On the “Curiosity” of Electrically Conductive Melt Processed Doped-Polyaniline/Polymer Blends versus Carbon-Black/Polymer Compounds

M. Narkis,1 M. Zilberman2 and A. Siegmann2

1 Department of Chemical Engineering and 2 Department of Materials Engineering, Technion-Israel Institute of Technology, Haifa 32000, Israel

© 1997 by John Wiley & Sons Ltd.

No. of Figures: 4 No. of Tables: 0 No. of Refs: 16

KEYWORDS: electrically conductive polymer blends; polyaniline; conductive blends

Carbon black/polymer conductive compounds have been known and commercially used for many years, and their scientific background is quite well established and documented. In contrast, polyaniline/polymer blends (PANI/polymer) processible via dry (solvent-free) melt-shaping methods are still relatively unknown, insufficiently understood, and only a single commercial PANI/polymer blend for dry melt processing is presently commercially available (PANI/PVC, Zipperling, Germany). In this communication, a mechanism of PANI structuring in dry melt-processed PANI/polymer systems is suggested. In addition, the differences between these two conductive “fillers” (carbon black and PANI) in melt blending and processing, and the rules governing their mode of dispersion in the solidified polymer matrix, which determines the blends conductivity levels, are discussed. In future papers, detailed experimental evidence, supported by molecular modeling calculations, for the PANI/polymer systems, will be presented to support the ideas expressed in the present communication further.

Conducting carbon blacks (CB) often consist of elongated aggregates (low aspect ratios) composed of very small (nanometric) primary particles sintered together. Upon melt blending with a polymer and processing, the CB may undergo deagglomeration, aggregate erosion and fracturing, and reagglomeration, resulting in either a uniform or more often a nonuniform distribution of the black particles [1, 2]. The level of the particle distribution nonuniformity varies and, as a rule, higher nonuniformity levels result in higher conductivity levels owing to the formation of conducting paths [3, 4]. For example, nonuniform distributions are formed in semicrystalline polymers, where carbon black particles are selectively located within the amorphous regions, and in polymers having low affinity to the surface of the carbon black particles [5]. Thus, in semicrystalline polymers and particularly in relatively nonpolar and low surface tension polymers, represented, for example, by polyethylene and polypropylene (PP), the tiny carbon black particles tend to segregate and even percolate, by forming conducting networks at extremely low content of the CB particles, e.g. 3 wt% Ketjenblack EC in PP [6], as in Fig. 1(a). Other parameters, such as melt-blending conditions including shear level and shear history, are less important within the practical acceptable regions of blending regarding the CB structuring and conductivity levels obtained. More uniform distributions of carbon black particles are obtained in amorphous polar polymers having higher surface tensions, similar to that of CB (~50 dyne/cm). Thus, by dispersing carbon black (Ketjenblack EC) particles in a soft, amorphous and polar random co-polyamide 6/6.9 (≡poly[HN–(CH2)5–CO]−co–[HN–(CH2)6–NH–CO–(CH2)7–CO]) [7,8], percolation has not been realized up to the
maximum possible carbon black content of 14 wt%, owing to the formation of uniform particle distributions, as in Fig. 1b. By replacing the amorphous co-polyamide with a semicrystalline polyamide, Nylon 6, percolation is realized at roughly 7 wt%, owing to the nonuniform distribution of the CB particles, located only within the amorphous regions. Interestingly, carbon black particles are very selective and are able to migrate easily during blending from one phase to another in immiscible binary polymer blends. Thus, by adding a polyamide component into a melt of a pre-compounded carbon black/polypropylene mixture, fast migration of the carbon particles from the polypropylene into the polyamide takes place [8].

