Polyaniline/PVAc Blends: Variation with Time of Structure and Conductivity of Films Cast from Aqueous Dispersions

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ABSTRACT: Recently, a polymerization process of Anilinium-Dodecyl Benzene Sulfonic Acid (DBSA) complex in an aqueous dispersion was developed in our laboratories. Simple mechanical mixing of the aqueous PANI–DBSA dispersion with a PVAc aqueous latex leads to highly conductive blends at low PANI–DBSA contents. The percolation threshold of the dried films is extremely low (~0.5 wt %). The combined aqueous PVAc/PANI–DBSA dispersions exhibit a gradually decreasing electrical conductivity accompanied by a gradually increasing viscosity, with the storage time. However, an aged cast film from these blends maintains its electrical conductivity with time. These phenomena are associated with acidic hydrolytic reactions of the ester group, resulting in the formation of vinyl acetate–vinyl alcohol copolymer and evolution of acetic acid, and also the interaction of the DBSA surfactant with the PVAc, causing swelling and disintegration of PVAc particles. A chemical structural model describing these changes with storage time is suggested. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 760–766, 2001

Key words: polyaniline; PVAc latex; aqueous dispersion; blends; conductivity

INTRODUCTION

The applicability of Intrinsically Conductive Polymers (ICP), such as polyaniline (PANI), is restricted by their poor processability and the resulting mechanical properties. Numerous studies have been conducted, and methods developed for the improvement of PANI processability. One method for processing PANI without altering its structure is by blending with a conventional polymer. These blends are designed to combine the desired properties of both components, i.e., electrical conductivity of PANI along with processability and physical properties of the matrix polymer. In most studies of electrically conductive PANI-containing blends, blending was performed in a solution or via melt blending. A less common method for blending is through dispersions mixing.

Synthesis of colloidal PANI particles[1–5] and their application in polymer/PANI blends[6–13] have been of great interest. When colloidal particles of PANI are used to form polymer/PANI blends, fine conductive paths may generate and high conductivity levels may be realized already at low PANI contents.

Two main approaches in the preparation of PANI containing colloidal blends can be distinguished. Blends have been prepared by polymerizing aniline in the presence of the matrix polymer latex[6–10] or by simple mechanical mixing of a colloidal PANI dispersion with a matrix polymer latex.[11–13] Because aniline polymerization is affected by many parameters, for example, pH level, aniline–oxidizer ratio,[14] the second route, polymerizing aniline separated from the matrix polymer, enables efficient control of the polymerization process.

Gospodinova et al. obtained PANI-containing blends by simple mechanical mixing of a colloidal PANI–DBSA (Dodecyl Benzene Sulfonic Acid) dispersion with a solution of the host polymer (PVAL dissolved in water and EVA dissolved in xylene) followed by solution casting.[11] Haba et al. developed a unique polymerization process of anilinium–DBSA salt (no organic solvents and surfactants are required) in an aqueous dispersion.[5] The mechanical mixing of a PANI–DBSA aqueous dispersion with an aqueous emulsion of another polymer, for example, polyacrylates, PMMA, and PS, leads to highly conductive dried blends at very low PANI–DBSA contents. The percolation threshold of such blends is extremely low (~0.5 wt % PANI–DBSA).[12,13] Haba et al. also found that the conductivity level of the various blends is independent of the polymer matrix nature. This stems from a segregation mechanism in which the PANI–DBSA particles "feel" the character of the particle's surface and not the specific polymer and thus segregate accordingly.[12,13]

Film forming polymer/PANI blends prepared via the aqueous dispersion method, have a utilization potential in various applications, such as conducting paints, conducting adhesives, and antistatic coatings. The coagulated and dried powdery blends can be used in melt processing procedures.

In this article the method of anilinium–DBSA polymerization in an aqueous medium[5] was utilized to form polymer/PANI–DBSA blends focusing on PVAc/PANI–DBSA blends prepared via the aqueous dispersion mixing method. The stability of the electrical conductivity under different environmental conditions was investigated and is reported in the article.

EXPERIMENTAL

Materials

Poly(vinyl acetate) (PVAc) aqueous latex (50 wt % solid content, at approximately room temperature T_g) was supplied by Tambour, Israel.

