Thermal Dynamic Processing of Polyaniline with Dodecylbenzene Sulfonic Acid

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ABSTRACT: To attain an intrinsically conductive and processible polymer, polyaniline (PANI)/dodecylbenzene sulfonic acid (DBSA) blends of several compositions were processed at various elevated temperatures in a Brabender plastograph. The blends' temperatures during processing, as affected by the blends' composition and initial process temperature, were monitored. Accordingly, the process includes the following main stages: heating the blend, exothermic PANI-DBSA doping reaction accompanied by a paste to a solidlike transition, and plasticization of the resulting PANI/DBSA complex by the excess DBSA. Composition analysis of the process products sampled at the various stages showed that the initial blends, prior to their thermal processing, already consisted of partially doped PANI particles, having a core/shell structure; the core consists of $PANI_{base}$ and the shell of $PANI(DBSA)_{0.32}$ complex. In addition, at the paste-to-solidlike transition, the doping reaction is completed; further mixing does not affect the complex composition, but results in conductivity reduction. The morphology of the blends sampled at the various processing stages was studied by electron microscopy. From the conductivity and processibility point of view, optimal PANI/DBSA blend composition and processing temperature were identified. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 2199–2208, 1997

Key words: polyaniline; doping; thermal process; electrical conductivity

INTRODUCTION

The demand for electrically conducting processable materials having a combination of balanced mechanical properties, using conventional thermoplastic processing machines, is steadily increasing. To achieve such a goal, electrically conductive fillers, such as carbon black, metallic powders, and electrically conductive flakes and fibers (aluminum, carbon, stainless steel, etc.) have been used. Recently, the inherently conducting polymers (ICPs) are making their first steps

in such applications.[1] The specific processing method may have a dramatic effect on the electrical performance of the moldings obtained, thus a compound consisting of a polymer and a particulate-conducting filler may show significant conductivity in a compression molded part, but may perform as an insulator by injection molding. The ICP materials can often be dissolved with the matrix polymer in common solvents, followed by forming a thin liquid layer of the solution and evaporation of the solvent; this technique is suitable for the preparation of conductive thin films of polymer blends. The same compounds are usually unsuitable for melt processing due to insufficient thermal stability of the ICPs and lack of the fine dispersion, leading to the unique formation of con-

tinuous structuring and the derived conductivity characterizing the solution method.

Polyaniline (PANI), is normally available as a powder of an emeraldine salt doped with mineral acids, the conductivity of which is due to protonation of iminic nitrogen sites in an oxidation state. Such doped PANI materials are often insoluble in common solvents and decompose prior to melting and plastic flow. Actually, upon heating, PANI may undergo changes, generally leading to dedoping, up to the state of a fully dedoped emeraldine base, an insulative material.[2-5] Redoping of PANI with functionalized organic acids[6-8] results in doped PANI of better thermal stability, and processability both via solution casting from nonpolar or moderately polar organic solvents,[6-9] and melt processing.[10-12] Low PANI percolation concentrations (6–10 vol %), were reported for submicron PANI particles dispersed in polar matrices via melt blending.[13] An efficient doping method of PANI with dodecylbenzene sulfonic acid (DBSA), by refluxing followed by heating, was recently reported.[14] Such doping routes affect the stiff chain conformation into a more flexible one, which may enhance its crystallizability.[8,14,15] In another doping approach,[10-12] the PANI–DBSA compound was prepared in the absence of solvents by heating at elevated temperatures, namely through thermal doping. In both the solution and thermal processing, excess DBSA is necessary.[6-12] The complexation reaction exhibits an exothermic peak $\sim 150°C$ where the pastelike consistency transforms into a solidlike material. The peak location depends on the PANI/DBSA ratio. At the phase transition the conductivity increases from a level typical of ionic conduction of liquid DBSA to the level of an electronically conducting doped PANI, with a characteristic conductivity of 1–20 S/cm.[11,16,17] An important issue is the PANI/DBSA ratio regarding the conductivity level and material consistency achieved, despite the fact that a fully doped state conforms to a PANI/DBSA molar ratio of 1 : 0.5. By using an excess amount of DBSA, a plasticizing effect is actually realized, which eases melt processing, and can be followed by dynamic testing (T_g decreases with excess DBSA). For example, at a molar ratio of 1 : 0.7, the T_g is $\sim 135°C$, whereas without a DBSA excess, molar ratio 1 : 0.5, the T_g is $\sim 230°C$.[16,18,19] Another important finding is by X-ray studies,[10,17] revealing for the material after thermal doping (with excess DBSA presence) a layered structure with 2.7-nm spacing between layers, as opposed

to a three-dimensional close packing unit-cell structure. A layered structure obviously enhances processability. No layered crystalline structure is found in the absence of excess DBSA and the PANI(DBSA)$_{0.5}$ complex was therefore non-heat-processable.[10] However, a close examination of the published scientific literature and patents often seems to be rather confusing. The objective of the present study is to investigate the dynamic high-temperature doping process of PANI with DBSA and the associated reaction product transformations.

