

Electrical Characterization of Polyaniline-Based Adhesive Blends

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ABSTRACT: Preparation and processing of conductive blends based on doped polyaniline (c-PANI) or *tetra*-aniline (c-TANI) with epoxy resins is described. The dedoping of c-PANI by the epoxy hardener, in the process of the blend curing, has been investigated by UV-vis-NIR spectroscopy. Classical amine hardeners lead to a quick increase of the blend resistivity during its processing, which can be correlated with the observed spectral features, characteristic of the deprotonation of c-PANI. For these reasons, for further investigations, BF₃-amine complexes have been selected as curing agents. Using these hardeners and tuning the curing conditions (temperature and time), it is possible to obtain blends with resistivities down to 10² Ω·cm, depending on the type of the epoxy resin used. In general, resins with higher epoxy network densities give c-PANI-based blends

of lower percolation thresholds. The effect of the c-PANI processing solvent on the resistivity of the resulting blend is even more pronounced than the epoxy network density. In particular, blends processed from toluene show much higher resistivities than those processed from tetrahydrofuran (THF) or ethylacetate (EA). Above the percolation threshold, c-TANI-based epoxy blends show at least three orders of magnitude higher resistivities than their c-PANI analogues. They are however technologically interesting, because they are not very sensitive to the processing/curing conditions and show lower percolation thresholds. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1965–1973, 2011

Key words: adhesives; blends; conjugated polymers; percolation; electrical measurements

INTRODUCTION

Intrinsically conductive polymers (ICPs) have received much attention in the last three decades for many applications related to organic electronic devices such as organic light emitting diodes, organic field effect transistors but also in other technological fields as antistatic coatings, and electromagnetic shielding layers. More generally, they can be used in all devices, which require the application of materials combining enhanced electrical conductivity with specific properties of polymers.^{1–3} Recently, a particular interest has emerged for electrically conductive blends⁴ with a particular emphasis on epoxy-based adhesives containing polyaniline (PANI)-based ICP fillers^{5–7} Epoxy resins combined with PANI (as top-coated layers or in a form of blends) are also widely studied as new anticorrosion materials.^{8–15} Such blends are very attractive for the possibility to adjust and control the resistivity of the adhesive in a very wide range (10⁻² – 10¹⁵ Ω·cm) by modifying the filler-to-matrix ratio, the conducting polymer-doping level, and the processing conditions. In addition, contrarily to the case of metal particles filled adhe-

sives, improved mechanical and electrical properties are expected due to a more similar chemical nature of the matrix and the conducting filler. When processing such blends, three particular issues have to be addressed: the chemical reactivity and miscibility between both constituents of the adhesive blend and the value of the percolation threshold. It is known that the conductive (doped) form of PANI undergoes dedoping in the presence of common amine epoxy hardeners that inevitably leads to an uncontrollable increase of the blend resistivity. The dedoping can be avoided either by using an appropriate complex BF₃-amine hardener^{8,10} or an anhydride type hardener,^{6,16} but still several problems concerning the miscibility of the components and the blend processing have to be resolved.

The main goal of the research presented here was to develop a conductive blend easy to process and showing reproducible electrical properties. As the conductive component of the blend, we have selected PANI (or its oligomeric analog—tetraaniline) protonated with diesters of sulfosuccinic acid, because this form of PANI is known to combine solution processibility with good mechanical and electrical properties of the resulting material. This is important not only for the development of conductive adhesives showing the conductivity in the range of 10⁻⁵–10⁻⁷ S/cm¹⁷ but also for the elaboration of systems in which the electrical and mechanical

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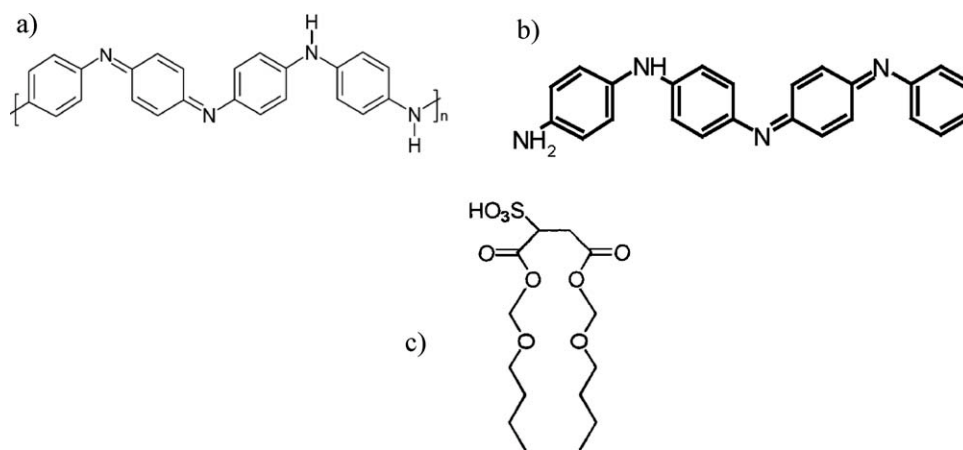