Polymerization of Aniline

Anilinium–Dodecyl Benzene Sulfonic Acid (DBSA) complex (needle-like salt particles formed by reacting aniline with DBSA) was polymerized in an aqueous dispersion according to the process developed in our laboratories.[5] Aniline (12 g) and DBSA

(43.2 g) at a stoichiometric ratio were dissolved and reacted in water (1200 g) for 3 h at room temperature to form a homogeneous milky dispersion of particles of the anilinium–DBSA complex. The dispersion temperature was then maintained at ~0°C, and a solution of ammonium peroxydisulfate (30 g dissolved in 100 g water) was added dropwise. Polymerization was carried out at ~0°C for 5 h, forming a green, stable PANI–DBSA dispersion containing ~1.8 wt % doped PANI (determined by complete precipitation with water).

Blend Preparation

PVAc/PANI–DBSA blends were obtained by simple mechanical mixing of the aqueous PANI–DBSA dispersion with the aqueous PVAc latex. Free-standing PVAc/PANI films were obtained by casting the aqueous blends onto glass substrates, gently evaporating the water on a hot plate at 40°C, and vacuum drying.

Morphological Characterization

High Resolution Scanning Electron Microscopy (HRSEM) of freeze fractured films was performed using a Leo Gemini-982 machine, at an accelerating voltage of 1 kV, using the SE IN-LENS technique. The samples were placed on a carbon tape for observation.

Rheological Behavior

The rheological behavior of the combined PVAc/PANI–DBSA mixtures in the aqueous state was studied using an Epprecht-Rheomat 15 (Contravas AG) concentric cylinders rheometer.

Conductivity Measurements

The electrical conductivity of films (up to 10^{-7} S/cm) was measured using the "four probe technique" (ASTM D 991-89). The electrical conductivity of less conductive films was measured using the DIN 53596 technique.

RESULTS AND DISCUSSION

Upon mixing a PANI–DBSA dispersion with the PVAc latex, a visually homogeneous and stable blend is obtained. Such blends are film forming at room temperature due to the low T_g of the PVAc matrix polymer. An interesting characteristic of
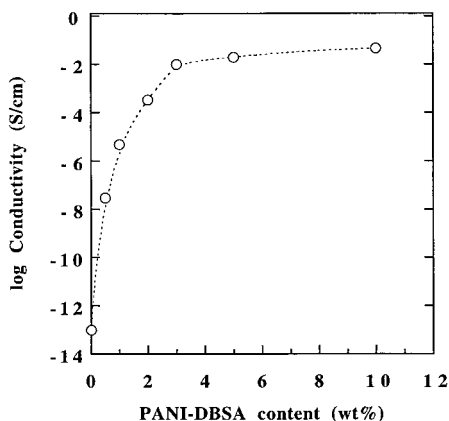
Figure 1 Electrical conductivity of PVAc/PANI–DBSA films vs. PANI–DBSA content.

the PVAc/PANI–DBSA films is their semitransparency.

The electrical conductivity of PVAc/PANI–DBSA films vs. the PANI–DBSA content is depicted in Figure 1. A conduction threshold (at 10^{-8} S/cm) is observed at an extremely low PANI–DBSA content (~0.5 wt %). The conductivity tends to level off at 10^{-2} S/cm above 3 wt % PANI–DBSA. According to Haba et al.,[12,13] the segregation process in the polymer/PANI blends obtained by the aqueous dispersions mixing method depends upon the different surface characteristics of the PANI–DBSA and the matrix particles. Hence, PANI–DBSA blends with different latex polymers may show similar electrical conductivity behavior, particularly if the same surfactant has been used in the latex polymers synthesis.

The featureless surface morphology of the film-forming PVAc latex is depicted in Figure 2(a). Clearly, the low T_g (~28°C) of the PVAc has ensured an efficient particles coalescence so that the individual primary sub-micron particles are no longer discernible (the PVAc film was very sensitive to the scanning electron beam, despite the low, 1 kV, voltage used). The PVAc/PANI-DBSA (97/3) film [Fig. 2(b)–(d)] exhibits a complex morphology. It consists of both rather smooth areas [Fig. 2(b)] similar to that of PVAc film and hexagonal-like structures. A higher magnification [Fig. 2(c) and (d)] reveals that the blend film also contains partially coalesced PVAc primary spherical particles, ~2–3 μm in diameter. This is in agreement with the observations that the last stage of latex film formation involves hexagonal structure formation and coalescence through self-