EXPERIMENTAL

PANI was produced on a pilot-plant scale in an aqueous sulfuric acid medium, using ammonium persulfate as an oxidant, by chemical oxidation polymerization yielding batches of 1–1.2 kg.[20] PANI emeraldine base powder (PANI-base) was prepared by dedoping the PANI-H$_2$SO$_4$ powder with ammonium hydroxide ($\sim 1\%$ aqueous solution) in a stirred reactor for 3 h. The dedoped material was precipitated, filtered, rinsed with water and acetone, and finally dried under vacuum at 40°C. Technical DBSA was used as received. A sample of dry PANI-base powder was mixed with a known quantity of DBSA until a pastelike consistency was achieved. A Brabender mixing head, maintained at a constant temperature, was charged with 30 g of the paste. The material's temperature in the mixing head was continuously recorded. The process was interrupted at different predetermined mixing times for sampling. The resulting reaction product at each stage was cooled to ambient temperature and ground, yielding a powder of PANI(DBSA)$_x$ complex with excess DBSA (DBSA$_{free}$). To investigate the stoichiometric ratio in a PANI(DBSA)$_x$ complex, a water-rinsing procedure to remove the excess DBSA was applied, leaving only the DBSA complexed with the PANI imine groups.[17]

Strips of the reaction products (12.0 × 1.3 × 0.25 cm) were prepared by room temperature compression molding at a pressure of 250–800 atm. Small strips of the washed complex (2.6 × 1.5 × 0.25 cm) were also prepared by room temperature compression molding at a pressure of 800 atm. The strips' conductivity was measured using a four-probe method. Depending on the resistivity level, either a Sorenson power supply (low resistivity) or a high, 240 V, voltage supply
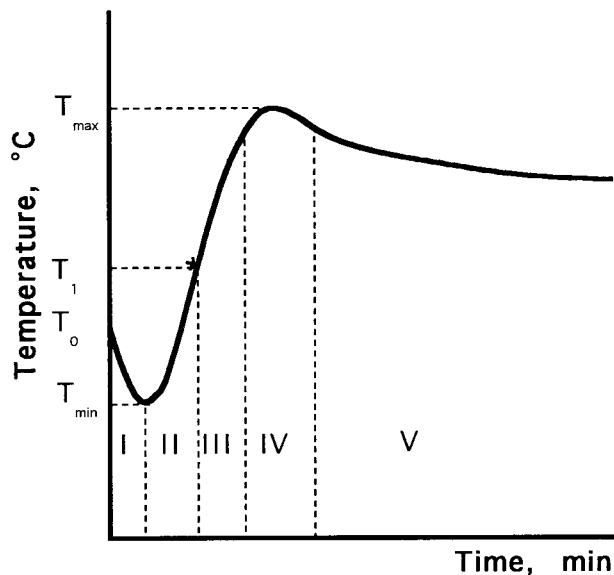
Figure 1 Schematic description of the temperature profile in a Brabender mixing head during the dynamic thermal processing of PANI/DBSA mixtures.

was used with a Keithley autoranging electrometer 175 (low resistivity) or Keithley electrometer 614. The morphology was studied using a Jeol 5400 scanning electron microscope (SEM).

RESULTS AND DISCUSSION

The starting material was a H_2SO_4-doped PANI (0.32 : 1 mole ratio), a dark green fine powder which may be compressed into a strip, exhibiting a conductivity of 0.2 S/cm. Dedoping yields a brown fine powder which was used for the present series of thermal dynamic doping experiments. The PANI/DBSA weight ratio in the premixed paste was 1 : 3, in the reported optimal ratio range.[10,11,17] Assuming a similar level of doping as in the initial H_2SO_4-doped PANI implies a PANI-$(DBSA)_x/DBSA_{free}$ ratio of 57 : 43, similar to the reported value of 56 : 44.[16,17,19]