Polyaniline, PANI, powders represent a remarkably different case. In addition to being organic materials and having various possible morphologies, they are heavily doped with different inorganic or organic acidic dopants. The size of PANI primary particles and PANI aggregates is larger than the size of conducting CB particles. The reported most common dopants are sulfuric acid, hydrochloric acid, p-toluene sulfonic acid (pTSA), dodecyl benzene sulfonic acid (DBSA) and camphor sulfonic acid (CSA) [9, 10]. The dispersibility, in a given polymer, of doped PANI materials mainly depends on the dopant’s nature, the specific matrix and the compositional used [11–13]. Thus, PANI/H_2SO_4 materials, known to be practically insoluble in most organic solvents, disperse in an organic molten polymer similarly to an inorganic filler. The PANI/H_2SO_4 particles certainly undergo fracturing in an intensive mixing step, yet these fractured rigid particles do not form conductive segregated structures, as the fine CB particles do. Thus, expected percolation levels are close to the predicted values, 16–30 vol.%, depending on the particle’s shape and specific distribution in a given matrix. Doped polyacetylene powders, also known as insoluble materials, are expected largely to behave like PANI/H_2SO_4 particles, namely as a filler, in melt blending with another polymer.

The organic dopants, pTSA and DBSA, and the doping level confer new properties on the doped PANI materials, including partial solubility in some solvents, e.g. PANI–pTSA in DMSO and m-cresol, and PANI/DBSA in toluene. PANI–pTSA is expected to behave somewhat differently from PANI/DBSA in various matrices owing to the long aliphatic group present in DBSA, which makes it less suitable for a PS matrix and other polar matrices, but more suitable for PE matrices. This difference may already show in the process of fracturing of the relatively large doped PANI aggregates during the melt-blending operation via intensive mixing. The level of fracturing obtained in the PANI particles (generally described as rupture and erosion) depends on the specific matrix and doped PANI used; on the matrix viscosity, the level of shear and time experienced, and on the adhesion level between the doped PANI particles and the matrix [14]. A doped PANI/polymer system of a higher interaction level, higher adhesion, will show a higher level of fracturing, in a given matrix, owing to better interphase shear stress transferability. Nevertheless, even in conductive blends where severe fracturing of the doped PANI particles has taken place during the intensive melt-mixing step and fine particles resulted in, it is still difficult to observe conducting networks by microscopical techniques.

It is thus suggested that a yet nonobservable, by optical and scanning electron microscopy, very fine short-range fibrillar-like morphology exists in the melt-processed blends, presumably interconnecting the observable fine discretely dispersed particles. This cooling rate-dependent morphology has been formed during the cooling step, following the melt-processing step. This could stem from partial dissolution, in the molten matrix, of doped PANI molecules, very probably the shorter chains. Then, upon cooling, some of the dissolved molecules may remain so; however, some precipitate out to form a fibrillar structure. Recall that structured doped PANI/polymer systems are obtained through solution casting and solvent evaporation, which form fibrillar-like networks. In this case the PANI molecules and matrix are both dissolved in a common solvent and an observable fibrillar structure of PANI tiny particles distributed within the matrix is formed during solvent evaporation, owing to the relatively low system viscosity, as schematically shown in Fig. 2(a). The effect of the relatively slow cooling step of a hot PANI/polymer melt is similar to the previous effect of solvent evaporation. The system undergoing cooling, however, is highly viscous permitting only the formation of short-range, very fine, fibrillar structures interconnecting the discretely dispersed PANI particles and thus forming continuous conducting paths. Therefore, at least a three-level structural hierarchy is expected (molecular, fibrillar-
like and discrete particle dispersions) as schematically shown in Fig. 2(b).

A behavior similar to the solution cast samples, Fig. 2(a), was reported for solid-plasticizer/polymer systems (e.g. tetra-bromoxylene/polystyrene, TBX/PS) where at the elevated processing temperature TBX dissolution into the PS matrix has taken place followed by precipitation out and formation of segregated fine crystalline morphologies, upon slow cooling [15]. The contribution of the PANI molecules remaining dissolved in the solid matrix to the system’s conductivity is assumed to be negligible. Electron microscopy studies in our laboratories have revealed that doped PANI, with pTSA or DBSA, underwent fracturing to significantly different levels in different polymers. Thus, fine particles were observed in a polycaprolactone, PCL, or co-poly-amide matrix, whereas large PANI–pTSA particles were observed in polyethylene, Fig. 2(b) and (c). The PANI–pTSA/polyethylene blends remained insulative up to high PANI–pTSA contents (close to the predicted percolation value), very probably owing to the lack of doped PANI–pTSA molecule dissolution and subsequent formation of the previously described particle–particle interconnecting, short-range, fine structures. In contrast, conducting blends containing structures of fine PANI–pTSA particles, interconnected by PANI–pTSA fibrils, are formed in PANI–pTSA/co-polyamide and PANI–pTSA/PCL systems.