diffusion into an homogeneous, isotropic film.[15] In immiscible emulsion blends no diffusion across the interface occurs, thus, leading to poor properties of the resulting blend.[15] The HRSEM micrographs (see Fig. 2) confirm that the PANI–DBSA phase is heterogeneously distributed throughout the PVAc matrix. The poor coalescence of the PVAc particles in some parts of the film is caused by the presence of PANI–DBSA particles among the PVAc particles. The relatively large diameter of the PVAc spherical particles (~2–3 μm diameter compared with a typically submicron diameter) observed in the PVAc/PANI–DBSA blend is attributed to the PVAc particle's swelling. This phenomenon will be further discussed below.

Two procedures (described in Fig. 3) were employed to monitor the stability of the electrical conductivity of the PVAc/PANI (97/3) blend: (a) Procedure 1: (film aging)—conductivity measurement in 30 days intervals of the cast film, preserved at room temperature; and (b) Procedure 2: (aqueous PVAc/PANI–DBSA blend aging)—every 30 days films were cast from the original aqueous blend and their electrical conductivity was measured.

The conductivity results are depicted in Figure 4. The PVAc/PANI–DBSA (97/3) aged film (procedure 1) maintained its electrical conductivity during the monitored period, while the conductivity of the aged PVAc/PANI–DBSA (97/3) aqueous blend (procedure 2) significantly decreased during the same monitored storage time. The initial conductivity of the PVAc/PANI–DBSA (97/3) blend was 0.05 S/cm, and after a 120 days storage period it reached a value of 2×10^{-5} S/cm. This electrical conductivity reduction was accompanied by a significant increase of the blend's viscosity (Fig. 5) and by evolution of a strong smell of acetic acid. The viscosity of the aqueous PVAc/PANI–DBSA blend increased by more than an order of magnitude after a 90 days storage period (Fig. 5). For comparison, the rheological behavior of a PVAc/DBSA blend (without PANI) was also characterized. Addition of an equivalent concentration (to the DBSA concentration in the PVAc/PANI–DBSA (97/3) blend) of DBSA to the PVAc latex resulted in a significant viscosity increase after a 90 days storage period (Fig. 6). It is thus concluded that the DBSA presence (presumably the DBSA excess) within the PVAc/PANI–DBSA (97/3) blend is responsible for the observed viscosity increase. Two possible chemical reactions are suggested to occur between the DBSA—a strong acid, and the PVAc particles in the latex (Fig. 7).
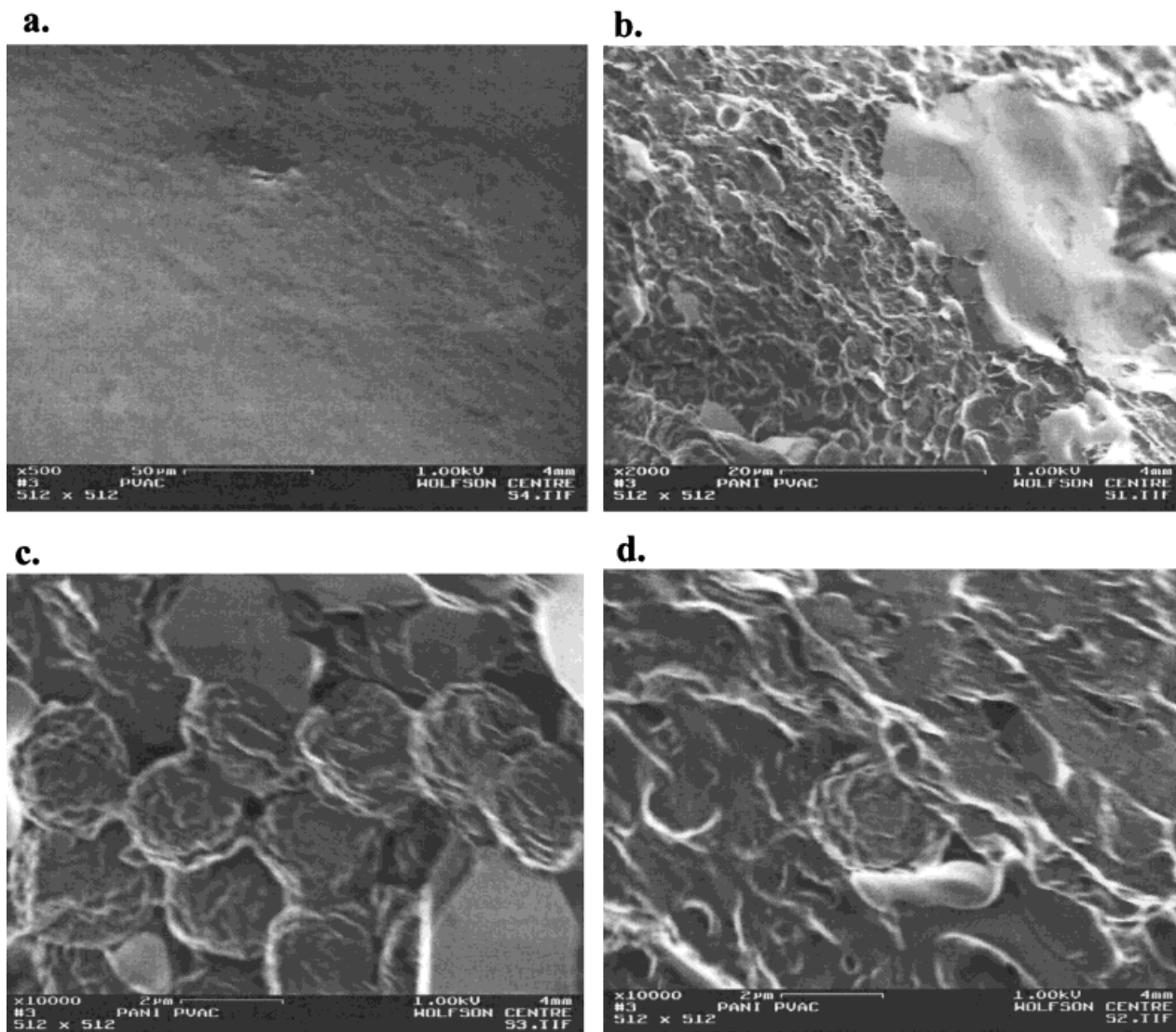
Figure 2 HRSEM micrographs of freeze-fractured surfaces: (a) PVAc film, (b, c, d) PVAc/PANI–DBSA (97/3) blend at different magnifications.