The thermal process was carried out in a Brabender plastograph kept at a constant desired temperature, T_0. The thermal process may be divided, according to changes in the material's temperature (measured at the mixing head inner wall), into the following stages (Fig. 1): In the first stage (stage I), the initial temperature decreased to T_{min}, as a result of charging the paste, followed by a temperature rise to T_1 ($>T_0$) at which the paste was observed to transform into a

semi-solid state (stage II). At this point the temperature rise was accelerated (stage III), peaking at T_{max} (stage IV). During the following continuous mixing (stage V) the temperature decreased, attaining a steady state value, significantly higher than T_0. It should be mentioned that upon the cessation of mixing during any of the last two stages, the material's temperature dropped to T_0. Hence, the exothermic doping reaction was practically completed prior to stage III and the stage III–IV temperatures are only determined by T_0 and the excess heat generated due to the mixing. The Brabender torque during the first three process stages increased with mixing time, reaching its upper limit; the material's temperature at that point, T_2, was recorded. Therefore, as seen in Figure 2, in the low initial temperature experiments ($T_0 < 132°C$) the process could not be continued all the way through, and even the exothermic peak (stage IV) could not be reached. In the high initial temperature experiments ($T_0 > 140°C$), however, the process could be continued as desired. Interestingly, the value of $T_2 - T_0$ was found to be approximately constant for all experiments (Fig. 3).

As can be seen in Figure 3, the transition temperature from a paste to a "solid," T_1, and the peak temperature, T_{max}, both increase with increasing the initial process temperature, T_0. As will be discussed below, the optimal value of T_1, as the end product's conductivity is concerned, for the 1 : 3 PANI/DBSA system and the presently used mixing conditions is 143°C, in agreement with reported thermoelastic measurements.[16] Fig-
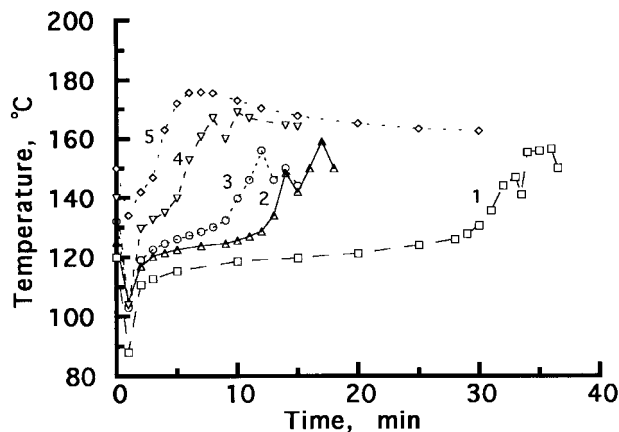

Figure 2 Temperature profiles in a Brabender mixing head during the dynamic thermal processing of a 1 : 3 PANI/DBSA mixture, at an initial temperature of (1) 120, (2) 125, (3) 132, (4) 140, and (5) 150°C.
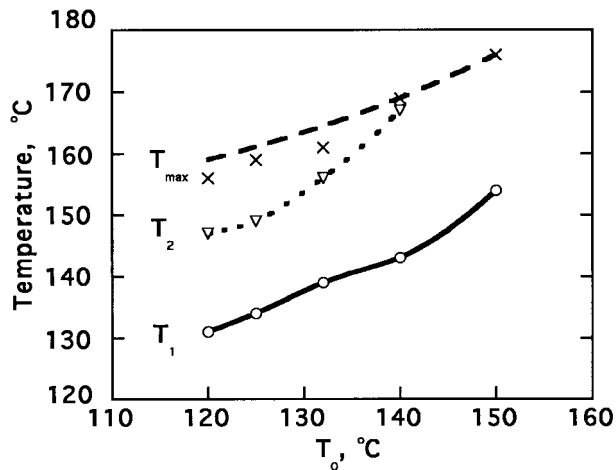
Figure 3 Characteristic temperatures of the dynamic thermal process of a 1 : 3 PANI/DBSA mixture, as affected by the initial process temperature, T_0.

ure 4 depicts the effect of PANI/DBSA ratio on the material's temperature in the Brabender chamber during the thermal doping process for $T_0 = 140°C$. Increasing the ratio from 1 : 3 to 1 : 2 does not significantly affect the solidification temperature. However, the maximal exothermic temperature is substantially higher, i.e., 14°C, for the 1 : 2.5 PANI/DBSA system than for the other two compositions. The low DBSA (1 : 2) containing system was transformed into a powder immediately after the paste-to-solid transition and, therefore, its temperature decreased upon further mixing, attaining a steady-state temperature of T_0 and, thus, exhibiting a relatively low T_{max} value. The lower T_{max} value for the higher DBSA-containing system (1 : 3 as compared to 1 : 2.5), is a result of the DBSA plasticization effect. In addition, reduction of the DBSA content resulted in a significant increase of T_{min} to the point that, for the 1 : 2 system, stage I and stage II of the process were almost indistinguishable.