Figure 1 (a) Polyaniline base in the oxidation state of emeraldine, abbreviated as PANI, (b) *tetra*-aniline in the oxidation state of emeraldine (abbreviated as TANI), and (c) protonating agent: dialkoxyester of sulfosuccinic acid. The conductive form of PANI and TANI is obtained by protonation of their imine nitrogen with dialkoxyester of sulfosuccinic acid. In the subsequent text, the conductive forms of the polymer and oligomer used will be termed c-PANI and c-TANI.

properties of the resulting materials would be relatively insensitive to eventual changes in processing conditions. This is not trivial, because the macroscopic conductivity of such blends is governed by the percolation threshold. Moreover, the system is PANI-dedoping sensitive. To minimize this phenomenon, which has a negative impact on its conductivity, we have tested the effect of different hardeners, epoxy resin as well as the influence of the solvent used, and the temperature of curing on the properties of the resulting blends. These studies were supported by the electrical characterization of the resulting adhesive and the investigation of its dedoping by the UV-vis spectroscopic measurements. In addition, we have carried out similar studies for tetraaniline (c-TANI)—a low-molecular weight analog of c-PANI. To the best of our knowledge, very few studies have been reported on adhesive blends prepared from low-molecular weight analogues of c-PANI, that is, oligoanilines.¹⁸

EXPERIMENTAL

Materials

Adhesives used in this study are commercial epoxy products supplied by Epotek Company. Three products were selected, the first being a common epoxy, the second, and the third containing a Lewis acid-based hardener, which should not dedope the conductive polyaniline (c-PANI): (1) "E730" in with an epoxy-based polymer including a cresol novolac, epichlorohydrin, and bisphenol A and a classical amine hardener (polyamide resin), (2) "H 61" with a resorcinol diglycidyl ether as base polymer and a complex BF₃-amine hardener with a 120°C minimum curing temperature, and (3) "OM100" with a epichlorohydrin and bisphenol A and 1,4 butanediol

diglycidyl ether as base polymer and a complex BF₃-amine hardener, which cures at room temperature. A BF₃-amine complex hardener purchased separately from Air Products company (namely Anchor 1115) was also used.

c-PANI was purchased from Paniplast company¹⁹ in a form of dispersions in ethyl acetate (Paniplast Sol-P2-AE [10 wt %]), tetrahydrofuran (THF; Paniplast Sol-P2-TH [10 wt %]), or toluene (Paniplast Sol-AP1-TL [9 wt %]). The polymer contained special plasticizing dopants leading to conductive products with improved mechanical properties.^{19–21} Two forms of the conductive filler were supplied: (1) PANI in the oxidation state of emeraldine protonated with the dialkoxyester of sulfosuccinic acid dispersed in the above solvents and (2) tetramer of aniline (c-TANI) dispersed in THF (Paniplast Sol-P2-TTR-TH [7 wt %]) in the same oxidation state and doped with the same protonating agent (see Fig. 1 for the chemical formulae).

Blends preparation

c-PANI and c-TANI were supplied as dispersions in various solvents of increasing boiling point: THF, ethylacetate (EA), and toluene (bp of 66, 77, and 110°C, respectively). Two mixing procedures were applied depending on the type of the epoxy resin used: single epoxy component (H61) or two-component epoxy (E730, OM100). In the first case, the solvent was first evaporated at moderate temperature (just below the boiling point) from the c-PANI or c-TANI dispersions until less than 5 wt % of its original content. This gave a dispersion showing medium "honey"-type viscosity that could be easily further mixed with the right proportion of H61 single component using a magnetic stirrer. In the second case,

