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Polymer 43 (2002) 5493–5499

polymer

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Thermal treatment and dynamic mechanical thermal properties of polyaniline

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Received 1 February 2002; received in revised form 12 June 2002; accepted 19 June 2002

Abstract

Thermal transitions of polyaniline in the emeraldine base form (Pani-EB) were studied by DMTA using two series of thermally treated samples. In the first series the specimens were annealed at 70 °C for 5, 15 min, 1 and 3.5 h. In the second they were submitted to annealing at 100 °C during the same periods of time plus a 24 h treatment. Two transitions were observed at sub-zero temperatures and were attributed to the motion of solvated water and solvent (NMP). The glass transition and the highest temperature relaxation, assigned to crosslinking depended on the degree of solvation resulting from the thermal treatment. A linear contraction of Pani-EB films with residual water evaporation was reported for the first time. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Polyaniline; Thermal treatment; Dynamic mechanical thermal analysis

1. Introduction

Polyaniline (Pani) is one of the most investigated intrinsically conducting polymers due to its easy synthesis and good conductivity. The ability to process Pani into tough, free standing, air stable films has been a fundamental factor for the intense research and great number of published material related to this promising conducting polymer. One of the difficulties associated with the processing of conjugated polymers is the poor solubility in common, volatile organic solvents. Pani in its emeraldine form (Pani-EB) is commonly processed by dissolving the polymer in *N*-methylpyrrolidone (NMP) or *m*-cresol, both high boiling point solvents, resulting in cast films containing a non-negligible amount of residual solvent, often associated with residual water from the polymerization reaction. Thus, the resulting Pani film usually contains a considerable amount of NMP, about 18% by weight. This is due to the high boiling point of NMP (202 °C) and the presence of the hydrogen bonding interaction of the carbonyl group with the NH group in Pani. The carbonyl shifts in the infra red absorption of NMP/water and NMP/Pani mixtures provided further evidence for hydrogen bonds between these compounds [1]. The effect of residual solvent on the thermal properties of Pani has been addressed by several authors [2–9]. Residual solvent also affects electrical conductivity [10–13] and degree of crystallization and crystalline structure [14] apart from mechanical and thermal properties, such as dynamic mechanical, as discussed in this contribution.

In a recent communication, MacDiarmid et al. [14] have demonstrated that Pani-EB films cast from water containing NMP solutions showed photoluminescence at a 401 nm. This lead to the proposition that Pani-EB is a block copolymer, containing leucoemeraldine, emeraldine and pernigraniline segments, formed through water-assisted tautomerism processes.

By means of DMTA the relaxations in the chemically synthesized Pani-EB cast films from MNP solution have shown that NMP has a strong plasticizer effect, resulting in decreases in T_g in a linear fashion, as described by Wei et al. [2], (ranging from 220 to 120 °C for 0 to 20% NMP). These results were corroborated by Chen (140 and 180 °C for NMP contents of 15.3 and 9%) [1]. Lower values as 99 °C have also been reported [6]. However, information about the combined effect of residual NMP/water is much more scarce and controversial and the results seem to depend strongly on the experimental conditions. Pani is a very hygroscopic polymer and the amount of retained water is affected by ambient conditions, annealing temperatures and time. The occurrence of two kinds of bound water has been reported

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0032-3861/01/$ - see front matter
PII: S0032-3861(02)00401-9

