

## Preparation of conducting polysiloxane/polyaniline composites

Katarzyna Depa,<sup>1</sup> Adam Strachota,<sup>1</sup> Jaroslav Stejskal,<sup>1</sup> Patrycja Bober,<sup>1</sup> Věra Cimrová,<sup>1</sup> Jan Prokeš,<sup>2</sup> Miroslava Trchová,<sup>1</sup> Miroslav Šlouf,<sup>1</sup> Jiří Hodan<sup>1</sup>

<sup>1</sup>Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovsky sq. 2, 162 06 Prague 6, Czech Republic

<sup>2</sup>Faculty of Mathematics and Physics, Charles University in Prague, V Holešovičkách 2, 180 00 Prague 8, Czech Republic

Correspondence to: A. Strachota (E-mail: strachota@imc.cas.cz)

**ABSTRACT:** Polysiloxane/polyaniline microcomposites were prepared, in which polyaniline particles act as filler, thus combining the mechanical properties of polysiloxane matrix with conductivity of polyaniline. Two syntheses were evaluated: (1) homogeneous dispersion of a polyaniline colloid in the reaction mixture from which the polysiloxane matrix subsequently formed, and (2) the blending of previously prepared dry polyaniline particles with a liquid oligomeric siloxane resin followed by cure (“heterogeneous method”). Both methods lead to composites with evenly distributed filler. Electrical conductivity was achieved above 40 wt % of polyaniline, which is better obtained by the “heterogeneous” method. During the composite cure, the polyaniline particles, which are softer than the matrix, act as a catalyst and cause more efficient matrix crosslinking, thus leading to somewhat raised moduli. Although particulate fillers usually deteriorate the impact toughness, in the case of the prepared composites, the impact toughness was preserved due to the softer consistence of the filler, which hinders crack propagation. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2015, 132, 42429.

**KEYWORDS:** coatings; composites; conducting polymers; synthesis and processing

Received 5 January 2015; accepted 27 April 2015

DOI: 10.1002/app.42429

### INTRODUCTION

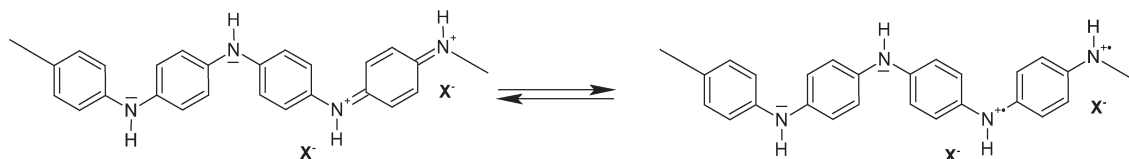
Polyaniline (PANI) is one of the most popular electrically conducting polymers and attracts considerable research interest since the late 1980s. It is characterized by a high conductivity in the partly oxidized and protonated emeraldine state<sup>1,2</sup> (Scheme 1), where the unpaired electrons, polarons, act as charge carriers. Polyaniline ranks among the semi-flexible rod polymers and its processibility is limited, except for a few cases reported in the literature.<sup>3–5</sup>

Polyaniline is conveniently prepared by the oxidation of the inexpensive aniline monomer with suitable oxidants, such as ammonium peroxydisulfate.<sup>6</sup> The oxidation mechanism is relatively complex<sup>7</sup> and includes aniline radical cations which further react to oligomers and finally to polyaniline. A unique feature of polyaniline is, that it can occur in three idealized oxidation states<sup>8,9</sup>: colorless leucoemeraldine, the partly oxidized emeraldine (green salt or blue base) or the fully oxidized pernigraniline (blue salt or violet base). The partly oxidized emeraldine in the salt form is an electric semiconductor, while all other forms are non-conducting. Although polyaniline can be oxidized up to pernigraniline, it is resistant to degradative oxidation.<sup>10</sup> The pH-dependent redox- and optical (color) switch-

ing makes polyaniline attractive for applications like acidobasic sensors,<sup>11</sup> for detections of gases, for example, ammonia,<sup>12,13</sup> or atmospheric humidity,<sup>14</sup> or of biologically active compounds.<sup>4</sup> The redox chemistry also makes polyaniline an attractive material for supercapacitors.<sup>15–17</sup> Due to its conductivity, reducing ability, and its content of mobile counter-ions, the polyaniline is applicable in corrosion protection of metals, for example, for steel, either as neat polyaniline,<sup>18–20</sup> or as additive in coatings.<sup>21–23</sup> Also non-ferrous metals like Ag, Cu<sup>24</sup> or Al<sup>25</sup> can be protected by polyaniline.

Polysiloxane resins (also called silicone- or polysilsesquioxane resins; see Scheme 2), are silicon–organic thermosets. These compounds were first described in 1901, and they gained practical importance after the development of the Müller-Rochow synthesis (in 1940) of the polysiloxane precursors, the methylchlorosilanes.

The thermo-mechanical properties of the polysiloxanes can be widely varied by the choice and the ratio of linear and branching comonomers. In contrast to the related silicone oils, which are typically prepared by anionic ring-opening polymerization,<sup>26</sup> the polysiloxane resins are usually produced by the so-called **sol-gel process** of suitable silicon compounds, such as chlorides



**Scheme 1.** Molecular structure of polyaniline (emeraldine salt form).  $X^-$  is an arbitrary counter-ion.

or alkoxides, with final cure via annealing at moderate temperatures. The latter process starts with hydrolysis of dissolved monomers to silanols, followed by their condensation, which results in the formation of gels or colloids.<sup>27</sup> Since the 1980's, the sol-gel process became a popular synthetic route to inorganic and organic-inorganic hybrid materials, or to ceramics (cold synthesis), starting from silicon- and/or from other metalloid- or metal alkoxides.<sup>28–30</sup> Analogous reactions of alkoxy-silane-terminated organic monomers or macromonomers,<sup>31–33</sup> or of OH-functional oligomers with alkoxy-silanes<sup>34</sup> yield hybrid organic-inorganic copolymers with tunable properties. In the case of the sol-gel process of alkoxy-silanes, which was also employed in this work (see Scheme 5 further below), the nature of the catalyst and water concentration are the most important synthesis factors.<sup>35–37</sup> The acidic catalysis<sup>38–40</sup> leads to moderately branched products with unreacted hydroxyl groups in early and medium reaction stages. Such intermediates can be isolated and stored as liquid “precursor resins,”<sup>41</sup> prior to final cure by polycondensation. In contrast to this, the alkaline catalysis<sup>42,43</sup> is known to yield compact and highly condensed polysiloxane particles in early reaction stages, which subsequently precipitate. The latter effect can be of use for the preparation of well-defined silica or of polysiloxane nano- and micro-particles.<sup>44</sup>

The polysiloxane resins are typically heat- and acid-resistant and find numerous applications,<sup>45,46</sup> for example as electrical insulation, electronics coatings (demanding applications,  $T = -65$  to  $315^\circ\text{C}$ ), hydrophobic glass coating, as matrix in laminates and particulate-filler composites; elastomeric polysiloxane resins are attractive materials for rubber molds. An important application is the use of polysiloxane resins in varnishes and paints (sometimes in the form of blends with other polymers), also for coating of metals, which is related to the topic of this work.