To study the material's doping progression during the thermal dynamic process, the latter was interrupted at different stages for sampling. The initial premixed paste did not consist of any neat PANI-base particles, but rather particles with bound DBSA, as evident by the dry particles' weight following water wash. A 1 : 0.28 PANI/DBSA ratio was found in the as prepared paste and 1 : 0.30 and 1 : 0.32 PANI/DBSA ratio in pastes stored at ambient temperature for a day and 2 weeks, respectively. SEM micrographs (Fig. 5) show a different appearance of the washed pre-

mixed paste particles when compared to the PANI-base particles; it appears as if the PANI particles are just externally coated. It is, therefore, proposed that the particles in the initial paste have a core/shell structure. The shell, 35−40 wt % of the material, consists of a fully doped conducting PANI(DBSA)$_x$, engulfing the insulating PANI-base core particles. This washed fine bluish powder, actually a blend of PANI-base and PANI-doped, exhibits a conductivity of 6.3×10^{-3} S/cm.

Following charging of the Brabender mixing head, preheated to a desired temperature, with this premixed paste, the paste temperature increases and the thermal doping reaction, accompanied by heat generation, takes place (stage II), yielding a fully doped PANI(DBSA)$_x$ complex. As mentioned above, when T_1 is reached, the PANI-(DBSA)$_x$ and DBSA$_{free}$ mixture turned into a semisolid state consistency, resulting in a marked torque increase. All samplings during stages III−V, for all the T_0 and initial PANI/DBSA ratio (1 : 2−1 : 3), were found (Table I), following the removal of the free DBSA, to be represented by complex PANI(DBSA)$_x$, with an average x value of 0.32 (rather than the theoretical value of 0.5), a doping level close to that of the original PANI-(H$_2$SO$_4$)$_{0.316}$. Hence, the chemical reaction between PANI-base and DBSA was completed already in the beginning of stage III of the process,
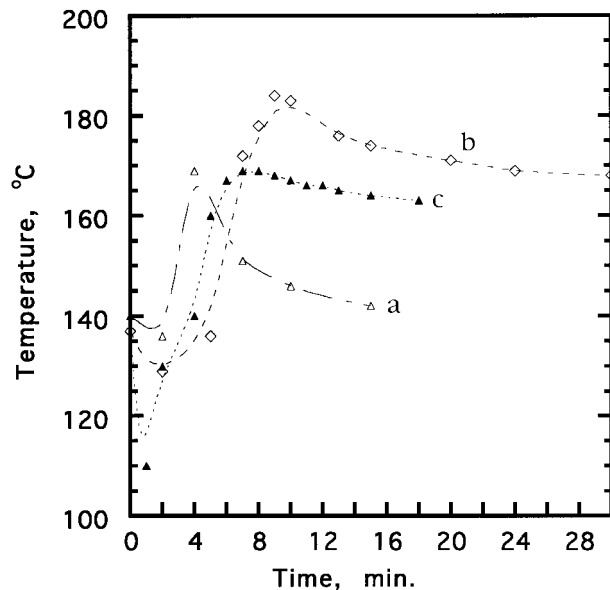

Figure 4 Temperature profiles in a Brabender mixing head during the dynamic thermal processing at T_0 = 140°C of (a) 1 : 2, (b) 1 : 2.5, and (c) 1 : 3 weight ratio PANI/DBSA mixtures.
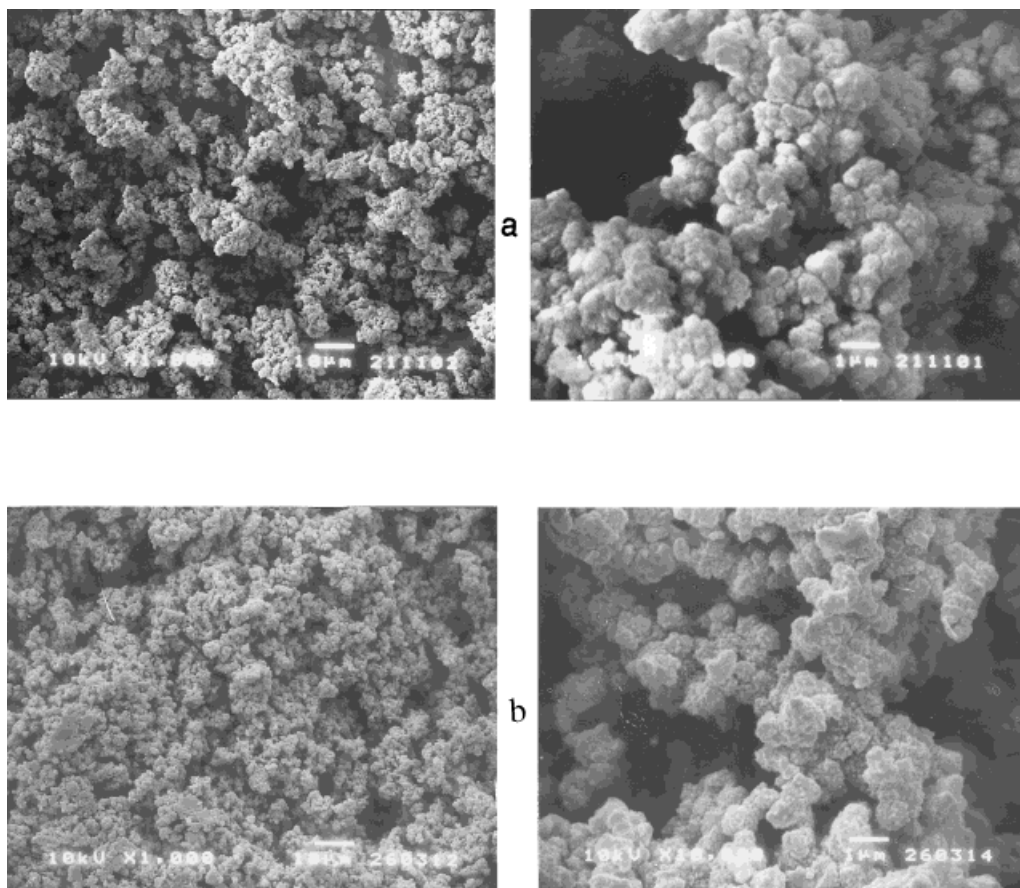
Figure 5 SEM micrographs of (a) PANI-base and (b) PANI-base/PANI(DBSA)$_{0.32}$ mixtures (initial paste, prior to thermal processing, of a 1 : 3 PANI/DBSA weight ratio, after the removal of DBSA$_{free}$).