The first, acidic hydrolysis of the ester groups, resulting in the formation of a vinyl acetate–vinyl alcohol copolymer and acetic acid. The second possible reaction can be regarded as an exchange reaction, where DBSA attacks the ester group while it is bonded to the PVAc molecule along with the production of acetic acid. These two chemical reactions may occur simultaneously. The formation of the vinyl acetate–vinyl alcohol copolymer converts an insoluble PVAc polymer into a partially water soluble vinyl acetate–vinyl alcohol copolymer (PVAl), with a gradually increasing solubility with the increasing hydrolysis level into hydroxyl groups. The observed viscosity increase of the aqueous PVAc/PANI–DBSA blend
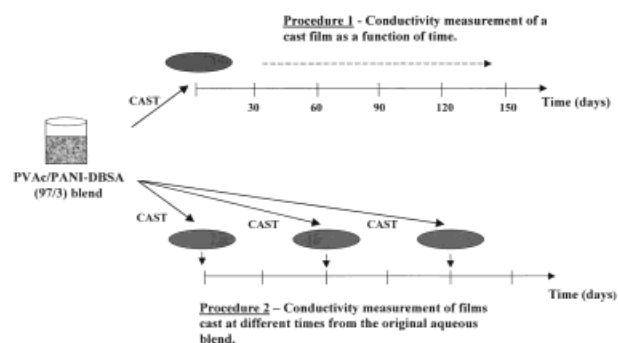

Figure 3 Schematic description of the two procedures employed for monitoring the electrical conductivity stability with time of a PVAc/PANI (97/3) blend.
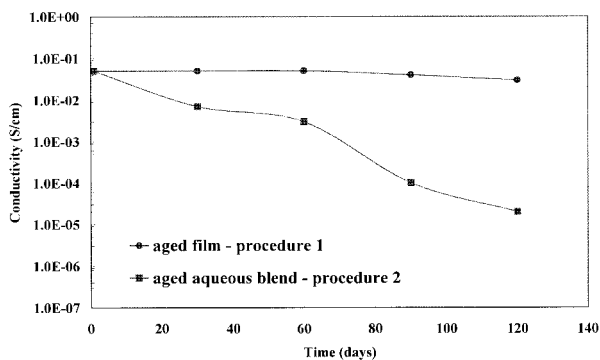
Figure 4 The conductivity of PVAc/PANI–DBSA (97/3) films as function of storage time.