Only very few papers have been published so far about polysiloxane-polyaniline composites, which are studied in this work. The mentioned publications were concerned with the electromechanical response of elastomeric crosslinked polydimethylsiloxane with polyaniline nanofiller.<sup>47–49</sup> Distantly related systems, which employed a different matrix or a different filler, have been investigated as anticorrosive coating<sup>50</sup> or as elastic and inert electrode for neural stimulation.<sup>51</sup> Attractive applications of polyaniline composites with polymeric matrices include pH sensors (polyvinylbutyral/PANI<sup>52</sup>), polyaniline/graphene nano-sandwiches with valuable electrochemical properties,<sup>53</sup> or protective coatings.<sup>21,22</sup>

In their previous work, some of the authors investigated synthesis routes to PANI,<sup>6,7,9,54</sup> its properties<sup>9,10</sup> and its potential applications,<sup>13,23</sup> in another, they optimized the synthesis of polysiloxanes, which were subsequently pyrolyzed to silicon oxy-

carbide glasses.<sup>41,55–57</sup> As part of the latter investigations, the authors also prepared polysiloxane composites with epoxy powder as a sacrificial organic filler,<sup>58</sup> in order to obtain highly porous pyrolytic SiOC foams as final product.

The aim of this study was to use the experience gained in the authors' previous work, in order to prepare polysiloxane/PANI composites, which would combine the conductivity and the anti-corrosion effect of the polyaniline filler with the mechanical properties and the thermal and chemical stability of polysiloxane thermosets, envisaging a future potential application as protective coating.

## EXPERIMENTAL

### Polyaniline Powder Synthesis

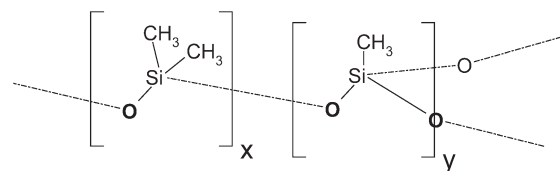
Polyaniline powder was prepared at room temperature with a standard procedure<sup>6</sup> by oxidizing 0.2M aniline hydrochloride (Fluka, Switzerland) with 0.25M ammonium peroxydisulfate (APS; Lach-Ner, Czech Republic) in water (Scheme 3). The polymerization of aniline was completed within tens of minutes; the mixture was left to stand at room temperature for 24 h. The green solids were collected on a filter, rinsed with 0.2M hydrochloric acid, acetone, and dried at room temperature over silica gel.

### Polyaniline Colloid Solution in Water

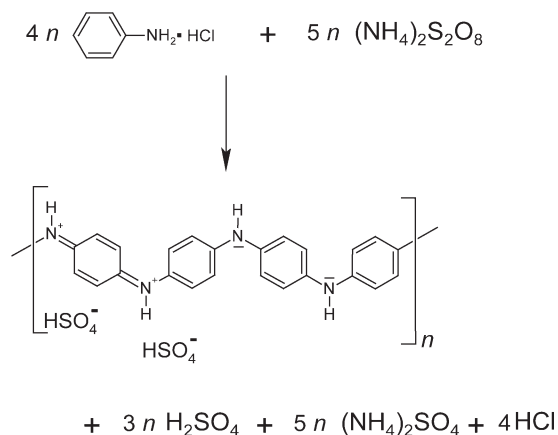
Colloidal polyaniline dispersions (Scheme 4) were prepared by the oxidation of 0.2M aniline hydrochloride with 0.25M ammonium peroxydisulfate in the presence of 2 wt % of poly(*N*-vinylpyrrolidone) (PVP; Type K-90, Fluka, Switzerland) in water at room temperature.<sup>54</sup> The volume of the reaction mixture was 100 mL. The resulting dark green aqueous colloid contains 2 wt % polyaniline and 2 wt % PVP. For some experiments, polyaniline colloids with 4 and 6 wt % concentration of polyaniline were prepared by gradual water evaporation via bubbling of air through the solutions and solvent mass-loss determination.

### Neat Liquid Siloxane Resin Preparation (Precursor Resin<sup>41</sup>)

Triethoxymethylsilane (T), dimethyldiethoxysilane (D), sulfuric acid and sodium hydrogen carbonate were purchased from Sigma-Aldrich and used as received without further purification. Triethoxy(methyl)silane and dimethyldiethoxysilane were mixed, (Table I) and the necessary amount of water containing



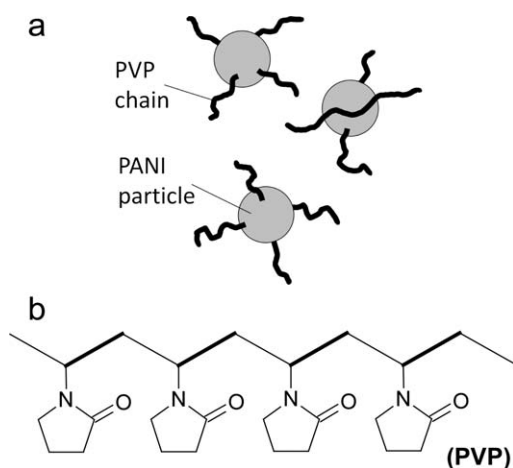
**Scheme 2.** Example of a polysiloxane resin: The random copolymer  $[\text{Si}(\text{CH}_3)_2\text{O}]_x[\text{Si}(\text{CH}_3)_3\text{O}]_y$ .



**Scheme 3.** Polyaniline synthesis via oxidation of aniline with peroxydisulfate in acidic conditions.

4 wt % sulfuric acid as catalyst was added. The mixture, originally separated in aqueous and organic phases, was stirred without heating for 10 min. During that time, at one moment a complete homogenization accompanied by heat evolution was observed. Thereafter, the reaction mixture was stirred for 30 min on a heating plate kept at 130°C in order to remove by evaporation the formed ethanol, the excess water, and the condensation water. Finally, the raw liquid resin was cooled to room temperature. It still contained water droplets and sulfuric acid.