Table I   Results After Water Extraction

PANI/DBSA (weight ratio)	Conductivity Before Washing (S/cm)	T_0 (°C)	Process Stage	Final DBSA Content (molar fraction)	Conductivity After Washing (S/cm)
1 : 3	0.074	120	III	0.36	0.19
1 : 3	0.20	125	III	0.37	0.53
1 : 3	0.50	132	III	0.37	1.30
1 : 3[a]	8.00	140	III	0.32	0.92
1 : 3	13.00	140	III	0.33	1.10
1 : 3	1.50	140	IV	0.36	0.49
1 : 3	0.10	140	V	0.34	0.18
1 : 3	7.00	150	III	0.34	1.10
1 : 3	0.30	150	IV	0.32	0.41
1 : 3	0.0005	150	V	0.36	0.08
1 : 2.5	0.0003	140	V	0.31	0.01
1 : 2	0.10	140	III	0.35	0.21

[a] Product sampled at $T_1 = 143°C$.

Table II   Plasticization of a 57 : 43 PANI(DBSA)$_{0.32}$/DBSA$_{free}$ Mixture During Dynamic Thermal Processing

T_0 (°C)	Sampling	Product Appearance	Softening Ability	Molding Pressure (atm)	Conductivity (S/cm)
140	III	green fine powder	weak sintering	550[a]	13.0
140	IV	gray fine rubberlike powder	sintering	275	1.5
140	V	gray rubberlike powder	strong sintering	275	0.1
150	III	green fine powder	weak sintering	485[a]	7.0
150	IV	gray rubberlike powder	plastic flow	315	0.3
150	V	black rubberlike worms	plastic flow	275	0.0005

[a] Brittle molded strips.

as also suggested above, based on the material's recorded temperature. Beyond this stage, at $T > T_1$, plasticization of the doped PANI by the DBSA$_{free}$ is the main process taking place. Hence, the accelerated material's temperature rise to T_{max} is mainly determined by heat generation accompanying the resulting high torque during mixing of the very viscous material, in addition to the heat generated during the chemical doping reaction.
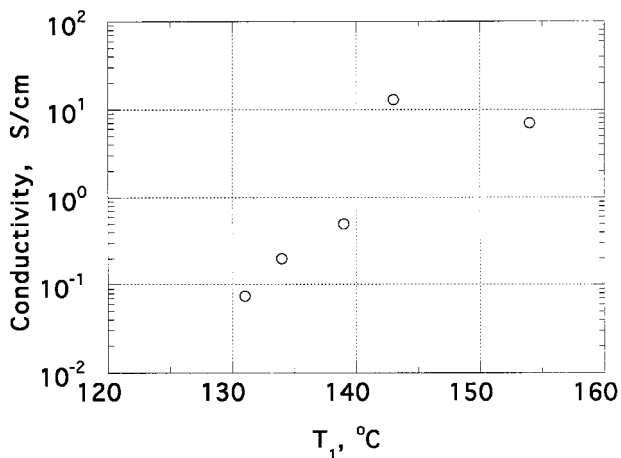
The consistency of stage III material was that