[7]. The first form of absorbed water is weakly bound and mild treatments such drying at 70 °C during 20 min or at ambient temperatures under dry nitrogen flux are sufficient to remove entirely this component of absorbed water. Reversible weight changes in the polymer upon drying and wetting at about 30 °C [7] with determined activation energy of 3–5 kcal/mol (13–22 kJ/mol) have been established [7,15]. Matveeva et al. [7] supposed the existence of another form of water reversibly absorbed at the imine nitrogen with an activation energy of 15–18 kcal/mol (63–75 kJ/mol). A mechanism of the interaction between water and the polymer chain has also been proposed [7,16]. At first hydrogen bonds are formed and then water molecules dissociate. It was also assumed that absorbed water in Pani-EB and its removal cause structural changes in the polymer chains [17,18]. In spite of these results no evidence of thermal relaxations in DSC or DMTA has been reported, which could be assigned or correlated to polymer bound water or NMP molecules. In a general way the main thermal transitions found in undoped Pani-EB are the following: (1) a low relaxation located in the range − 86 to − 65 °C which has been tentatively assigned to torsional motions of the aromatic ring in the polymer chain [3] or to local motions of the more flexible amine units [1]; (2) the residual solvent dependent glass transition temperature, as above mentioned and (3) a transition located at temperatures above 180 °C which has been attributed to crosslinking and decomposition. Transitions for the crosslinked material have been reported to occur at a wide range (265 °C [3], 188–201 °C [1], 250 °C [4]) and the residual NMP in the films has been invoked to assist crosslinking in the Pani film by first forming hydrogen bonds with the amine groups of the polymer, or by the formation of aggregates through hydrogen bonding or pseudo-protonation [19]. The removal of the residual solvent in the film acting as plasticizer could also leave a free space allowing the motion of macromolecular segments [20,21]. Other processes as reorganization of the polymer chains [2], formation of new bonds [21] post-polymerization from approximately 250–340 °C have been suggested [5]. Crosslinking was also supposed to be both physical at about 180 °C [3,9,22,23] and chemical over 200 °C [1–3,8,9,17]. The temperature strongly depended on the Pani-EB form (powder, tablet or film) and on the environment [17]. It was supposed that the process proceeds at the imine nitrogen atom [24–26] resulting in a three dimensional polymer structure of the phenazine type [6,21,24–27].

The effect of the solvent and water in the final properties of Pani is therefore a matter of prime importance for the understanding of the thermo- and mechanical behavior of this material and consequently for the practical utilization of the polymer. Due to the lack of agreement in this matter we decided to perform DMTA analysis in samples that were systematic annealed below and in the vicinity of the glass transition during determined periods of time. The results gave evidence of water and NMP correlated transitions, and we also report for the first time the contraction effect verified when the solvent is fully removed, which has implications for technological developments of Pani as a film.

2. Experimental

2.1. Materials

Aniline (Vetec) was distilled twice under vacuum and stored in a refrigerator. Ammonium peroxydisulfate and *N*-methylpyrrolidone (analytical grade, Merck) were used without purification.

2.2. Polymerization procedure

Pani powder in emeraldine form was synthesized by chemical oxidation of aniline (4 mol) with ammonium peroxydisulfate (1 mol) as oxidant in hydrochloric acid solution (1 mol/l) [2]. The mixture was constantly stirred in an ice/salt bath for 15 min. The precipitate was washed with 0.1 mol/l HCl aqueous solutions until the filtrate was colorless. It was treated with 0.1 mol/l NH_4OH, filtered and dried to obtain the emeraldine base powder. These conditions were the same described in the literature [28] which gave a $M_w = 35\,000$. Recent results relate that the polymer properties begin to level up from 8-mers [29], in contrast with previous results that refer to 30–70 monomeric units [30]. No information about the entanglement molecular weight could be found in the literature.

2.3. Film preparation

Pani-EB was dissolved in NMP (2%, w/w) and filtered. The films were prepared by casting a Pani solution in NMP and drying at 65 °C for 60 h. These films were later submitted to thermal treatment at 70 or at 100 °C during predetermined periods of time.

2.4. Thermal characterization

The TG 209 and DMA 242 coupled modules of Netzsch–Thermisch Analyse were used to perform the thermal analyses. For the thermogravimetric tests (TGA) a heating rate of 20 °C/min was used with a nitrogen flow of 15 ml/min from room temperature to 450 °C. A heating rate of 20 °C/min was also used, to compare with DMA results.

The mechanical dynamic characterization (DMA) was performed in the tension mode, under a steady load of 1.78 MPa and a dynamic stress of 1.98 MPa, under a nitrogen flow of 50 ml/min. The sweepings were made in the temperature interval of − 150 to 250 °C at a heating rate of 2 °C/min at a frequency of 5 Hz. The dimension of the samples used in the characterization by DMA was (4.8 × 10.0 × 0.65) mm.

2.5. Computer generated image of Scheme 2

For the simulation of the Pani molecule alone and solvated it was used the HYPERCHEM PRO-6 program, allowing the optimization of the distance between Pani and solvating NMP and water molecules, as well as Pani conformation.