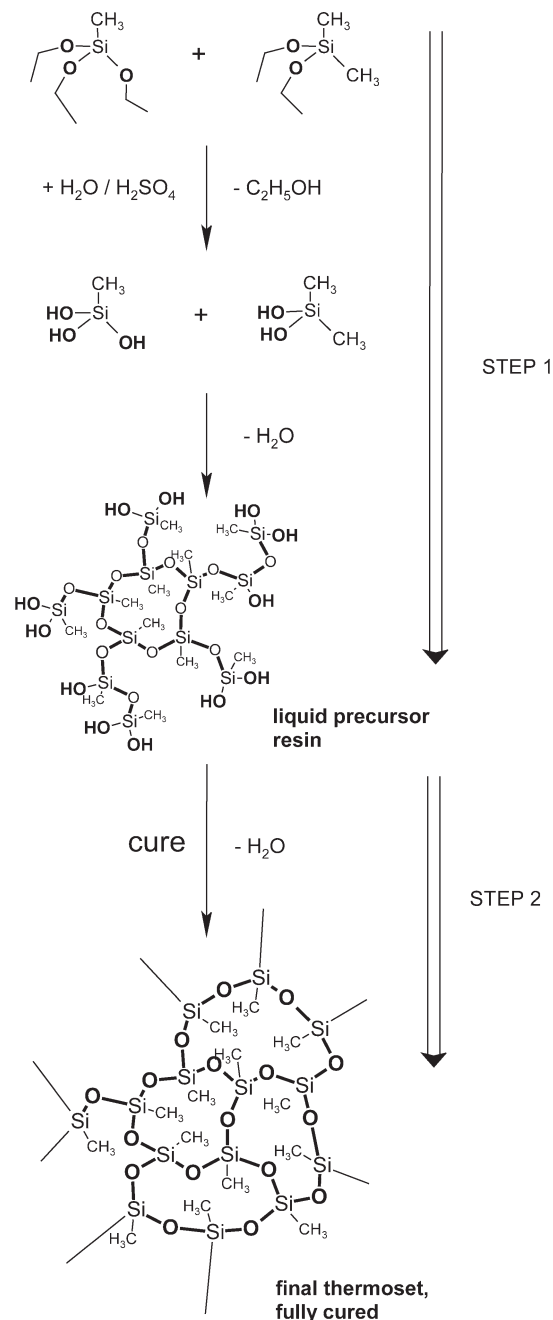
The raw resin was subsequently diluted by addition of 5 mL of toluene, and the sulfuric acid was removed by the addition of a 1.3-fold mole excess of powdered sodium hydrogen sulfate. The aqueous phase formed by the neutralization separated from the toluene phase and was removed. The precursor resin solution (50 wt %) was then ready for long-term storage. In order to prepare solvent-free precursor resins, toluene was removed prior to resin use on a rotary evaporator under vacuum at 35°C. In this way, a neat, viscous and catalyst-free liquid precursor resin was obtained, which also displayed some limited storability at -20°C. Precursor resins with monomer ratios T2D1, T3D1, and T4D1 were prepared.



**Scheme 4.** Stabilization of polyaniline colloid with polyvinylpyrrolidone.

### Homogeneous Preparation of Polysiloxane/PANI Composites

The “homogeneous” synthesis of the polysiloxane/PANI composite containing 3 wt % polyaniline was performed in a similar way like the synthesis of the neat liquid siloxane resin, with some important changes: In place of water acidified with sulfuric acid, aqueous 2 wt % polyaniline colloid was used, which already is acidic. The neutralization and dilution step at the end of the synthesis was always skipped, to avoid the conversion of conducting polyaniline salt to a non-conducting base. The oligomeric composite resin was poured into a mold and cured. Experiments were carried out also with 4 and 6 wt %



**Scheme 5.** Sol-gel synthesis of the polysiloxane matrices used in this work, starting from alkoxy silanes.

**Table I.** Composition of the Prepared Polysiloxanes and of Polysiloxane/PANI Composite Samples

Neat polysiloxanes					
Sample name <sup>a</sup>	"T" (g)	"D" (g)	H <sub>2</sub> O (g)	H <sub>2</sub> SO <sub>4</sub> (g)	Neat product obtained (g)
T2D1	7	2.90	6.4	0.27	4.09
T3D1	7	1.94	5.8	0.24	3.60
T4D1	7	1.45	5.6	0.23	3.36
Polysiloxane/PANI composites					
Sample name <sup>a</sup>	"T" (g)	"D" (g)	2% PANI colloid in H <sub>2</sub> O (g)		
T2D1/PANI (3%)	7	2.90	6.4		
T3D1/PANI (3%)	7	1.94	5.8		
T4D1/PANI (3%)	7	1.45	5.6		
Polysiloxane/PANI blends					
Sample name <sup>a</sup>	Neat precursor resin (g)		PANI powder (g)		
TxDy/PANI (30%)	3		1.29		
TxDy/PANI (40%)	3		2		
TxDy/PANI (50%)	3		3		

<sup>a</sup>Sample names description: "TxDy": the coefficients x, y after the monomer symbols (T, D) describe the ratios between the monomer units; PANI polyaniline filler.

polyaniline colloids, yielding 6 and 9 wt % polyaniline in the resulting composites.

#### **In Situ Preparation of Composites with Higher PANI Loadings**

For obtaining medium and higher concentrations (10–30 wt %) of polyaniline in the composites, a modification of the above procedure was tested. In place of the higher-concentrated polyaniline, a suspension of the neat polyaniline powder in water was used. The polyaniline dispersion in the reaction mixture was provided by constant sonication in ultrasonic bath and intense mechanical stirring at room-temperature and during the 130°C heating step.

#### **Blending Neat Liquid Siloxane Resin with PANI Powder**

Polysiloxane/PANI composites with high polyaniline contents were prepared by mechanical blending of dry powdered polyaniline and of the neat catalyst-free liquid siloxane resin T2D1, T3D1 or T4D1 in order to obtain 30, 40 or 50 wt % of polyaniline in the matrix. The blending was done by shearing the raw mixture on a Teflon plate, using a doctor blade until homogeneity of the components was achieved. The paste-like composite was then ready for pressing into mould and cure.

#### **Cure of Liquid (Precursor) Resins**

The neat or composite liquid precursor resins were put into a mould and left to gel for 3 days at room temperature, and thereafter the solid resins were post-cured at for 24 h at different temperatures: 60, 120, 160 or 180°C. The post-cure temperature of 60°C was found to be the optimal one. For the conductivity tests, samples of circular platelet shape were pre-

pared in the moulds (10 mm diameter and 2.5 mm thickness), for the thermomechanical analysis rectangular-platelet-moulds were used (30 × 10 × 2 mm<sup>3</sup>), while for the impact toughness tests, beam-shaped specimens sized 50 × 6.3 × 2.5 mm<sup>3</sup> were prepared.