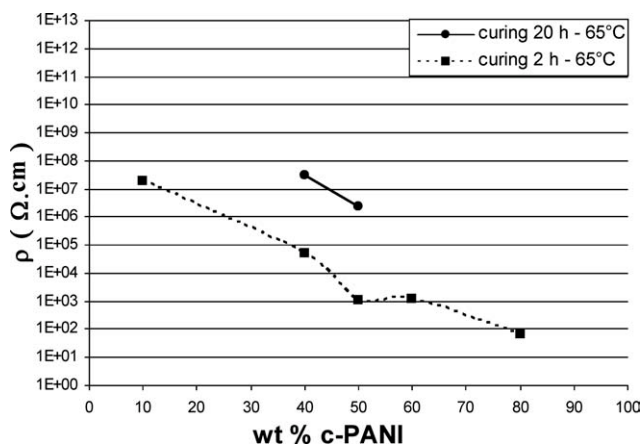


Figure 2 Resistivity of conductive blends cured at 65°C prepared from E 730 epoxy, a common amine hardener, and c-PANI dispersed in THF as a function of c-PANI content for two different curing times (square plots : 2 h and round plots : 20 h).

c-PANI or c-TANI dispersions were first mixed with the base polymer epoxy (also referred as Part A) in appropriate proportions to obtain the aimed composition; then, the solvent was evaporated to also less than 5 wt % of its original content. Finally, they were mixed with the proper quantity of the hardener, according to manufacturer recommendations. Note that, in the second case, the c-PANI or c-TANI/Part A blends without hardener were stable, at least for 24 h.

As a general rule, in the text and all figures, the content of the conductive phase in the blend is expressed as the ratio of the mass c-PANI (or c-TANI) to the total mass of the blend after the complete solvent removal.

Measurement methods

The prepared blends were deposited manually on a glass substrate to yield a thin homogeneous coating of ~ 50- μm thick. They were then cured at temperatures between room temperature and 125°C depending on the epoxy used. UV-vis absorption measurements were performed using a PerkinElmer apparatus. Electrical measurements were carried out using the four-point method in which the contact resistances can be neglected. In this method, the potential difference is measured for a defined injected current in the coating. For very high-resistivity materials, injection of the current becomes difficult, and the potential measurements were not carried out using the classical differential mode but on two separate lines to attest that the measurements were not perturbed by current injection. The present apparatus is capable of measuring resistivities up to $10^9 \Omega\cdot\text{cm}$. When the resistivity of the blend is higher than $10^9 \Omega\cdot\text{cm}$, it is displayed as $10^{12} \Omega\cdot\text{cm}$ on the

graphs, but it may range from 10^9 to $10^{15} \Omega\cdot\text{cm}$ as for instance in Figure 8.

RESULTS

Dedoping effect

First, adhesive blends were prepared from the E730 product, a common amine epoxy hardener, and c-PANI dispersion in THF. The resistivity has been investigated as a function of the c-PANI content in the cured state. The results obtained for two different curing times are presented in Figure 2. For three contents of c-PANI, the UV-visible absorption spectra were taken to follow the possible dedoping effect (Fig. 3).

Next, other blends were prepared using the same base polymer of the E730 epoxy (Part A) but replacing the amine hardener supplied with it (part B) by a complex amine- BF_3 (Anchor 1115 product). The results of the resistivity measurements are shown in Figure 4. It can be seen that even for a relatively prolonged curing time (24 h) and a high-temperature curing (125°C), the resistivity of the blend is stable.

It seems that the percolation threshold should be lower in the former case; however, it cannot be properly determined for the blend prepared with the common amine hardener, because its resistivity is not stable and increases with time due to the dedoping process (*vide infra*). Contrarily, a clear percolation threshold can be seen at the c-PANI content of ~ 25 wt % when the complex amine- BF_3 Anchor 1115 hardener is used.

In the next experiments, adhesive blends were prepared using another epoxy H61 with also a BF_3 -amine complex hardener (Part B supplied by the

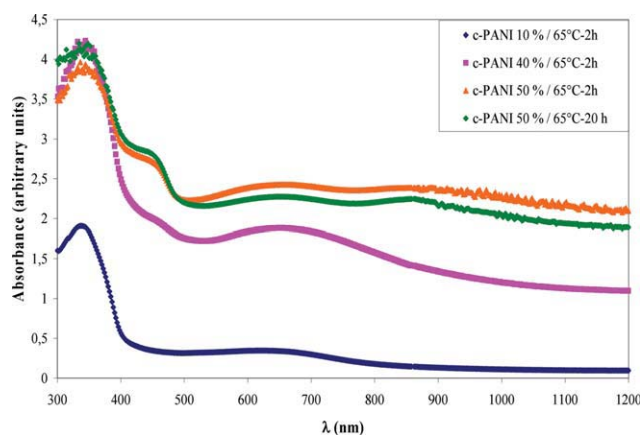


Figure 3 UV-visible absorption spectra of four conductive blends prepared from E 730 epoxy, a common amine hardener, and c-PANI dispersed in THF; dark blue line 10% of c-PANI cured at 65°C for 2 h; pink line 40% of c-PANI cured at 65°C for 2 h; orange line 50% of c-PANI cured at 65°C for 2 h; green line 50% of c-PANI cured at 65°C for 20 h. [Color figure can be viewed in the online issue, which is available at www.wileyonlinelibrary.com.]