3. Results and discussion

3.1. Thermogravimetric analysis (TGA)

Pani films, cast as described above were submitted to two series of thermal treatment: in the first the samples were annealed at 70 °C during 5, 15 min, 1 and 3.5 h. In the second treatment the films remained at 100 °C during 5, 15 min, 3.5 and 26 h. In Fig. 1 the corresponding thermogravimetric curves are shown. It was observed that the polymer undergoes three weight loss processes, which do not shift in temperature with the thermal treatment. The first loss, located in the range 20–120 °C, was attributed to the evolution of water molecules [2,3,6], the second in the range 120–250 °C was assigned to the loss of solvent and possibly to some water/NMP azeotrope, and the third, located at 250–360 °C is related to the release of NMP molecules hydrogen bonded to the amine groups of Pani. For films with 18% NMP Chen and Lee [1] reported that evaporation of NMP occurs in two stages, from 120 to 130 °C and from 240 to 480 °C. The TGA curves showed that the total weight loss was 15.95% for the as cast film and varied from 15.13% (5 min) to 9.89% (26 h) for the 100 °C regime and remained around 14.5% for the 70 °C regime.

In Fig. 1c the curves corresponding to the as cast films obtained with heating rates of 20, 2 °C/min (same as in DMA runs) and to the powder form of Pani (without residual NMP) are shown. It was observed that the curves related to different heating rates were comparable, although small differences appeared in the early stages of weight loss. On the other hand, the powder form showed only one weight loss process, which began at around 25 °C and went up to 150 °C. After this stage the sample weight remained essentially constant, with a weight loss of 1% in the range 150–370 °C. These results further corroborate the assignment of the second and the third weight losses of the cast films to processes involving NMP molecules.

3.2. Dynamic mechanical thermal analysis (DMTA)

Fig. 2 shows the variation of the loss modulus with annealing time for the two regimes (70 and 100 °C).

Three peaks can be clearly seen before the main transition at 100 °C: the first, in the −80 to −60 °C region (β), the second in the −20 to +2 °C (β′) and still another situated at 40–51 °C (β″). The β transition was also reported by Chen [1] for Pani films with NMP contents of