The conductivity results, shown in Fig. 3, are supported by the SEM micrographs shown in Fig. 4 (our preliminary TEM studies strongly indicate the presence of a short-range fibrillar-like structures). Figure 4(a) depicts large PANI particles detached from the PE matrix, whereas in PCL the same PANI disintegrates into barely observable tiny particles, wetted and covered by the PCL matrix, Fig. 4(b).

Contrary to the PANI–pTSA/co-polyamide conductive blends, carbon black/co-polyamide blends are insulative owing to the formation of uniform CB particle distributions. The foregoing description explains the presently practical availability of only a single commercial doped PANI/PVC material for melt processing [16]. This product probably consists of doped PANI–pTSA which has sufficient partial solubility in the plasticized PVC to generate a morphology consisting of the structural hierarchy described, which is needed to form a conducting network in the blend. In addition to plasticized PVC, PETG and PMMA are also mentioned as candidate polar matrices for highly conductive thermoplastic polymer blends with doped PANI [16]. Contrary to these PANI-containing systems, these two polymers each combined with carbon black will undoubtedly show high percolation concentrations. Our own experience has shown that polystyrene is a good candidate as a host matrix for PANI–pTSA (polystyrene is also a good host matrix for CB) probably because of its aromatic nature, consistent with the aromatic dopant. Thus, increased polarity and aro-

**FIGURE 2.** Schematic representation of doped PANI distribution in a host matrix: (a) solution cast; (b) melt blended, PANI–pTSA/PCL (dissolved molecules, ~); (c) melt blended, PANI–pTSA/polyethylene.

**FIGURE 3.** Conductivity of PANI–pTSA/PCL and PANI–pTSA/polyethylene blends.
maticity enhance the potential of a polymer to serve as a suitable host matrix for PANI doped with pTSA. In such systems, PANI molecular weight should play an important role, particularly the soluble fraction of the shorter chains. Thus, a broad molecular weight distribution containing a low molecular weight tail, or a bimodal distribution is desired. Plasticizers may play important roles in both enhancing dissolution of doped PANI molecules in the hot melt and in reducing the processing temperature—the latter is of importance to preserve conductivity.

In summary, considerations of carbon black distribution and doped PANI distribution in a given polymer matrix are remarkably different and may even represent opposite cases. In the CB-containing systems there are obviously no solubility effects, and structuring of the CB particles occurs during the melt-processing step. Further structuring, of the CB particles, takes place during the cooling step, mainly in semicrystalline matrices. In the doped PANI/polymer systems, the doped PANI component, probably the shorter chains, may partially dissolve in the melt and upon cooling partially precipitate out to form a fine, short-range, fibrillar structure bridging the discretely dispersed doped PANI particles, resulting in a conducting network represented by this two-level hierarchy. The levels of fracturing and dissolution, in a given matrix, of the doped PANI particles and molecules, respectively, strongly depend on the dopant nature. The more complex distribution of doped PANI and CB particles in a given continuous matrix, through melt blending, seems to explain the less sharp insulator-conductor transition in the former. Doped PANI/polymer systems produced through solution blending (a single fibrillar-like structure is generated) show sharper insulator-conductor transitions. The rules set forth in this communication are believed to be useful for further understanding the behavior of doped PANI/polymer blends and for the development of new useful commercial thermoplastic and thermosetting highly conductive blends.

ACKNOWLEDGMENTS

The support of the University of Drexel-Technion Foundation (Harry Stern Program for Innovative Academic Initiatives) and the Israel Ministry of Science is greatly appreciated.

REFERENCES

14. I. M. Zloczewer and Z. Tadmor, Mixing and Compounding of Polymers, Ch. 3, Hanser Publisher, Munich (1994).

**FIGURE 4.** SEM micrographs of fracture surfaces (liquid nitrogen, 20 wt% PANI) of: (a) PANI-pTSA/polyethylene and (b) PANI-pTSA/PCL blends.