Figure 6   The conductivity of 57 : 43 PANI(DBSA)$_{0.32}$/DBSA$_{free}$ weight ratio mixtures, sampled at stage III, as affected by the paste-to-solid transition temperature, T_1.

of a brittle "fused" cake, which was easily stripped of the mixing head walls. After grinding, the fine green powder could be compressed into a strip, for conductivity measurements, only under a relatively high pressure. Quite different was the cake obtained at stage V for the 1 : 3 ($T_0 = 150$°C) and 1 : 2.5 ($T_0 = 140$°C) PANI/DBSA systems. These cakes appeared softer and more ductile and their stripping off from the mixing head was quite difficult. Upon grinding at ambient temperature, chopped rubbery particles, rather than brittle powder, resulted, which could be compressed into a strip already at a relatively low pressure. Upon aging at ambient temperature some of the free DBSA exuded to the sample's surface. It should be mentioned that stage IV material exhibited an intermediate behavior. It can, therefore, be concluded that the plasticity of the reaction products [blends of PANI(DBSA)$_{0.32}$ complex with DBSA$_{free}$] is quite high in systems which underwent the exothermic peak temperature, hence, doped and plasticized. Moreover, the conductivity of the reaction products depends on the material's transformation at T_1 and its plasticity. Interestingly, the conductivity of samples prepared at T_0 of 140 and 150°C and which experienced T_{max}, is drastically reduced upon continuation of mixing from stage III to stage V (Table II). In an attempt to clarify the cause for this conductivity reduction, reaction products sampled at stages III and IV (T_0 of 140 and 150°C) were annealed in an air oven at 170°C for 30 min. This thermal treatment resulted in
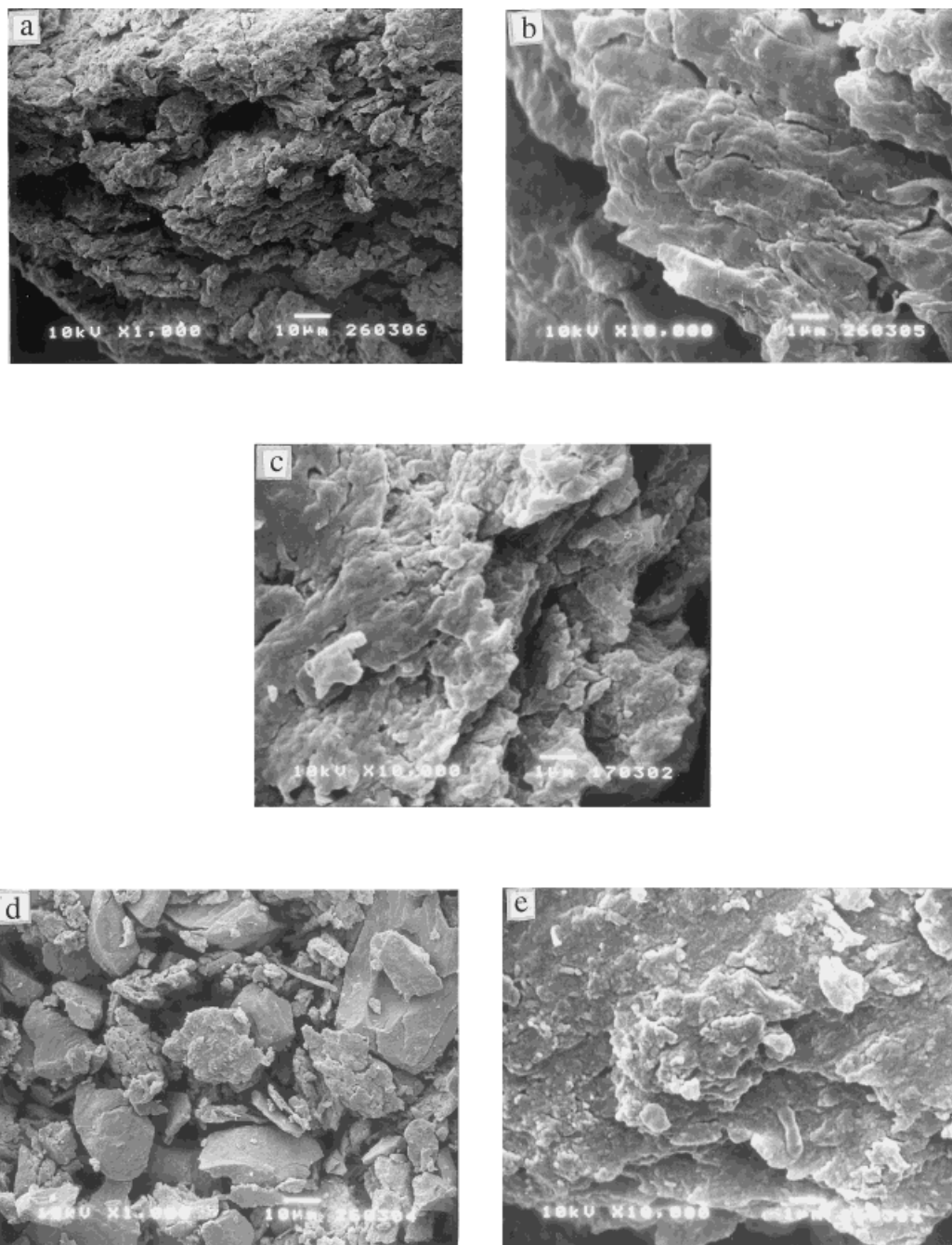
Figure 7 SEM micrographs of PANI(DBSA)$_{0.32}$ complexes sampled at stage (a,b) III, (c) IV, and (d,e) V of the thermal process, after the removal of DBSA$_{free}$ (initial 1 : 3 PANI/DBSA weight ratio; initial process temperature $T_0 = 140°C$).