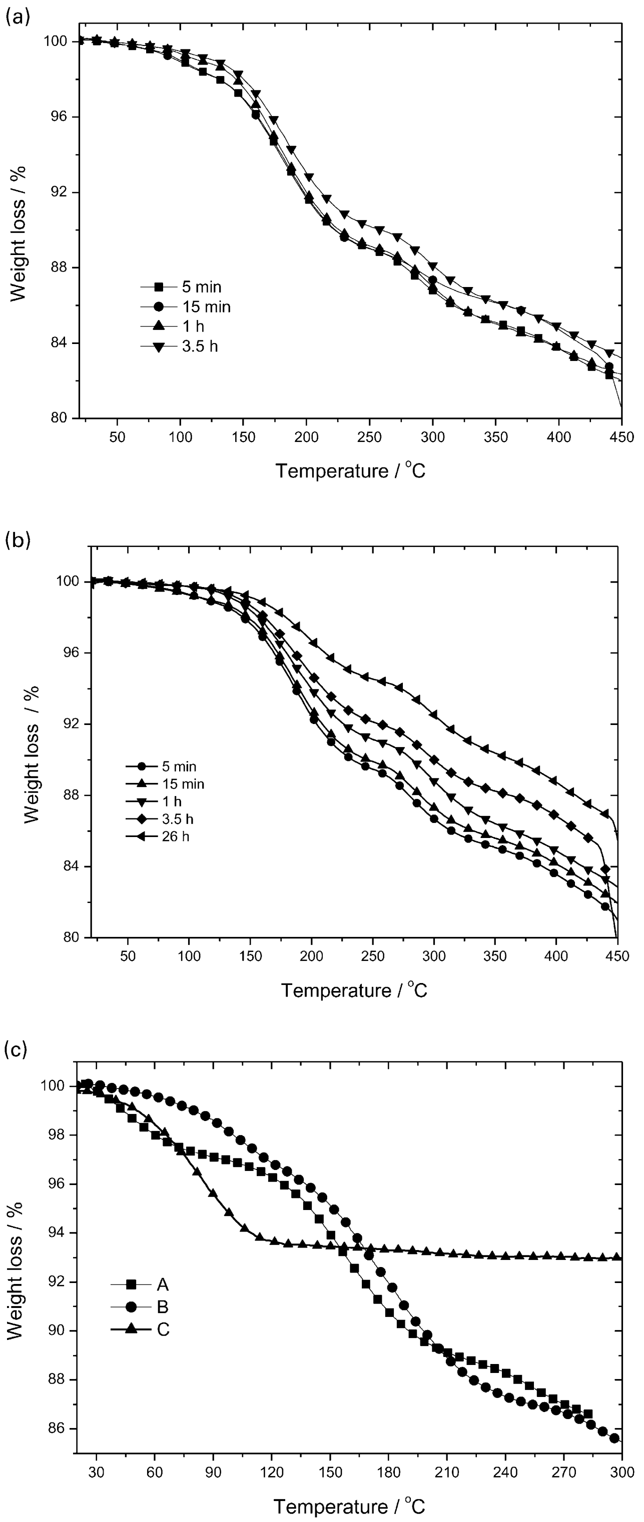


Fig. 1. TGA curves for Pani-EB: (a) films annealed at 70 °C, heating rate 20 °C/min; (b) films annealed at 100 °C, heating rate 20 °C/min; (c) as cast film, heating rate 20 °C/min (A), as cast film, heating rate 2 °C/min (B), and power, as precipitated from the reaction medium, heating rate 20 °C/min (C).

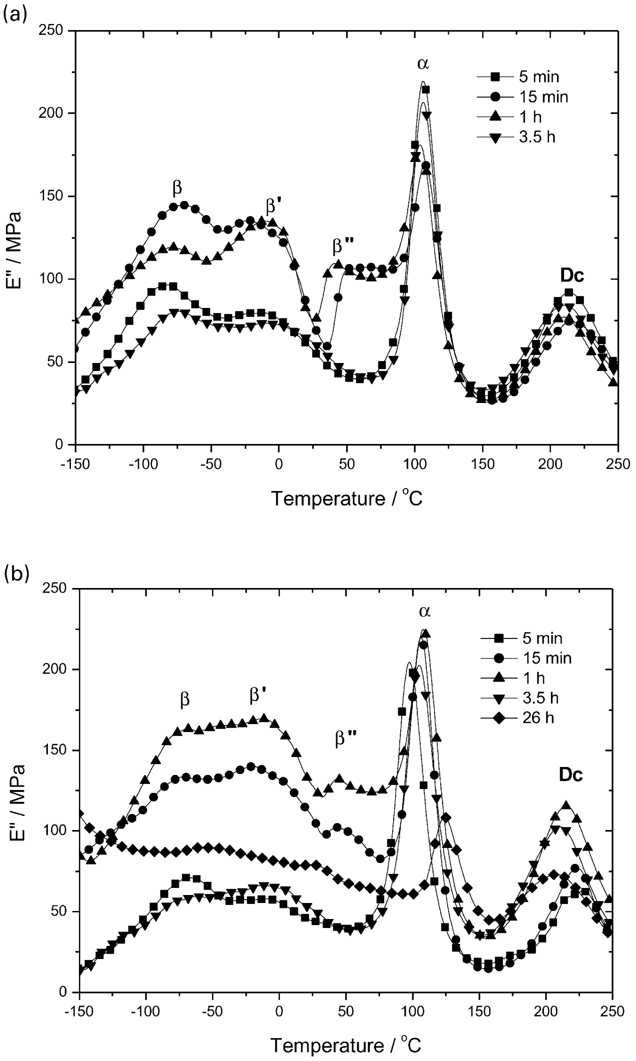
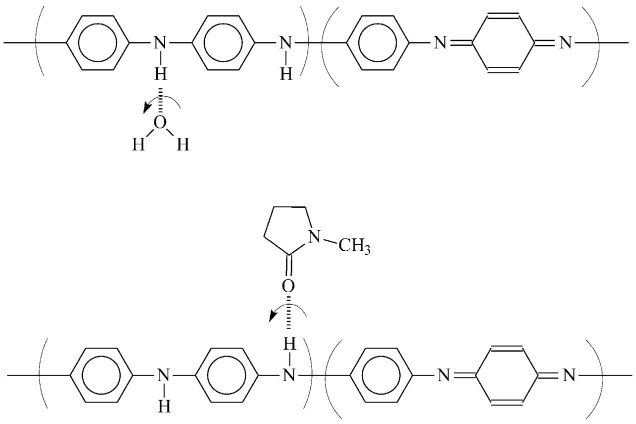


Fig. 2. Loss modulus E'' for Pani-EB films thermally annealed at 70 °C (a) and 100 °C (b).