#### **Morphology**

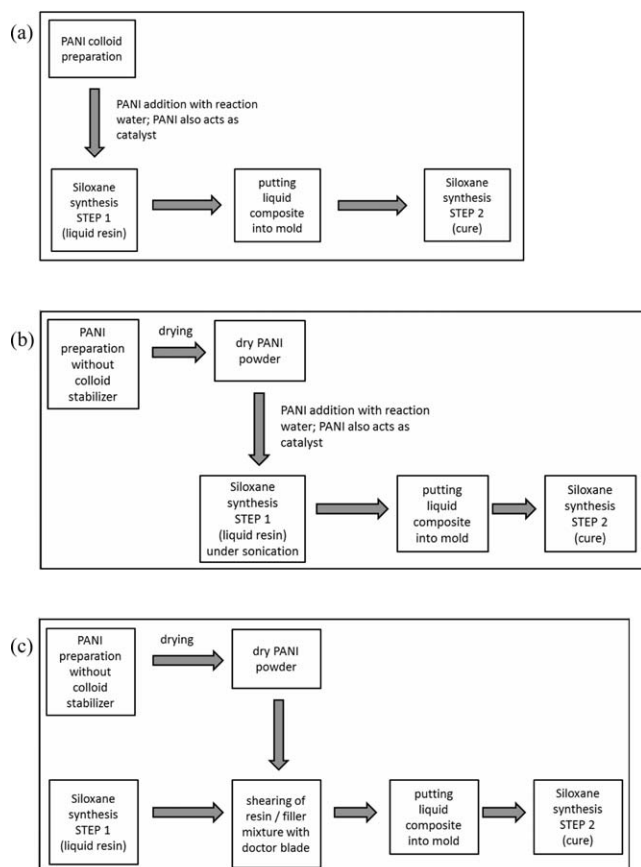
Samples for transmission electron microscopy were cut to ultrathin slices with an ultramicrotome Ultracut UTC (Leica). The slices were transferred onto supporting copper grids, and observed using the JEM 200CX microscope from JEOL. The microphotographs were obtained with a DXM1200 NIKON digital camera and their brightness and contrast were adjusted by standard software.

#### **FTIR Spectroscopy**

FTIR spectra have been recorded with a Thermo Nicolet NEXUS 870 FTIR Spectrometer (Madison, WI, USA) using a DTGS detector in the wavenumber range from 650 to 4000 cm<sup>-1</sup>. Golden Gate Heated Diamond ATR Top-Plate, MKII Golden Gate single reflection ATR system (Specac, Orpington, UK) was applied for the measurements of spectra of samples of square platelet shape, approximately 5 × 5 × 1 mm<sup>3</sup>, by the ATR spectroscopic technique. All spectra were corrected for the presence of moisture and carbon dioxide in the optical path.

#### **Dynamic-Mechanical Thermal Analysis (DMTA)**

DMTA measurements were carried out using an ARES-G2 from TA Instruments. The samples were of rectangular platelet shape (30 × 10 × 2 mm<sup>3</sup>). An oscillatory shear deformation with a



**Scheme 6.** Tested pathways of polysiloxane/PANI composite synthesis: (a) “Homogeneous” preparation: dispersion of a polyaniline colloid in the early homogeneous (sol) stage of the polysiloxane matrix synthesis; the polyaniline colloid simultaneously introduces water needed for the sol–gel process and also serves as the acidic catalyst (protonated polyaniline). (b) *In situ* preparation of composites with higher polyaniline contents (10–30 wt %): addition of polyaniline powder along with water; sonication was employed for enhanced dispersion. (c) “Heterogeneous” preparation procedure: mechanical blending of fine polyaniline powder with a liquid precursor siloxane resin.

constant frequency of 1 Hz was applied and the temperature was increased with the heating rate of  $3^{\circ}\text{C min}^{-1}$ . Shear modulus  $G'$ , loss modulus  $G''$  and  $\tan(\delta)$  were recorded in the temperature range from 30 to  $180^{\circ}\text{C}$ .

### Impact Toughness

The Charpy unnotched impact strength was determined on unnotched beam-shaped specimens sized  $50 \times 6.3 \times 2.5 \text{ mm}^3$ , which were tested on a CEAST Resil Impactor Junior, from CEAST, Italy, (now part of Instron, USA) at room temperature,  $\approx 25^{\circ}\text{C}$ , in the edgewise impact mode, with an impact energy of 0.155 J (hammer mass: 1.096 kg, speed:  $0.5 \text{ ms}^{-1}$ ). The data sampling rate was 600 kHz. Average toughness values were calculated from results obtained with five specimens of each sample.

### Conductivity Determination

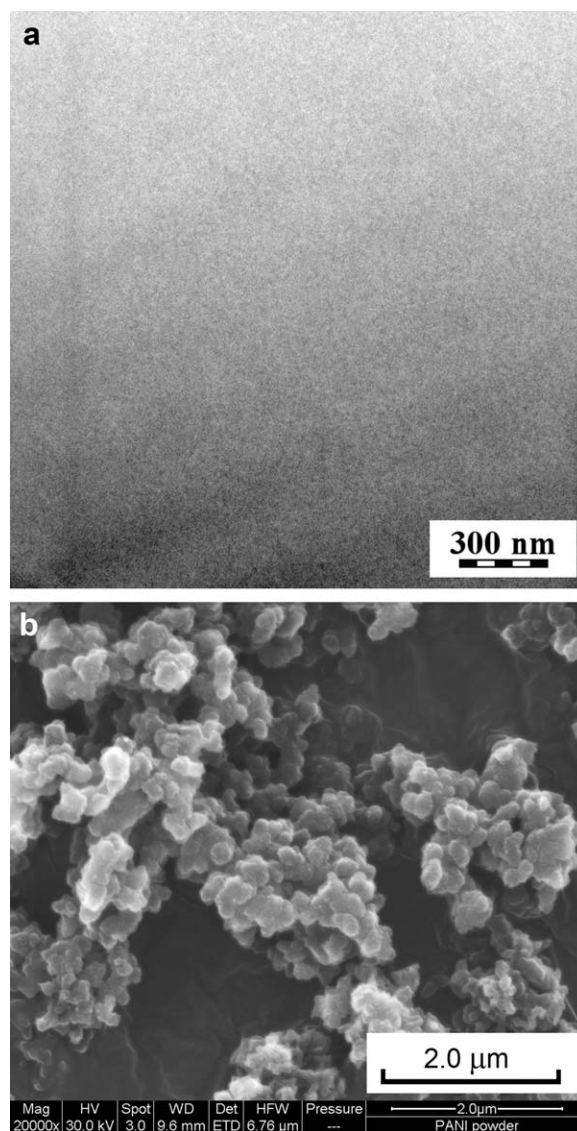
The conductivity of polysiloxane/PANI composites was measured by a four-point van der Pauw method, using a SMU

Keithley 237 as the current source and a Multimeter Keithley 2010 as voltmeter with a 2000 SCAN 10-channel scanner card. Circular pellet samples with 10 mm diameter and 2.5 mm thickness were used for the experiments.

## RESULTS AND DISCUSSION

### Polyaniline Dispersion in Polysiloxane Resins

Several procedures of polysiloxane/PANI composite preparation were tested (Scheme 6). The polyaniline filler was added either in the initial stage of the matrix synthesis, or after its partial polymerization. The **polyaniline filler** was always prepared separately from the polysiloxane matrix (Scheme 3). In order to finely disperse smaller polyaniline amounts (3–9 wt %), a polyaniline colloid stabilized by PVP was prepared. For composites with higher filler loadings, a finely powdered polyaniline with sub-micrometre particle size [Figure 1(b)] without the PVP was used.