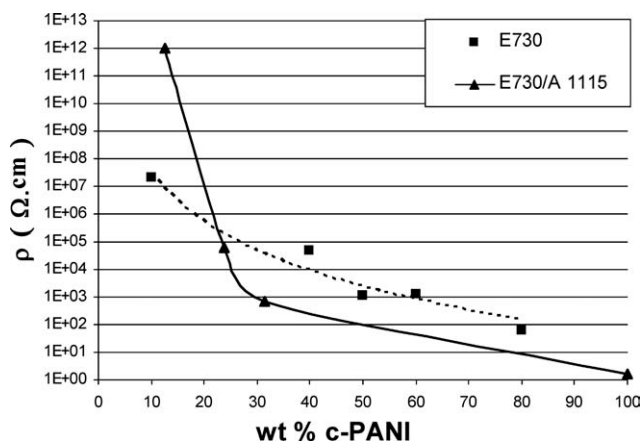


Figure 4 Resistivity of conductive blends prepared from (i) E730 epoxy, common amine hardener, and c-PANI dispersed in THF—curing 2 h/65°C (dotted line/square plots) and (ii) E 730 epoxy, BF₃-amine complex hardener (A1115), and c-PANI dispersed in THF—curing 24 h/125°C (full line/triangle plots)—as a function of c-PANI content.

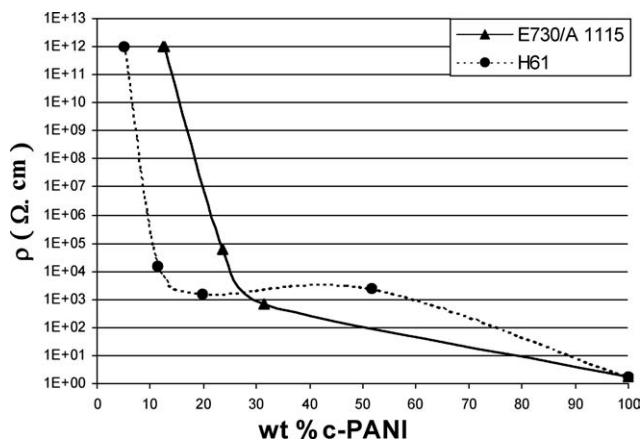


Figure 5 Resistivity of conductive blends prepared from (i) E730 epoxy, BF₃-amine complex hardener (A1115), and c-PANI dispersed in THF—curing 24 h/125°C (full line/triangle plots) and (ii) H61 epoxy, BF₃-amine complex hardener, and c-PANI dispersed in THF—curing 20 h/125°C (dotted line/round plots)—as a function of c-PANI content.

producer) and c-PANI dispersed in THF. The resistivity is still stable, as in the previous case, but the percolation threshold is lower, around 15% (see Fig. 5).

Influence of the solvent

It is expected that the chemical nature of the solvent may strongly influence the blend processing and its morphology in the cured state; thus, it can have a significant effect on the final resistivity. In Figures 6 and 7, the results of the resistivity measurements, carried out for the blends obtained from H61 and E730-Anchor 1115 epoxies, respectively, and c-PANI

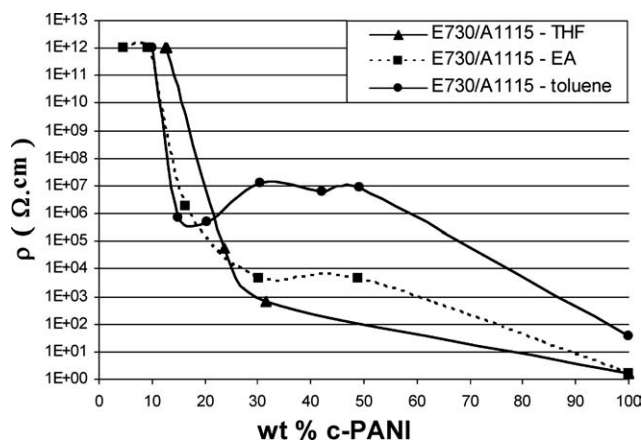


Figure 6 Resistivity of conductive blends cured 24 h/125°C and prepared from E730 epoxy, BF₃-amine complex hardener (A1115), and c-PANI dispersed in THF (triangle plots), EA (square plots) or toluene (round plots), as a function of c-PANI content.