an insignificant reduction in conductivity and a weight loss of 14%, presumably due to water evaporation. Following 2 weeks of storing the annealed samples at ambient conditions, most of the conductivity loss was regained, probably due to moisture absorption. The partial conductivity loss during the process stages beyond stage III, not directly related to just annealing, may stem from exudation of the excess DBSA to the particles' surface. As seen in Figure 6, the conductivity of stage III material attains a maximum value for the $T_1 = 143°C$ sample. This temperature is in agreement
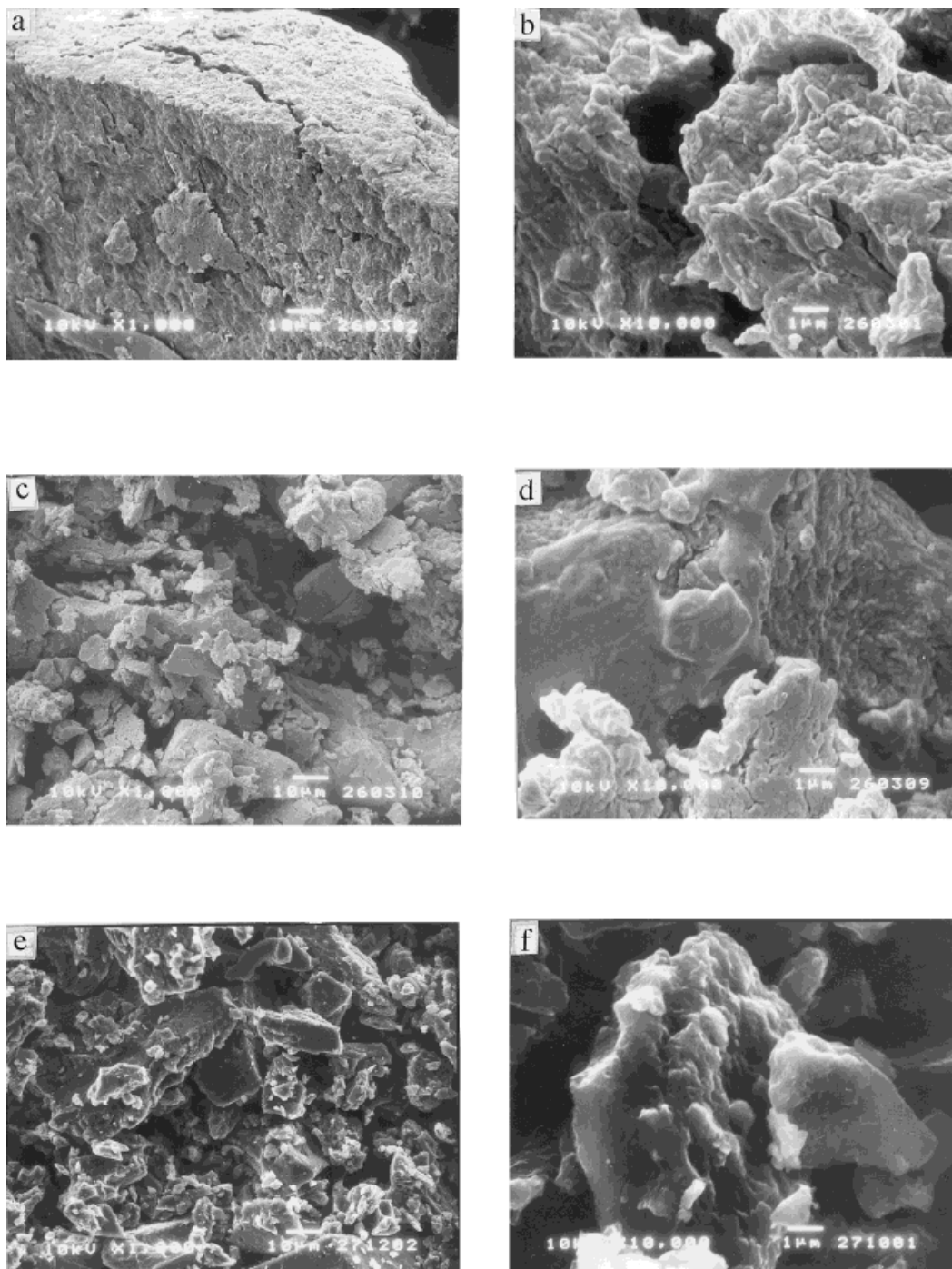
Figure 8   SEM micrographs of PANI(DBSA)$_{0.32}$ complexes sampled at stage (a,b) III, (c,d) IV, and (e, f) V of the thermal process, after the removal of DBSA$_{free}$ (initial 1 : 3 PANI/DBSA weight ratio; initial process temperature $T_0 = 150°C$).