Figure 6 Viscosity vs. shear rate of a PVAc/DBSA dispersion as function of storage time.

with storage time is the result of the gradually increasing dissolved PVAl concentration in the water. The foregoing explanation is further supported by a literature report stating that some surfactants, such as sodium dodecyl sulfate (SDS) and sodium dodecylbenzene sulfonate (DBS), tend to interact with PVAc, causing solubilization of the insoluble polymer and thus leading to an increasing viscosity.[16] Edelhauser explained that anionic surfactants, such as SDS and DBS, interact with PVAc latex particles in a two-step mechanism including surface adsorption followed by surfactant penetration into the interior of PVAc particles. The surfactant and water cause swelling and gradual disintegration of the outer parts of the particles.[17] Based on the chemical structure resemblance of DBS and DBSA, the aging process taking place in the aqueous PVAc/PANI–DBSA blend is suggested to include the following chemical structural changes (Fig. 8). Scheme A in Figure 8 describes the structure of PVAc (depicted in the left column) and PANI–DBSA (depicted in the right column) after the blending stage. The blend
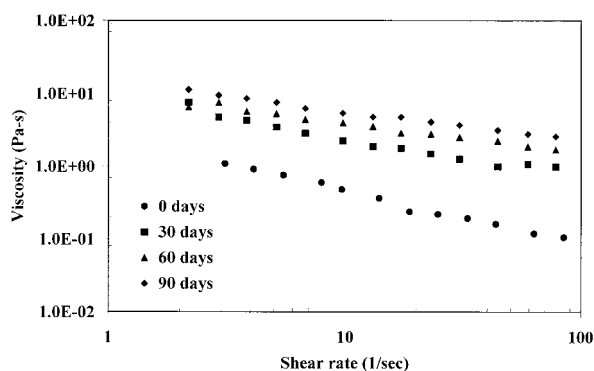
consists of PVAc particles, PANI–DBSA particles and "free" DBSA suspended in water. The excess DBSA in the original PANI–DBSA dispersion forms micellar structures and also acts as a surfactant, which stabilizes the dispersion of the PANI–DBSA particles (the structure of the neat

Figure 5 Viscosity vs. shear rate of the PVAc/PANI–DBSA (97/3) dispersion as function of storage time.