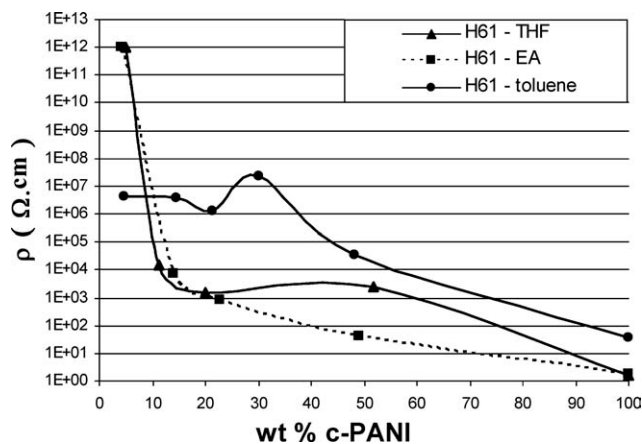


Figure 7 Resistivity of conductive blends cured 24 h/125°C and prepared from H61 epoxy, BF₃-amine complex hardener, and c-PANI dispersed in THF (triangle plots), EA (square plots), or toluene (round plots), as a function of c-PANI content.

dispersed in THF, ethyl acetate, or toluene, are shown. For THF and EA, the behavior is similar; however, the use of toluene leads to a significant increase in the blend resistivity in the c-PANI content range between 30 and 60 wt % for the E730/A1115-based blend. As for the H61-based blend, we have a similar behavior using the toluene solvent, but the high-observed resistivity only occurs in a c-PANI content range lower than 40% with a lower percolation threshold in this case.

Effect of the molecular weight

Oligoanilines are, in general, easier to process, and, for this reason, we have undertaken the task of the preparation of epoxy-based conductive blends with c-TANI instead of c-PANI. For the same doping level, c-TANI is however less conductive than c-

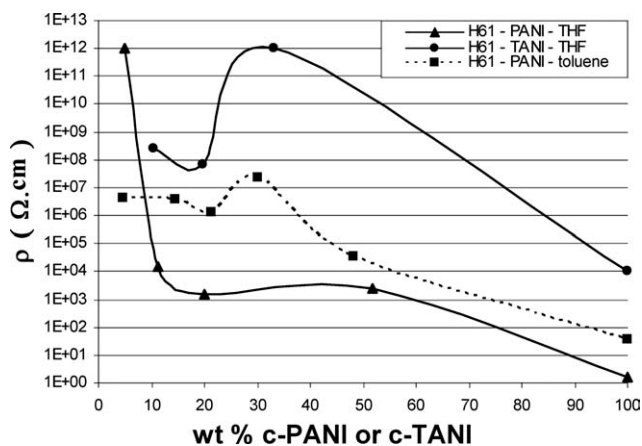


Figure 8 Resistivity of conductive blends cured 24 h/125°C prepared from (i) H61 epoxy, BF_3 -amine complex hardener, and c-PANI dispersed in THF (triangle dots), (ii) H61 epoxy, BF_3 -amine complex hardener, and c-TANI dispersed in THF (round plots), and (iii) H61 epoxy, BF_3 -amine complex hardener, and c-PANI dispersed in toluene (square plots) as a function of c-PANI or c-TANI content.

PANI; thus, higher resistivities are expected for the epoxy blends with the former. As seen from Figure 8, this is indeed the case.

Effect of the curing temperature

Curing of the OM 100 epoxy can be carried out at room temperature. The effect of the curing temperature (room temperature and 50°C, respectively, with in each case a curing time of 24 h) on the resistivity of the blends obtained from OM 100 epoxy, the same kind of BF_3 -amine hardener (Part B supplied by the producer), and c-TANI is shown in Figure 9. A slight increase of the blend resistivity is observed with an increasing curing temperature. Resistivity measurements carried out for the blend containing

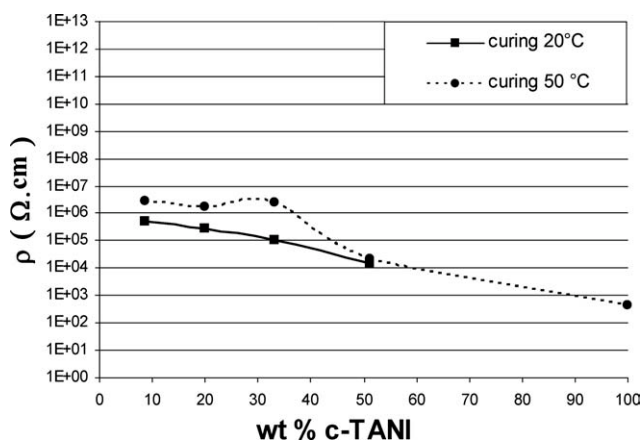


Figure 9 Resistivity of conductive blends prepared from OM 100 epoxy, BF_3 -amine complex hardener, and c-TANI dispersed in THF—curing at room temperature (square plots) or 50°C (round plots) during 24 h as a function of c-TANI content.