**Figure 1.** (a) TEM image of the neat T2D1 matrix and (b) SEM image of neat polyaniline powder.

The polysiloxane matrix was prepared by hydrolysis/condensation of alkoxy silane monomers, in a two-stage process (see Scheme 5 further below), in which a processible liquid resin is at first obtained, and subsequently cured in a mold to the final thermoset. At the start of the matrix synthesis (Scheme 5) it can be observed, that the monomers, triethoxymethylsilane and dimethyldiethoxysilane, at first repel water, but as the hydrolysis to hydrophilic silanols progresses, the incompatibility disappears, the reaction mixture becomes homogeneous and the hydrolysis is completed with heat evolution. Thereafter the polycondensation proceeds further (Scheme 5), and the growing branched siloxane oligomers eventually possess only few hydroxyl groups, but numerous methyl groups. The reaction mixture hence becomes increasingly hydrophobic again, and phase separation of water formed by condensation is observed as turbidity. Towards the end of the liquid matrix precursor synthesis (end of step 1 in Scheme 5), water is phase-separated and partly evaporated, and the liquid resin becomes homogeneous.

As the first filler dispersion method of polyaniline in polysiloxane, the “homogeneous preparation” was tested (Scheme 6a): A 2 wt % aqueous colloid polyaniline solution was substituted for water with 4 wt % sulfuric acid (Table I), which was added as reactant during the neat polysiloxane matrix synthesis.

The protonated polyaniline particles took over the role of the acidic catalyst. The filler particles easily disperse in the reaction mixture and do not appear to markedly separate even during the later hydrophobic stage of the sol–gel matrix synthesis. A micro-phase separation occurs, however, as observed by TEM (see below), and leads to the product classification as micro-composite, rather than nano-composite. By using the 2 wt % polyaniline solution, a final composite with 3 wt % of filler is obtained. More concentrated polyaniline solutions (4 and 6 wt %), were also tested in order to achieve higher polyaniline loadings (6 and 9 wt %, respectively). A further increase of filler loading was not accessible by this route, due to the limits of the colloidal polyaniline solubility.

In order to obtain polysiloxane/PANI composites with increased filler loadings (10–30 wt %), the above procedure was modified (Scheme 6b) by adding water and polyaniline powder instead of the colloidal polyaniline solution, and by enhancing the filler dispersion by applying ultrasonication in addition to stirring. However, the obtained filler dispersion was less than perfect, due to the aggregation of polyaniline particles. Additionally, the catalytic effect of large amounts of the filler on the resin cure led to rapid gelation in the later stage of the matrix sol–gel process at 130°C, thus making the pouring into mould of the polyaniline-filled liquid precursor resin problematic.

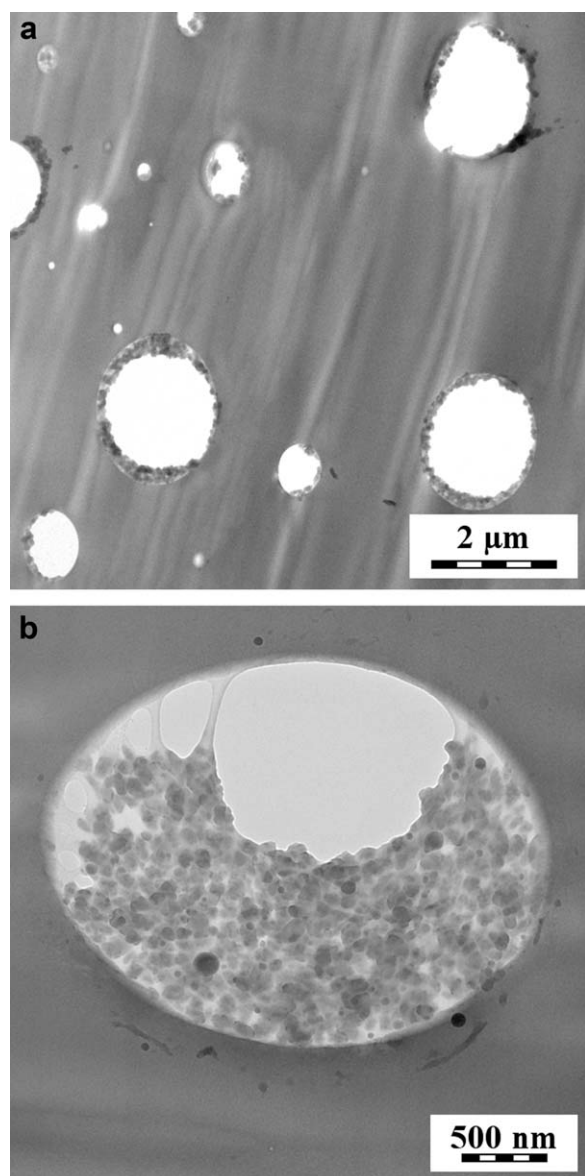
As an alternative preparation route, the “heterogeneous method” was tested: the blending of polyaniline powder with liquid siloxane precursor resin at room temperature via shearing with doctor blade (Scheme 6c). This route proceeded easily, the separately prepared liquid siloxane resins readily wetted the polyaniline micro-powder, and the obtained liquid (paste-like) composite precursors displayed some short-time stability at room temperature, which makes possible their comfortable

processing. The catalytic effect of the filler on the siloxane oligomers cure is visible even at room temperature, so that matrices with a high content of the branching monomer T (e.g., T4D1 in Table I) gelled relatively quickly, in about 7 min. Polysiloxane/PANI composites with high polyaniline contents (30, 40, and 50 wt %) and with regular filler dispersion were easily obtained by the “heterogeneous” method. On the other hand, this method is less suited for regular dispersion of small amounts of polyaniline, where the above “homogeneous preparation” is more feasible. The final cure temperature of the polysiloxane/PANI composites with high filler contents was optimized in view of its effect on the composite conductivity, and the temperatures 180, 160, 120, and 60°C were tested. The mechanical properties were not much affected by the final cure temperature, not least due to the strong catalytic effect of polyaniline on the cure. The optimization of the conductivity led to the choice of the cure temperature of 60°C as the most suitable.

Filler dispersion evaluation via TEM and light microscopy. The polyaniline filler dispersion in the composites was assessed by electron microscopy. TEM micrographs of the neat polysiloxane matrix illustrate its high homogeneity and the absence of any heterogeneous impurities [Figure 1(a)]. The polyaniline powder consists of rough irregular pieces up to 1 μm in size [Figure 1(b)], which are composed of smaller aggregated or fused grains sized 100–200 nm. The size of the particles in the polyaniline colloid (2 wt % polyaniline) appears to be similar to the size of the smallest grains in the polyaniline powder, namely around 200 nm, as can be seen on the example of an aggregated polyaniline domain [Figure 2(b)] formed from the colloid.