18–10%, and increased progressively from −86 to −65 °C. Its origin has been attributed to local motions of amine groups. β′ and β″ transitions were not observed before, to our knowledge. The location of β′ and β″ is sensitive to the annealing time for each exposure temperature, and is summarized in Table 1.



Scheme 1. Interactions between Pani and the solvents.

It can be observed that for both annealing regimes β and β′ increase with time of exposure and are thus related with the residual amount of water/NMP in the films. This rules out the possibility of assignment of this relaxation to localized motions of the benzene rings solely, and indicates that other species are involved in these relaxations. One possibility could be the rotation of solvated amine groups as suggested by Chen [1]. Another one, which seemed us more plausible would be the rotation of water or NMP molecules which are hydrogen bonded to the macromolecular chain, in analogy of the model presented by Lesueur [31] to explain the transition at −80 °C found in the DMTA analysis of polypyrrol, as illustrated in Scheme 1. The existence of two forms of residual solvent (free and hydrogen bonded NMP) has also been discussed in a recent publication [32].

In such a model, water molecules act as side units of the polymer chain. Thus, when hydration degree increases, the interchain distance is enlarged and water molecule motions become easier. This may explain the shift of β peak towards the lowest temperatures with increasing water content. The same reasoning could be applied to explain the origin of β′ assuming that the transition is due to the motion of hydrogen bonded NMP molecules. For annealing times of 15 min and

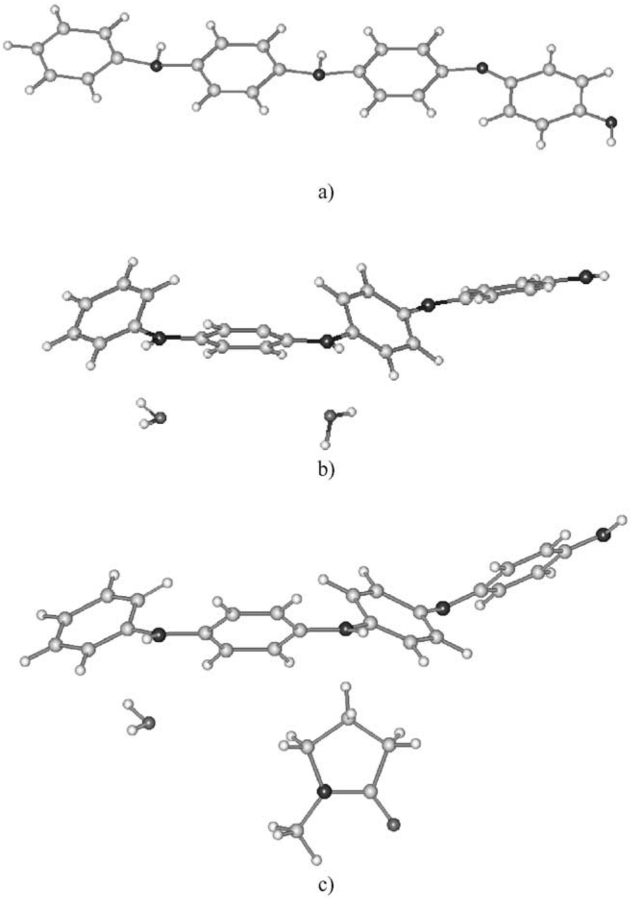
Table 1
DMTA thermal transitions of annealed Pani-EB

Sample	Transition (°C)									
	β-Transition		β′-Transition		β″-Transition		T_g		D_c	
As cast	−82.5		–		–		99.3		212.7	
Annealed	70 °C	100 °C	70 °C	100 °C	70 °C	100 °C	70 °C	100 °C	70 °C	100 °C
5 min	−81.5	−72.6	−13.9	−14.0	–	–	106.7	97.5	213.7	228.0
15 min	−76.0	−71.7	−12.1	−13.2	51.2	42.6	107.5	106.5	214.6	223.5
1 h	−75.5	−68.3	−10.2	−12.5	41.1	43.3	104.1	108.1	210.3	215.2
3.5 h	−72.0	−67.4	−7.2	−8.9	–	–	106.2	104.5	210.6	210.7
26 h	–	−55.1	–	–	–	–	–	124.0	–	207.7