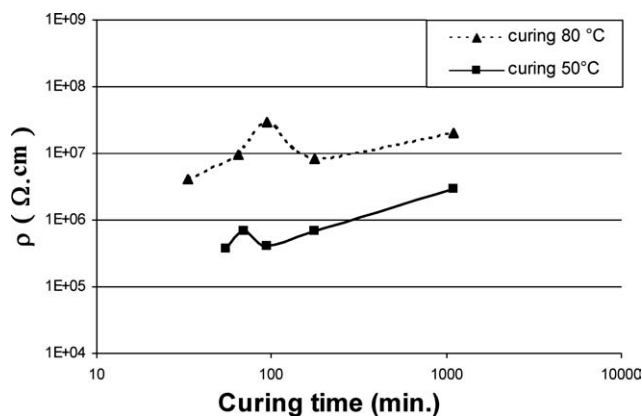


Figure 10 Resistivity of conductive blends prepared from OM 100 epoxy, BF_3 -amine complex hardener, and 30 wt % c-TANI dispersed in THF—curing at 50°C (square dots) or 80°C (triangle dots)—as a function of curing time.

30 wt % of c-TANI (cured at 50 and 80°C, respectively) performed for samples cured for different times show that the resistivity also increases with an increase in the curing time (cf. Fig. 10).

DISCUSSION

Dedoping

UV-vis-NIR is a very sensitive tool to investigate even small changes in the protonation state of PANI and its short-chain oligomers. In general, the undoped polymer shows two characteristic bands around 330 and 640 nm.²² In the case of the protonated (doped) c-PANI, two types of spectra are usually observed.²³ For c-PANI showing metallic type of conductivity (case of strongly delocalized polarons), a sharp peak at 440 nm is observed, accompanied with an adsorption tail increasing toward the NIR part of the spectrum. To the contrary for c-PANI exhibiting semiconducting type of electrical transport, three well-defined peaks can be distinguished in the UV-vis-NIR spectra: at 360, 440, and around 780–800 nm. As seen from Figure 3, the sample containing 10% of c-PANI is being totally dedoped within 2 h of the curing time, because bands characteristic of the protonated state are absent, and the only visible peaks can be attributed to the base (unprotonated) form of the polymer. The spectrum of the sample with 40% content can be considered as a superposition of the spectra characteristic of the protonated and unprotonated forms of PANI (note the presence of a clear absorption band at 440 nm originating from the electronic transition in the doped state). Thus, a coexistence of undoped and doped regions must be postulated; however, the doped “islands” do not completely percolate, because the macroscopically measured resistivity is

TABLE I
Chemical Formula and Composition of Base Prepolymers E 730,
H61, and OM 100 Epoxies

Epoxy base pre-polymer	Chemical formula	E730	H61	OIM 100
Epoxy function				
DGEBA = Poly(bisphenol A-co-epichlorohydrin), glycidyl end-capped		25–45%		65–85%
Resorcinol diglycidyl ether (RDGE)			100%	
Epoxy Cresol Novolac = Poly[(o-cresyl glycidyl ether)-co-formaldehyde] (ECN)		35–55%		
1,4 Butanediol diglycidyl ether (BDE)				15–35%


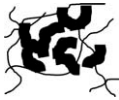
high in this case (cf. Figs. 2 and 3). For the sample containing 50% of c-PANI, the spectral changes induced by the extension of the curing time from 2 to 20 h are only minimal, the peak characteristic of the base (deprotonated) form is slightly better resolved at 330 nm. However, the peak corresponding to the polymer doped state at 440 nm is clearly visible in both cases. Nevertheless, the resistivity increases by three orders of magnitude after extended (20 h) curing. In terms of the percolation approach, this means that the small connectivity between the conductive "islands" has been at least partially lost. Taking into account the shape of a typical percolation curve, this process can be induced by a very small decrease in the content of the conductive phase.