In the case of the “homogeneously” prepared composites with 3 wt % polyaniline particles (Figure 2), micro-phase separation can be observed in the apparently homogeneous composite. The submicrometre polyaniline particles join to larger domains of 0.7–1.5 μm size, obviously as the result of siloxane oligomers hydrophobicity in the later part of the stage 1 of the polysiloxane matrix formation (Scheme 5). The product is a typical micro-composite with a particulate filler [Figure 2(a)]. Due to the globular structure and to the different mechanical properties of the filler and the matrix, the most of the polyaniline domains fall out of their positions during the cutting of sample slices for the TEM analysis [Figure 2(a)] and only few partially preserved domains could be observed [Figure 2(b)]. The shape of both single polyaniline particles (cubes) as well as of the polyaniline domains (spheres) would require high filler loadings (around 60 vol %) to achieve filler percolation and conductivity. Only up to 9 wt % (ca. 9 vol %) contents are accessible by the “homogeneous” preparation procedure. This procedure is hence suitable for the preparation of low-concentration polysiloxane/PANI composites, which inherit only the optical properties of polyaniline.

The polysiloxane/PANI composites prepared by the heterogeneous method (30, 40, and 50 wt % polyaniline, in T2D1, T3D1, and T4D1 resins), by blending polyaniline powder with liquid oligomeric siloxanes display a rough break surface, with the pattern [scanning electron microphotograph: Figure 3(a)] resembling the neat polyaniline particles [Figure 1(b)]. These



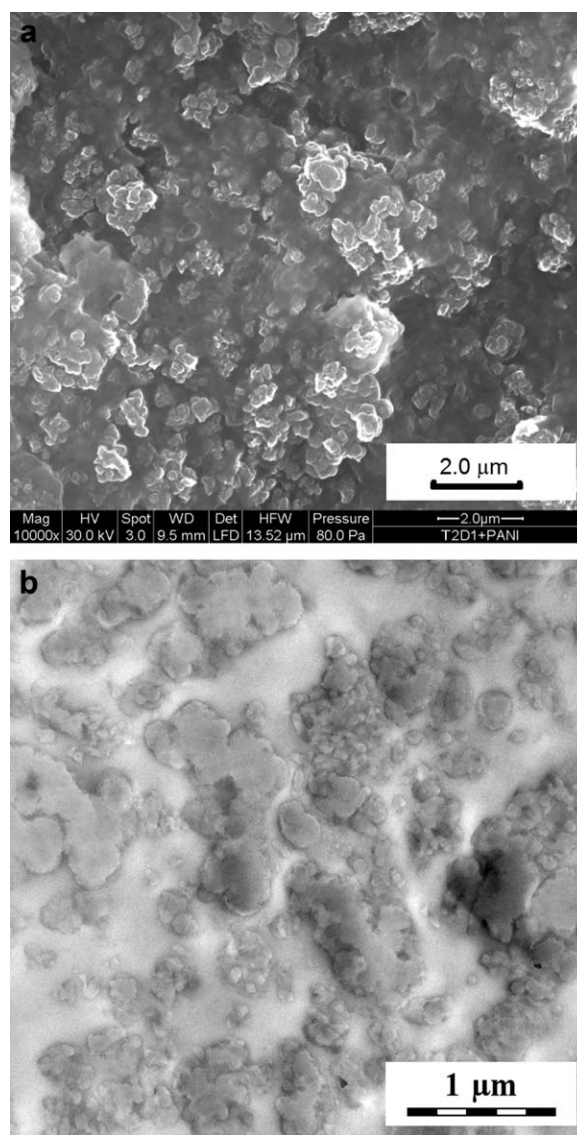
**Figure 2.** TEM images of (a) the T2D1/PANI composite with broken-off polyaniline domains and (b) a nearly intact polyaniline domain in T2D1/PANI, consisting of aggregated polyaniline nanoparticles.

micrometre-sized irregular aggregate particles can be seen also in the transmission electron microphotograph of a thin composite slice [Figure 3(b)], as the darker domains. The high content and the somewhat irregular shape of the polyaniline microparticles lead to the desired morphology of interpenetrating co-continuous phases, and to the percolation and consequent conductivity of the polyaniline phase.

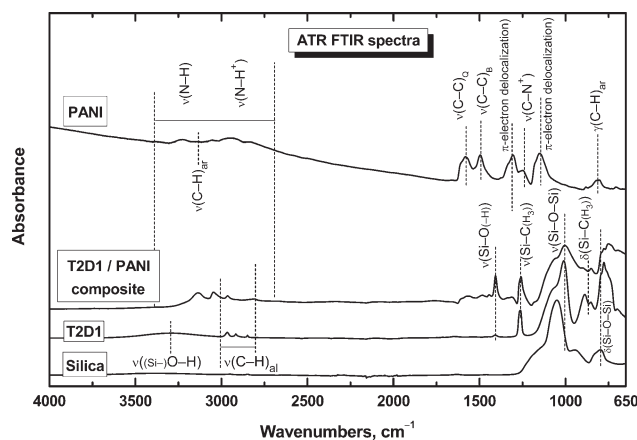
The morphology of the polysiloxane/PANI composites prepared by the “heterogeneous” method was not influenced by the matrix composition (T2D1, T3D1 or T4D1) and was also very similar at filler loadings of 30, 40, and 50 wt % polyaniline. The conductivity measurements (see below) demonstrated, that percolation of the polyaniline particles is lost between 40 and 30 wt % of the filler.

### Polysiloxane-Polyaniline Interactions as Observed by FTIR Spectroscopy

IR spectroscopic investigations (Figure 4) were performed in order to evaluate matrix-filler interactions. IR absorption bands related to the polysiloxane matrix (spectrum “T2D1” in Figure 4) are observed at 1265 (Si–C stretching vibration), 1010 (with a shoulder at 1055  $\text{cm}^{-1}$ ; both are Si–O–Si stretching vibrations), 890 (Si–C bending), 798 and 753  $\text{cm}^{-1}$  (both are Si–O–Si bending vibrations). The bands characteristic of pure silica, situated at 1055 and 798  $\text{cm}^{-1}$  (Si–O–Si stretching and bending vibrations) are well detected in the spectrum of polysiloxane matrix in slightly shifted positions. Bands assigned to C–H stretching of methyl groups of T2D1 are detected between 2964 and 2848  $\text{cm}^{-1}$ . The spectrum of a standard polyaniline film<sup>59</sup> contains absorption bands in the region 3400–2800  $\text{cm}^{-1}$  which are connected with nitrogen-containing groups, such as the secondary amine –NH– and protonated imine –NH<sup>+</sup>–. (spectrum



**Figure 3.** (a) SEM and (b) TEM of the composite made by blending the T2D1 resin with polyaniline.



**Figure 4.** ATR FTIR spectra of polysiloxane/PANI composite, of neat polyaniline filler, of the matrix, and of silica ( $\text{SiO}_2$ ). Abbreviations:  $\nu$ , stretching;  $\delta$ , in plane deformation;  $\gamma$ , out of plane deformation; ar, aromatic; al, aliphatic; B, benzenoid ring; Q, quinoid ring.