1 h a transition is observed at 44–47 °C (β″). Its presence is reproducible in both annealing regimes. A similar transition was found for polypyrrol (named Ds) [31]. It could be guessed that its origin is correlated with a particular water/NMP composition, but its nature is still unknown. Comparing the DMTA curves for the treatments at 70 and 100 °C (Fig. 2 and Table 1) one can observe that the β transition values for the 100 °C treatment are higher than those of the corresponding to the 70 °C treatment. This agrees with the assumption that the transition is due to the rotation of bound water molecules, as already discussed, that is, higher hydration shifts β to lower temperatures. On the other hand, β′ values in the 100 °C regime are lower than those of the 70 °C treated samples. This could be explained by the following reasoning: the release of water molecules would provide more available sites for NMP solvation, resulting in a higher degree of solvation by NMP molecules in the more extensively dried samples, reducing β′. The peaks corresponding to β and β′ in the samples submitted to annealing at 100 °C are less resolved than those of the 70 °C, reflecting a broader degree of mixture of solvation states. The residual solvents exert a strong influence over the conformation of Pani-EB. In the computer-generated representation of the isolated molecule its conformation is essentially planar. When water or NMP molecules are put in the vicinity of the aminic nitrogen (in a distance optimized for the minimum energy situation) a dramatic deviation of planarity is observed, as illustrated in Scheme 2. One could speculate that these differences in conformation should influence the DMA response, but at present we do not have experimental evidence to access this possibility.

The glass transition temperature (α) remains more or less constant for samples annealed at 70 °C, but with long heating times (24 h, 100 °C) it undergoes a sharp rise indicating the evaporation of plasticizing NMP molecules. The last transition, located at the highest temperatures (D_c), assigned to crosslinking reactions, occurs at lower temperatures for the 70 °C annealed samples. The assignment of D_c to decomposition, as it is assumed in Ref. [6] was ruled out by the results of the TGA, since the powder sample remained stable up to around 400 °C, as shown in Fig. 1c(C). This relaxation has also been attributed to another glass transition temperature [4] resulting from the motion of chain segments between crosslinks. With increasing temperature, the chemical crosslinking starts to take place and results in a partially crosslinked Pani. This partial crosslinking restricts the mobility of the polymer molecules and decreases the free volume, resulting in a rubbery polymeric state, decreasing the ability of individual polymer chains to slip past each other. However, as the temperature continually increases, the increase in mobility of the molecular chains is greater than the growth of the formation of crosslinks, and a secondary glassy phase to rubbery phase transition occurs [4].

To gain further insight on the origin of the D_c transition, the following experiment was performed: a non-annealed sample was scanned, and after cooling to ambient temperature, the sample was re-run (with the obvious corrections for the new dimensions) at the same conditions previously used. The dramatic differences between the two resulting curves, shown in Fig. 3 can be described as: transition β″, which firstly appeared as a shoulder, is much more intense, transition α is not seen, and D_c, if present, is



Scheme 2. Effect of the solvent on the Pani conformation: (a) Pani-EB, (b) Pani-EB/H_2O and (c) Pani-EB/H_2O/NMP.

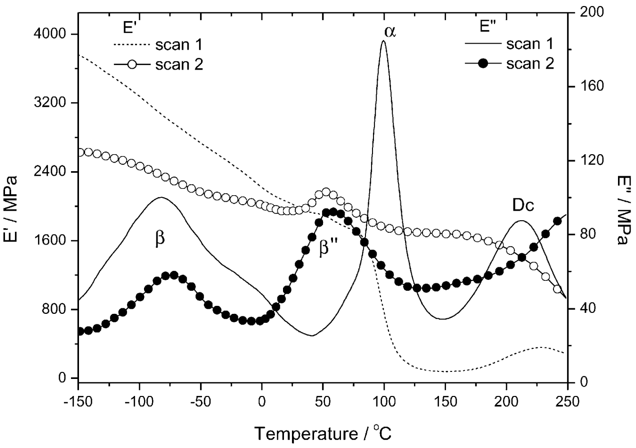
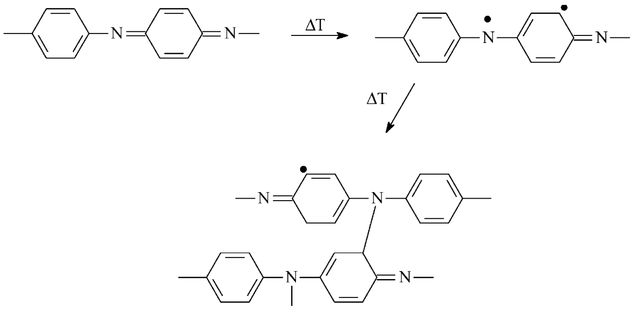


Fig. 3. Storage (E') and loss modulus (E'') for Pani-EB as cast film (first and second scan).