To assess the hypothesis, that the observed resistivity increase is caused by the deprotonation of c-PANI with the hardener containing strong bases, we have prepared c-PANI blends with the same epoxy resin but using an amine-BF₃ complex 1115 Anchor hardener (see Fig. 4), whose c-PANI deprotonation capability is reduced, as previously demonstrated for other type of epoxy resins.^{10,24,25} It is observed that, for this hardener, the resistivity remains at relatively low value, despite the fact that, for the amine-BF₃ complex, a much longer curing time was used (24 h). This means that, as expected, the protonation

state of c-PANI has not changed to a significant extent after extending curing. The same effect is observed when the same type of amine-BF₃ complex hardener is used with another epoxy resin, namely H61 epoxy (Fig. 5).

The results described earlier clearly indicate that the amine-BF₃ complex type is better suited than common amine hardeners. However, other factors must also be taken into account, for example, the epoxy network density. Figure 5 shows the resistivity data obtained for c-PANI blends prepared from two different epoxy resins (E730/A1115 and H61) using the same type of hardener (amine-BF₃). It is clear that the percolation threshold is significantly lower in the case of the H61 single component epoxy (~ 15%) than for the two component E730/A1115 epoxy (see Fig. 5). Because both blends were processed in the identical way (*vide infra*) from the same solvent, we believe that the resulting differences in the resistivity arise from different epoxy network density in both cases. There are two factors that determine the epoxy network density. First, referring to the chemical formula of the base prepolymer epoxies (cf. Table I), there is an increasing network density for DGEBA, BDE, RGDE, and ECN, respectively, if we assume that all the epoxy functions are implied in the curing process. E730 and OM 100 products are made of a blend of the base prepolymers displayed in Table I,

TABLE II
Possible Morphology of *c*-PANI Agglomerates in a Dense (H61 Based) or Relaxed (E730/A1115) Epoxy Network

Dense epoxy network		Smaller <i>c</i> -PANI aggregates with high aspect ratio (thick line) in a dense epoxy network = lower percolation threshold	H61 & <i>c</i> -PANI conductive adhesive
Relaxed epoxy network		Larger <i>c</i> -PANI aggregates with high aspect ratio (thick line) in a relaxed epoxy network = higher percolation threshold	E 730/A115 & <i>c</i> -PANI conductive adhesive

whereas H61 is made of a single prepolymer. We do not know exactly the composition of E730 and OM 100 products; but as judged from the data collected Table I, we may assume a decreasing interreticular distance and thus an increasing network density for OM100, E730, and H61.

Second, the epoxy network density is dependent on the crosslinking reaction rate. The curing is a thermally activated process, and thus a more dense network is expected with a high temperature due to the fact that it activates the epoxy sites reactivity and leads to a faster and a more complete curing degree. The recommended curing conditions of the H61 are 120°C to 60 min while it is 120°C to 4 h for the E730 base prepolymer using the A1115 complex BF₃-amine hardener. So, the curing rate of the E730/A1115 blend is lower than that of H61 one, and thus, the E730/A1115 epoxy network should be less dense than the H61 one. Therefore, both the chemical constitution of the prepolymer and curing rate favor a denser network for H61 when compared with E730/A1115. Note that, to ensure complete crosslinking, we have extended the curing time to 20 or 24 h. About 125°C curing temperature was used rather than 120°C to be just above the minimum curing temperature of 120°C. The lowering of the percolation threshold in denser H61-based blend can be explained by a more favorable aspect ratio in the conductive phase. Evidently, quick curing process leads to a denser crosslinking, and aggregates of conductive chains of *c*-PANI are relatively quickly entrapped in the epoxy network being formed. This quick curing may thus induce phase separation on a much more microscopic scale with possible shape anisotropy of the conductive phase. Slower crosslinking with lower network density leads, in turn, to a more significant isotropy of the conductive phase, because large *c*-PANI agglomerates of less elongated shape can be formed in this case. This can explain the differences in the percolation threshold as shown schematically in Table II. Similar effects, associated with the PANI aspect ratio, on the percolation threshold have previously been observed for epoxy resins containing dispersed PANI of different shape (particles, fibers, and wires).²⁶