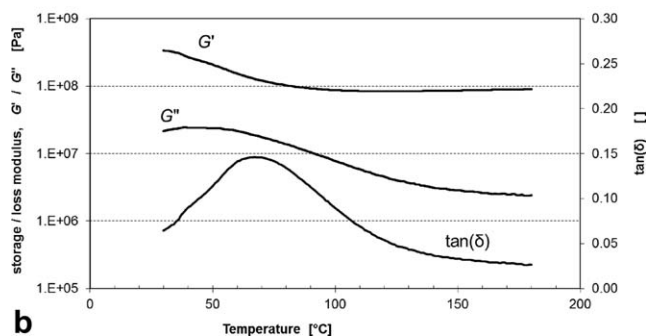
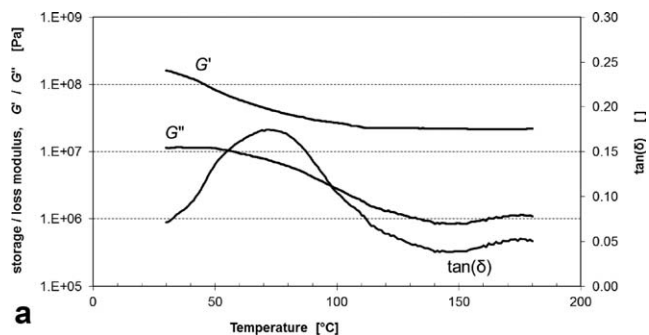
“PANI” in Figure 4). They reflect the organization of polyaniline chains within the film by hydrogen bonding involving these groups. They are enhanced in the spectrum of polysiloxane/PANI composite (spectrum “T2D1/PANI” composite in Figure 4). Two main bands with maxima situated at 1584 (with a shoulder at 1613  $\text{cm}^{-1}$ ) and 1495  $\text{cm}^{-1}$ , assigned to quinonoid and benzenoid ring-stretching vibrations, respectively, and the band with maximum at about 1306  $\text{cm}^{-1}$  corresponding to  $\pi$ -electron delocalization induced in the polymer by protonation, are well detected in the spectrum of composite. The band of C–N<sup>+</sup> stretching vibrations in the polaronic structure, observed in the spectrum of polyaniline at 1245  $\text{cm}^{-1}$ , the band at 1140  $\text{cm}^{-1}$ , which is related to the high degree of electron delocalization in polyaniline, and the bands corresponding to aromatic ring out-of-plane deformation vibrations situated in the region 900–700  $\text{cm}^{-1}$  are overlapped by the bands of the polysiloxane matrix.

The FTIR spectrum of the composites mostly corresponds to the simple addition of the spectra of polysiloxane matrix and of polyaniline. The peak near 889  $\text{cm}^{-1}$ , which is an absorption assigned to silanol OH groups, is somewhat broadened, which suggests an interaction between the silanol groups and the polyaniline filler by hydrogen bonding. A specific interaction is also supported by the appearance of a strongly enhanced peak at 1408  $\text{cm}^{-1}$ , which is found as a very weak absorption in T2D1. Generally, the polysiloxane/PANI composites prepared homogeneously (polyaniline colloid dispersion during matrix synthesis) as well as heterogeneously (blending) display very similar IR spectra. The spectra were not influenced by the presence or absence of filler percolation.

### Mechanical Properties

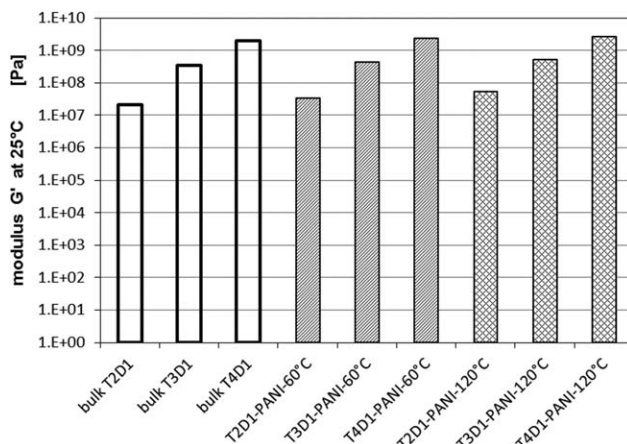
The dynamic-mechanical thermal analyses (DMTA; temperature dependences of storage shear modulus  $G'$ , of loss modulus  $G''$ , and of the loss factor  $\tan \delta$  in Figure 5) of neat polysiloxane matrices and of the prepared composites (see samples list in Table I) reveal the following trends:

All the samples except the most crosslinked matrix T4D1 display a **glass transition** and have relatively similar mechanical



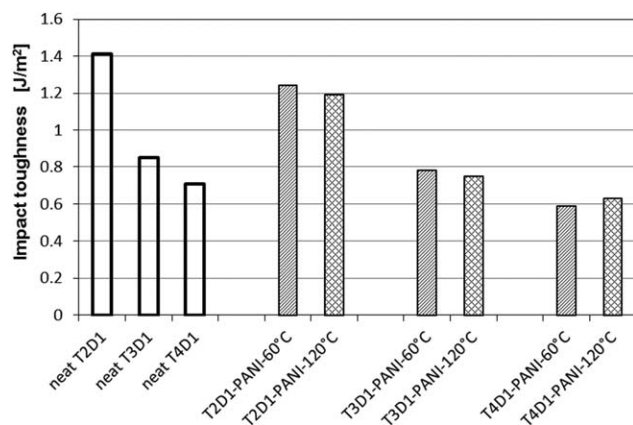
**Figure 5.** DMTA profiles of polysiloxane/PANI composites: (a) T3D1 neat matrix which is practically identical with the T3D1/PANI(3 wt %) composite prepared by the “homogeneous” route and (b) T3D1/PANI(50 wt %) composite prepared heterogeneously via blending.

properties, with storage and loss moduli in a similar range. In the case of neat T4D1, practically no glass transition was observed; this highly crosslinked material does not possess rubber elasticity. In less crosslinked matrices [T3D1, T2D1, see example in Figure 5(a)], or in all composites with higher polyaniline content, a glass transition is clearly observed. The glass transition temperatures  $T_g$  (determined as  $T$  at  $\tan \delta$  maximum) of all the studied samples are in the range 60–80°C. With the increase of the linear monomer (dimethyldiethoxysilane, “D”) content in the polysiloxane matrix, the  $T_g$  value slightly decreases. The addition of larger polyaniline filler amounts does



**Figure 6.** Shear storage moduli  $G'$  at 25°C of the tested polysiloxane matrices (cured at 120°C) and of the polysiloxane/PANI composites with 50 wt % polyaniline, cured at 120 and at 60°C.





