

After acceptance

Notification. You will be notified by the Editor of the acceptance of your contribution, and invited to send an electronic file of the accepted version to the Publisher, if this is not yet available. After acceptance any correspondence should be addressed to the Publisher at the coordinates below.

Page proofs are sent out to the Author in order to check that no undetected errors have arisen in the typesetting or file conversion process. In the proofs only typesetting errors may be corrected. No changes in, or additions to, the accepted paper will be accepted.

Copyright transfer. In the course of the production process the authors will be asked to transfer the copyright of the article to the publisher. This transfer will ensure the widest possible dissemination of information.

Electronic manuscripts

If possible, an electronic version of the manuscript should be submitted on a diskette together with the hard copies of the text and figures, or should be sent (after acceptance) by e-mail or on a diskette to the Publisher. It is the responsibility of the Author to ensure that the electronic version exactly matches the hard copy. No deviations from the version accepted for publication are permissible without the prior and explicit approval by the Editor. Such changes should be clearly indicated on an accompanying print-out of the file.

LaTeX articles and articles prepared with any of the well known word processors can be handled by the Publisher. Further information can be obtained from the Publisher.

Author benefits

No page charges. Publishing in Nuclear Instruments and Methods in Physics Research – Section B is free.

Free offprints. The corresponding author will receive 50 offprints free of charge. An offprint order form will be supplied by the publisher for ordering any additional paid offprints.

Discount. Contributors to Elsevier Science journals are entitled to a 30% discount on all Elsevier Science books.

Correspondence with the Publisher

After acceptance of an article any correspondence should be addressed to Elsevier Science B.V., NIM-B, P.O. Box 2759, 1000 CT Amsterdam, The Netherlands
Tel. +31 20 485 2500, fax +31 20 485 2431
e-mail nimb-j@elsevier.nl

North-Holland, an imprint of Elsevier Science