Effect of the solvent

There are no significant differences in the resistivity data obtained for blends made of ethyl acetate or THF-based *c*-PANI dispersions for both E730/A1115 and H61 epoxies (Figs. 6 and 7). Contrarily, for both epoxies, there is a huge increase (at least three orders of magnitude) in resistivity when using toluene-based dispersion. Because this effect is observed for compositions exceeding the percolation threshold, the observed differences must arise from different resistivities of the conductive phase (*c*-PANI) in the investigated blends. Toluene is known to be a poor processing medium for highly conductive forms of *c*-PANI, leading to pure *c*-PANI films of higher resistivity ($\sim 10^2 \Omega\cdot\text{cm}$).²⁷ This is usually ascribed to an unfavorable conformation of polymer chains in the *c*-PANI films processed from this solvent. UV-vis-NIR spectroscopic data obtained for such films clearly show that the charge carriers (polarons) are in this case strongly localized.²² Thus, its presence in the epoxy-*c*-PANI mixture, during the blending and curing, must inevitably lead to blends of higher resistivities. The high resistivity of toluene processed *c*-PANI is confirmed by the measurements carried out for pure *c*-PANI films (see Figs. 6 and 7). This effect is even more pronounced for medium *c*-PANI contents between 30 and 60% for the E730/A1115. This could be attributed to a strong phase separation of the *c*-PANI blend prepared in toluene in the epoxy resin matrix due to lack of miscibility. Only small differences in the resistivity are observed in E730/A1115 and H61 blends prepared from toluene dispersions of *c*-PANI. This means that, in this case, the solvent effect is more pronounced than that originating from the epoxy network density.

Influence of the molecular weight

Above the percolation threshold, the resistivity of a *c*-TANI-based blends is always higher than that of the *c*-PANI ones for the whole range of conductive filler content (Fig. 8). The conductive *c*-TANI fillers are short monodispersed molecules whose resistivity

is approximately at least three order of magnitude higher when compared with c-PANI doped with the same dopant and processed from the same solvent.^{18,27} Even if a similar charge carriers transport mechanism is expected in c-TANI and c-PANI, in the former, the resistance originating from the inter-chain hopping contributes more to the total resistance of the material, leading to its higher resistivity when compared with c-PANI. Therefore, we may assume that the observed higher resistivities of the c-TANI-epoxy blends have their origin in a significantly higher resistivity of the conducting phase.

Comparing the c-PANI and c-TANI-based blend, we have also observed, during curing, a more pronounced phase separation between the c-PANI filler and the epoxy contrarily to the case of c-TANI filler. This indicates that the compatibility of the epoxy and conductive filler is better in the latter. Such behavior is not unexpected taking into account that small molecules are in general better processible when compared with their high-molecular weight analogues, even if the solubility parameters are similar. This was already observed previously for c-TANI-based blends.¹⁹

Blends of c-TANI with OM 100 epoxy (see Table I) seem especially promising to achieve a stable resistivity in a large c-TANI content range with a medium obtained resistivity (see Fig. 9). For these reasons, we have undertaken the task of determining the temperature and time of curing on the resistivity of these blends (Fig. 9). They show higher resistivities than the corresponding c-PANI-epoxy blends; still, their resistivity above the percolation threshold ($10^{5-7} \Omega\text{-cm}$) is technologically interesting. First, we observe that, at the content of 10 wt % of c-TANI, the percolation threshold is not yet reached. This behavior is consistent with the previous study on oligoaniline/epoxy blends showing a very low-percolation threshold.¹⁸ This is of significant technological importance taking into account that the content of the conductive phase of rather poor mechanical properties should be as low as possible to obtain blends of mechanical properties typical of epoxy resins. This low-percolation threshold has been obtained for an epoxy resin showing a lower epoxy network density than other resins tested (see Table I). For c-PANI, such resins give rather large percolation thresholds. Second, technologically important feature of the c-TANI-OM 100 epoxy resins is their low sensitivity to the conditions of curing (temperature and time). In particular, an increase of the epoxy network density induced either by an increase of the curing temperature or by the extension of its time leads to relatively small changes in the resistivity. Last, technologically important feature is the almost unchanged resistivity in a large c-TANI content range from ~ 10 to 35 wt %.

CONCLUSIONS

To summarize, the results obtained in the course of the described research unequivocally show that there exists three crucial parameters determining the final resistivity of c-PANI (or c-TANI)—epoxy resin blends. The first is associated with the deprotonation of the c-PANI (or c-TANI) during the curing of the blend. This deprotonation, leading to a quick increase of the conductive phase resistivity, is caused by the hardener; therefore, a careful choice of this component must be undertaken. BF_3 -amine complex (such as Anchor 1115 for instance) is much better suited for this purpose than classical amine hardeners. Second, the percolation threshold in the blend depends on the type of the epoxy resin used. For c-PANI-based blends, lower percolation thresholds are obtained for resins with higher epoxy network densities. Third, the selection of the c-PANI processing solvent has an even more pronounced effect on the blend resistivity than the density of the epoxy network as observed for toluene-based blends. Finally, technological importance of c-TANI—epoxy resin blends should be pointed out, even though the obtained resistivities are much higher. They are easier to process and not very sensitive to the epoxy-curing conditions and c-TANI content variations.

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