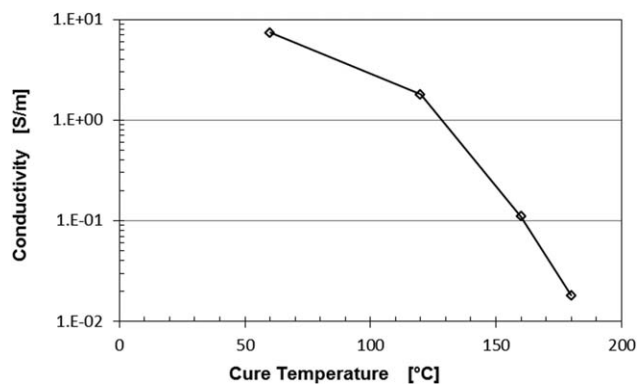
**Figure 7.** Impact toughness of the tested polysiloxane matrices (cured at 120°C) and of the polysiloxane/PANI composites with 50 wt % polyaniline, cured at 120 and at 60°C.

not markedly shift the  $T_g$ . Some broadening of the base region of the  $\tan \delta$  peak is nevertheless visible in case of high polyaniline content [Figure 5(b)].

The temperature dependences of the storage moduli  $G'$  indicate the following trends: An increasing content of the D monomer in the matrix causes a somewhat deeper step in the  $G' = f(T)$  curves, meaning some increase in rubber elasticity, which becomes more pronounced in the matrix T2D1. The cure temperature has only a moderate effect on the moduli, especially in the case of the composites: The 24 h cure is highly efficient even at the lowest tested temperature, 60°C. In case of the composites with higher polyaniline contents (heterogeneous preparation), the catalytic effect of the filler increases the efficiency of the cure. The moduli of a given sample slightly increase with the cure temperature. The addition of higher amounts of the polyaniline filler (e.g., 50 wt %, see Figure 6) also slightly raises the moduli, obviously due to the mentioned catalytic effect on the cure. On the other hand, the “homogeneously” prepared composites with low polyaniline loadings display identical moduli and DMTA curves like the neat matrices.

#### Effect of Polyaniline Particles on the Composites' Toughness.

An important mechanical characteristic is the impact toughness, which was determined for the neat polysiloxane matrices and for the most promising electrically conducting polysiloxane/PANI composites (Figure 7), by the Charpy unnotched impact test. The neat matrices display a decrease of impact toughness when the composition changes from the semi-elastic T2D1 to the glassy systems T3D1 and T4D1, decreasing from 1.4 to 0.71  $\text{Jm}^{-2}$ . The composites with 50 wt % polyaniline display somewhat smaller, but very similar impact toughness values like the



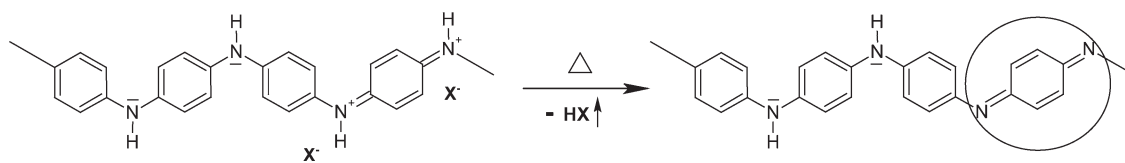
**Figure 8.** Dependence of the conductivity on the cure temperature for the composite T4D1/PANI (50 wt %).

neat matrices. The difference is the highest in case of the softer T2D1 matrix, while it is fairly small for the glassy matrices T3D1 and T4D1. Heterogeneities such like particulate fillers may support crack propagation, thus reducing material toughness.

On the other hand, soft particulate fillers can improve impact toughness by absorbing energy and spreading the tension of the propagating crack tip on the soft filler particles surface (e.g., styrene with polybutadiene particles). The investigated composites seem to be a border case between these two situations, where the impact toughness of the matrix is approximately preserved.

#### Conductivity

The neat polysiloxane matrices are good insulators and display negligible conductivities around  $1 \times 10^{-16} \text{ S cm}^{-1}$ . The polyaniline filler used in this work achieved a conductivity of  $1.1 \text{ S cm}^{-1}$ , measured on a pressed platelet sample, using the van der Pauw four-point method. Only the polysiloxane/PANI composites with the highest filler contents near 50 wt % were expected to achieve percolation and hence good conductivity. The effect of the cure temperature on the composites conductivity was hence tested on the system T4D1/PANI (50%). About 50 wt % of polyaniline was the highest filler loading, which was comfortably accessible by the heterogeneous (blending) preparation route. The results are displayed in Figure 8: At the relatively high cure temperature of 180°C, the achieved conductivity of the composite is  $1.8 \times 10^{-4} \text{ S cm}^{-1}$ . If the cure temperature is lowered to 160°C,  $1.1 \times 10^{-3} \text{ S cm}^{-1}$  are achieved. Between 120 and 60°C, high conductivities are reached,  $1.8 \times 10^{-2}$  and  $7.4 \times 10^{-2} \text{ S cm}^{-1}$ , respectively, which are fairly good in view of the original filler conductivity,  $1.1 \text{ S cm}^{-1}$ . The reason for the decreased conductivity after cure at high temperatures lies in the thermal



**Scheme 7.** Thermal elimination of the dopant acid from oxidized polyaniline, which leads to the fixation of the positions of quinoid structures in the polyaniline chain and to reduced conductivity.

deprotonation of polyaniline caused by the elimination of the acid constituting a salt with polyaniline (Scheme 7), due to which the electron resonance and delocalization, which is crucial for the electrical conductivity (see Scheme 1), is no more possible. The optimal cure temperature was hence found to be 60°C.

The limits of percolation for the investigated micro-powdered polyaniline filler were qualitatively tested on the T4D1/PANI (50%) system cured at 60°C. The specimens with 50 and 40 wt % polyaniline displayed an identical conductivity,  $7.4 \times 10^{-2} \text{ S cm}^{-1}$ , while the conductivity of T4D1/PANI (30%) was not measurable by the van der Pauw method. The percolation limit hence is located between 30 and 40 wt % polyaniline. The somewhat branched shape of the polyaniline microparticles as observed by TEM (Figure 1) can be helpful in establishing conduction paths.

The choice of resin type (T2D1, T3D1 or T4D1, tested with 50 wt % polyaniline) did not affect the conductivity (beyond the experimental error) at a given filler concentration.

## CONCLUSION

Polysiloxane–polyaniline micro-composites were successfully prepared using two methods: “homogeneous”: dispersion of a colloidal polyaniline solution in the reaction mixture of the polysiloxane matrix synthesis, yielding a liquid composite resin and subsequent cure; and “heterogeneous”: blending polyaniline powder and liquid siloxane resin and subsequent cure.

All the prepared composites display thermo-mechanical properties close to those of their respective matrices. The heterogeneously prepared composites keep the impact toughness of their respective polysiloxane matrices.

The heterogeneously prepared composites possess a good conductivity at filler loadings of 40 and more wt % polyaniline, while at 30%, the percolation (and hence the conductivity) is lost. The relatively low cure temperature of 60°C is required in order to reach the optimal conductivity.

The “homogeneously” prepared composites keep identical thermo-mechanical and electrically insulating properties like the corresponding neat matrices. Only the optical properties of polyaniline, the colour, are transferred to the composite.

## ACKNOWLEDGMENTS

The authors thank the Czech Science Foundation (107/12/2445 and 13–26542S) for the financial support.

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