Scheme 3. Crosslinking process of Pani.

shifted to much higher temperatures. These results seems to corroborate the assumption that at D_c the sample suffers a crosslinking process, with no apparent weight loss, since at this temperature range no noticeable change in the thermogram is observed (Fig. 1c). In fact, the crosslinking of Pani can be described as illustrated in Scheme 3, and for each crosslink formed only two hydrogen atoms are released.

For the non-treated Pani (Fig. 3), the β relaxation is located at −82.5 °C and β′ is seen as a shoulder. The broadness of these peaks reflect different degrees of solvation in the as cast film. The glass transition appears at 99.3 °C in agreement with reported data for NMP plasticized Pani [2]. D_c is seen at 212.7 °C. It is noteworthy that after the second DMTA scan the Pani films turned insensitive to solvents, indicating that the chains became completely crosslinked.

In Fig. 4 the storage modulus (E') curves are shown. The sharp drop at around 100 °C characterizes the glass transition in agreement with E'' results of Fig. 2. An increase in initial moduli values with annealing time is noticed for both 70 and 100 °C regimes and this can be explained by the replacement of evaporated water molecules by NMP in the solvation sites, allowing a better alignment of polymer molecules, which in turn would increase the resistance in the direction of the applied stress, since DMTA was performed in the tension mode. In the extensively dried samples (100 °C for 24 h) the solvent induced molecular ordering no longer is possible and the storage modulus decreases significantly. The increase in storage modulus above the α transition is attributed to the release of solvent during the scan, since it occurs at the same temperature range where the second weight loss (attributed to solvent evaporation), is observed.

Fig. 5 shows the variation of the sample linear extension (ΔL) in function of the temperature. Two observations should be pointed out regarding the linear expansion with temperature: (1) the annealed samples presented a linear expansion with temperature as shown in Fig. 5 (curves B and C), whereas the non-treated sample (curve A) showed a deviation of this behavior, that is, a reduction in linear expansion was observed, beginning at 40 °C and peaking at 74.4 °C. (2) the rate of expansion for the annealed samples shows a deviation in slope at around −15 °C, in the β′