with the temperature of transition to a conducting solid for a 1 : 3 PANI/DBSA system.[16]

It should be emphasized that the same conductivity reduction, as a result of mixing during the process stages IV and V, was also observed as a result of rinsing the DBSA$_{free}$, attaining a "neat" doped PANI (Table I). Thus, the conductivity of the reaction products was changed upon the re-

moval of the $DBSA_{free}$. Interestingly, also for the washed (excess DBSA free) doped PANI samples, the maximal conductivity was obtained for the sample which exhibited a transition temperature, T_1, in the optimal range of 139–143°C. Moreover, the presence of $DBSA_{free}$ in the reaction products prepared at nonoptimal temperatures and/or PANI/DBSA ratios reduces the conductivity compared to that of the washed $PANI(DBSA)_{0.32}$ complex (Table I).

As seen in Table I, the reaction product sampled at the transition temperature, $T_1 = 143$°C, was already a fully doped, conducting PANI(D-BSA)$_{0.32}$ complex and had, in the presence of excess DBSA, all characteristics of the solid material obtained in stage III of the thermal processes operated at all studied T_0 values. It seems, therefore, that most, if not all, the doping process was practically completed in stage II, before reaching T_1, and during further mixing, stages III through V, the complex is just being plasticized by the free DBSA. The complex by itself, after removal of $DBSA_{free}$, does not soften up to at least 230°C, whereas the reaction products of stages IV and V exhibit softening in the range of 145–150°C. A glass transition temperature of 133°C was reported[18] for a 1 : 2.5 PANI/DBSA system. It should be mentioned that in addition to the plasticization process, the complex may undergo some further changes during stages IV and V, as evidenced by the decreasing conductivity exhibited by materials sampled at these stages of the process (see Tables I and II). The plasticization process is reflected in the product morphology after the $DBSA_{free}$ removal (Figs. 7 and 8). The higher the doping temperature and the longer the mixing, the doped PANI seems better packed and more uniform; its appearance indicates that it underwent more ductile deformation. After de-doping the morphology of the resulting PANI-base was unchanged, similar to that of the material which underwent the above described transformation during the dynamic thermal doping and plasticization processes, as depicted in Figures 7 and 8.

The temperature changes of the material, recorded during the thermal doping process, are mainly a result of two processes, namely, chemical exothermic doping reaction and heat-generating shear mixing. Since the resulting composition of all doped PANI complexes is practically constant, the contribution of the doping reaction heat is similar in all the presently studied experiments.

As the PANI/DBSA ratio increases, corresponding to lower $DBSA_{free}$ content, T_{max} increases due to the higher heat generated by the mixing. Similarly, using a lower initial temperature, T_0, results in lower T_1 values, sharply increasing the viscosity of the reaction products and, thus, the resultant torque required for further mixing.

CONCLUSIONS

The thermal dynamic processing of PANI/DBSA mixtures results in a "fully" doped PANI already at a stage prior to the paste to solid consistency transition, at $T < T_1$. Plasticization of the fully doped PANI occurs upon further blending at $T > T_1$. Increasing the mixing duration, beyond doping, results in products of higher plasticity and lower conductivity. The optimal doping temperature, as far as the end product's conductivity is concerned, is mainly determined by the PANI/DBSA ratio, decreasing with increasing the PANI content. The peak material's temperature is determined by the process initial temperature, the doping heat of reaction, and the heat evolved due to shearing. The results of the present article are of technological interest and should be considered in the design of efficient industrial PANI thermal dynamic doping processes.

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