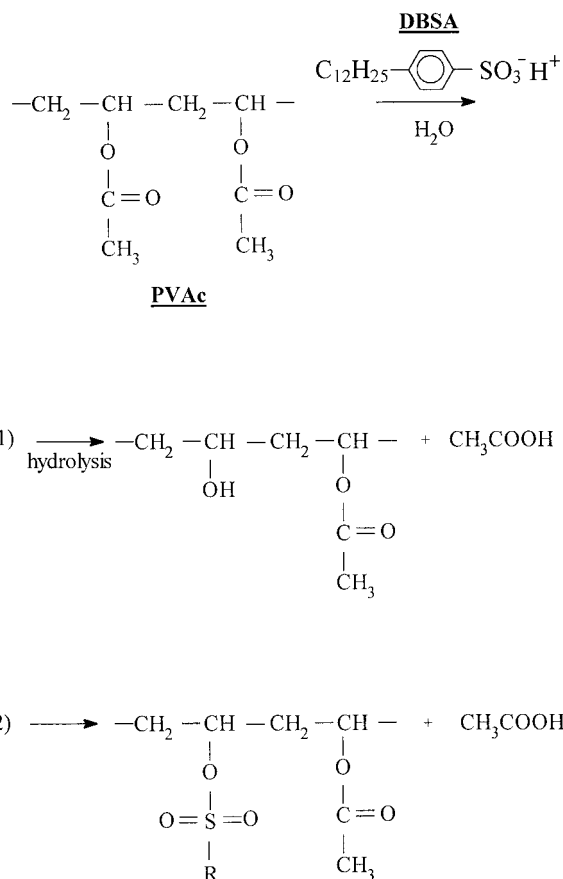**Figure 7** Suggested chemical reactions of PVAc in the presence of DBSA in an aqueous medium.
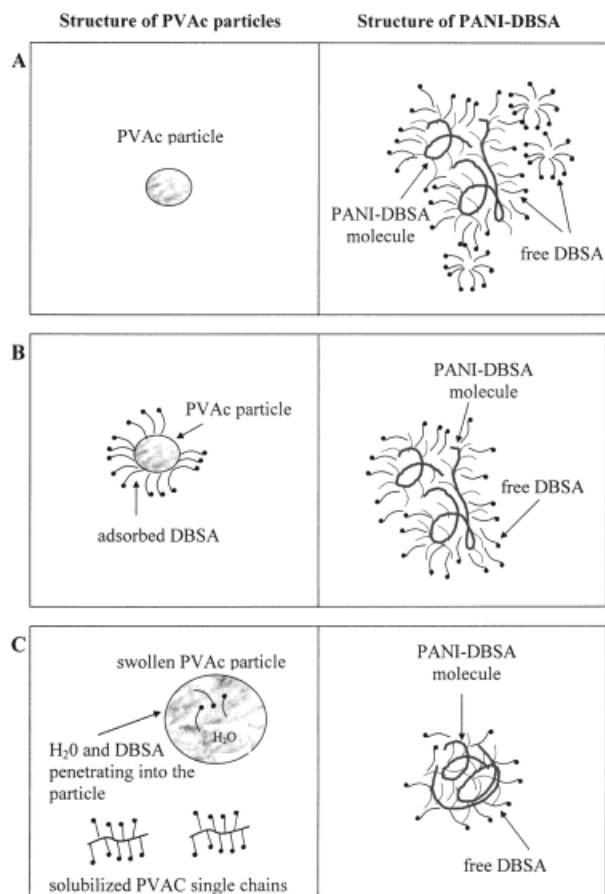
Figure 8 A schematic model describing structural changes taking place in the PVAc/PANI–DBSA dispersion with storage time.

PANI–DBSA dispersion was previously described[12]). Scheme B describes the blend's structure after a certain storage time has elapsed. Some of the "free" DBSA in the blend has been adsorbed on the surface of PVAc particles. The hydrophobic tail of the DBSA molecules is adsorbed onto the surface of the PVAc particle, while the hydrophilic groups turn to the aqueous phase. With time, the DBSA causes acidic hydrolytic reactions as was discussed above (according to Fig. 7). Scheme C depicts the blend's structure after a relatively long storage time of several weeks. DBSA molecules have penetrated into the interior of PVAc particles along with a certain amount of water. As a result, a substantial swelling of the PVAc particles takes place (as evidenced by the HRSEM micrographs). Concurrently, single PVAc chains from the swollen outer parts of the PVAc particles disentangle and "solubilize." The presence of the solubilized single

PVAc chains in the blend further induces the viscosity increase.

The reduced concentration of dissolved "free" DBSA molecules within the blend's aqueous medium can cause a significant change in the conformation of the PANI–DBSA chains. A progressive change in the molecular conformation of the PANI–DBSA chains, from "expanded coil" to "compact coil," may take place and thus reduce the interaction level between the hydrophobic polymer and the polar aqueous medium. Such conformation changes reduce the hydrodynamic volume of the PANI–DBSA particles and thus decrease the electrical conductivity level of the particles in the aqueous blend with storage time. These changes in the conformation of the PANI–DBSA chains do not affect the viscosity of the blend due to the relatively low concentration of PANI–DBSA particles in the blend. In a future article, unique blends of PANI–DBSA/polystyrene systems prepared via the aqueous dispersions mixing method followed by melt mixing will be described.

CONCLUSIONS

Cast PVAc/PANI–DBSA films obtained through an aqueous dispersion mixing procedure become conducting at very low PANI–DBSA content (~0.5 wt %) and attain conductivity levels of ~10^{-2} S/cm at ~3 wt % PANI–DBSA contents. The combined aqueous PVAc/PANI–DBSA blends exhibit upon storage a gradually decreasing electrical conductivity and increasing viscosity, accompanied by evolution of acetic acid. It is suggested that acidic hydrolytic reactions of the PVAc ester group and interactions of DBSA with the PVAc molecules are related to the observed aging effects.

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