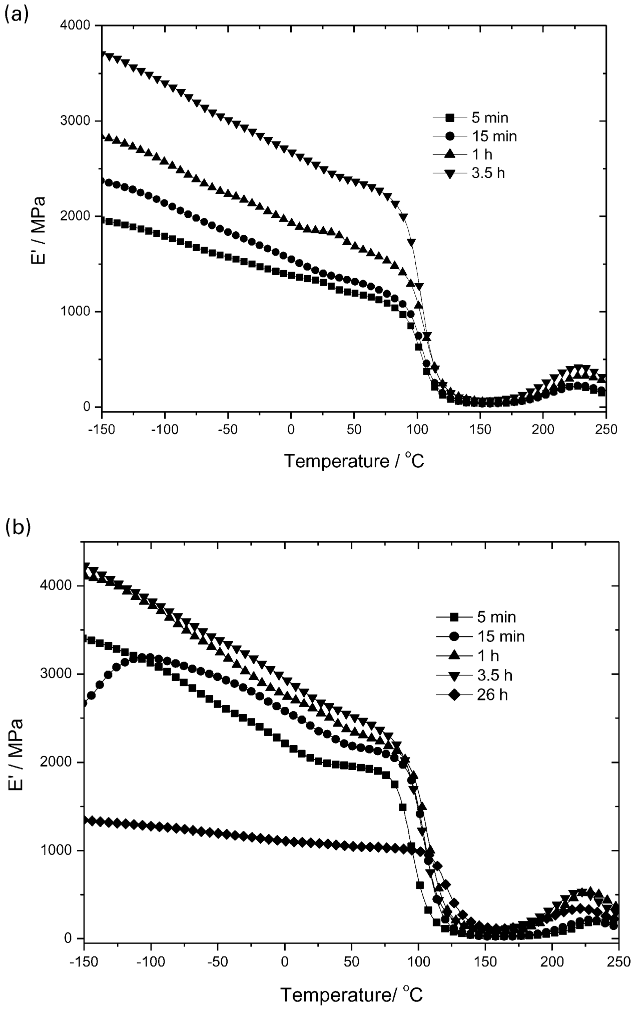


Fig. 4. Storage modulus for Pani-EB films thermally annealed at 70 °C (a) and at 100 °C (b).

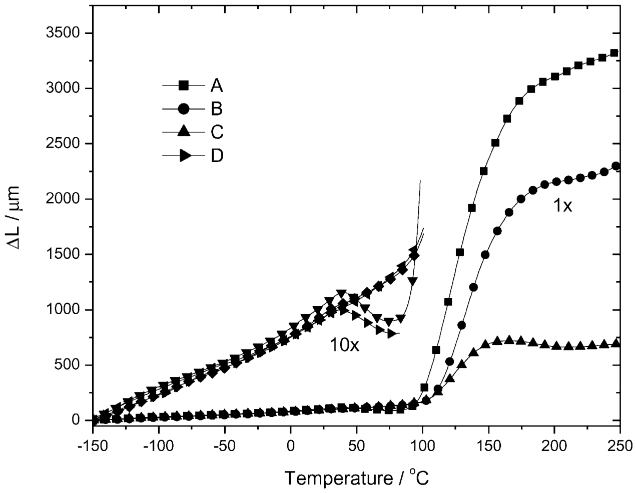


Fig. 5. Variation of the length with temperature for Pani-EB films. As cast film (A), films treated at 100 °C during 1 h (B), 3.5 h (C) and film (B) after exposure to ambient moisture (D).

region. These phenomena are related to the degree of solvation of Pani and are reversible. Curve D represents the behavior of the same sample used for curve B after exposure to ambient moisture during 4 days.

A rough estimate of the relative amounts of water and NMP can be made from the TGA scans. The weight loss of 3.65% at 120 °C suggests (by a trivial stoichiometry calculation) that each group of four aniline units is H-bonded with 1.5 water molecules, or with approximately 3 NMP molecules. With this result we could do calculations to evaluate the energetics of these H-bonded structures. We are aware that the proper procedure would involve optimization of a large number of conformers for the chain (one for each combination of the suitable dihedral angles between adjacent units), but at this point, for a first approach, we do not feel that this is necessary. With this reasoning, we optimized the geometry of a couple of complexes (the tetramer with one NMP molecule and with one water molecule) using AM1 semiempirical Hamiltonian [33]. The Schuster lengths have been frozen at 3.1 Å since it is well known that the H-bonds are not perfectly described by AM1 [33]. The optimized structures have the tilt angles close to 30°. This results matches that a recent X-ray diffraction study by Luzny et al. [13] as well as a detailed conformation analysis using AM1 [34]. The calculated energy of the H-bond between the tetramer and a water molecule is about 7.8 Kcal mol^{-1}, while the H-bond with NMP amounts to 9.8 Kcal mol^{-1}. This difference suggests that there is a preference for binding with NMP, which can be roughly estimated by assuming that there is only two possible states (tetramer H-bonded with NMP, and tetramer H-bonded with water). In a solvent mixture of NMP and water at 70 °C, the NMP forms H-bond with 95% of the available sites, and water forms H-bond with 5%. At 100 °C the ratio is very similar: NMP forms H-bonds with 93.7% of the available sites, and water forms H-bonded with 6.3%. Of course the actual situation is more complicated than that, as the actual polymer might present other features (e.g. non-bonded polymer, interchain linking). The above described calculation is given as first approach to quantify the results.

4. Conclusions

Thermal treatment is of prime importance in the performance of solvent cast Pani-EB films. The effects of residual water and solvent can induce modifications in the polymer structure leading to differences in polymer performance regarding to thermal mechanical responses. This implies that without a precise description of the conditions of film preparation the comparison of samples of different origin is of restricted meaning.

An assignment of distinct relaxation processes is proposed in which the solvent molecules act as side groups, with great distorting effect on the Pani-EB chains.

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