폴리비닐부티랄–폴리아닐린 복합체의 합성과 전기유변학적 특징 고찰

황지연, 장인배, 조민성, 최형진
인하대학교 화공·고분자·생물공학부

Synthesis and Electrorheological Characterization of Poly(vinyl butyral)(PVB)-Polyaniline(PANI) Composites

J.Y. Hwang, I.B. Jang, M.S. Cho, H.J. Choi
Department of Polymer Science and Engineering, Inha University, Incheon 402-751, Korea

Introduction

Polyaniline (PANI) is known to be one of the most useful conducting polymers for the various electrochemical and electronic applications because of its facile synthetic process, good environmental stability, low cost of raw material and conductivity control. PANI is also easy to polymerize by oxidation polymerization. For electrically conducting polymers in general, and PANI in particular, difficult processability due to their insolubility in common solvents should be overcome for their successful industrial applications.

To improve processability of the PANI (Aldissi M, 1993), various kinds of dopants instead of HCl such as benzenesulfonic acid, sulfosalicyclic acid, camphor sulfonic acid and dodecylbenzene sulfonic acid have been adopted. Nonetheless preparation of PANI dispersion is one of the most attractive approaches to improve the processability of PANI, since colloidal dispersions may be applied in place of completely dissolved solutions. The conducting polymeric submicron size particles are synthesized in the presence of a polymeric stabilizer, which adsorbs onto polymer nuclei and prevents their further aggregation via a steric stabilization mechanism. The macroscopic precipitation of polymer is prevented by the presence of the steric stabilizers such as poly(vinyl alcohol), poly(N-vinyl pyrrolidone), poly(vinyl methyl ether) and cellulose ethers. To enhance the dispersion stability of polyaniline, we used poly (vinyl alcohol) (PVA) (Stejskal *et al.*,1992) with hydroxyl groups as polymer stabilizer and obtained the PANI-PVA particles of a uniform nanometer size and a spherical shape prepared by the oxidative dispersion polymerization in acidic aqueous media. Note that the PVA possesses good film-forming ability, toughness and good biocompatibility. However PANI-PVA cannot be directly adapted to ER system without controlling conductivity because its conductivity is too high. Thereby, acetalization of PANI-PVA method is adopted as a substitute method for dedoping   in this study.

Experimental
Dispersion Polymerization

Polyaniline dispersion with poly(vinyl alcohol) as a steric stabilizer in acidic aqueous media was carried out by using oxidative dispersion method found in earlier references. PVA (molecular weight 70,000, degree of hydrolysis 98 mol %) was slowly dissolved in ionized water. The solution was heated up to 95℃ for 1 hour, cooled down at room temperature. 35 wt% HCl and aniline were added to solution and the reaction mixture was continuously stirring

at 0℃. An aqueous solution containing oxidant (ammonium peroxydisulfate) was added in drops for 60~90 min. The lightly yellow solution gradually darkened and turned emerald color over a period of 20 minutes and eventually turned dark green, which is a characteristic of doped polyaniline. This reaction mixture was then stirred for 24 hours at 0℃.

Synthesis of poly(vinyl acetals)

The acetalization (Toncheva et al.,1992) was carried out in reactor with PVA-PANI solution, equipped with mechanical stirrer, dropping funnel, reflux condenser and inlet for inert gas. The PVA-PANI solution which was included PVA and 35 wt% HCl as catalyst was prepared at 10℃. N-butyraldehyde was added to the solution at 10℃ for 60 min. With a progress of acetalization, the solutions became heterogeneous. This reaction mixture was then stirred for 3 hours at temperature from 10℃ to 55 ℃. The resulting dark green dispersions were filtered and washed by an aspirator. The separated PANI-PVB composite was then washed three times with deionized water.

Results and Discussion

PVA, like low-molecular-weight alcohols, is highly reactive lending itself to esterification, etherification and acetalization. Of these reactions, acetalization is of great importance in industrial applications. PANI-PVA solution prepared by the oxidative dispersion polymerization reacts with n-butyraldehyde in the presence of an acid catalyst, chiefly forming six-membered intramolecular acetal rings between the adjacent intramolecular hydroxyl groups. However, there is also the possibility of forming intermolecular acetal links between the hydroxyl groups causing intermolecular crosslinking. PAPVB composites with PAPVA series of several aniline/(aniline+PVA) wt% contents were synthesized from an acetalization reaction of a PVA with butyraldehyde. Codes and the relevant characterization data for samples used in this study are presented as PAPVB series. Numbers of immediately followed 'PAPVB' and 'PAPVA' denote the weight percent of aniline/aniline+PVA content in sample.

Composite particles of samples for various weight percent of aniline to PVA have been studied. At a low concentration, aniline was polymerized into the spherical nanoparticles in the case of PAPVA20 sample. The shape of particles synthesized at the other concentrations was expected to slightly derivate from the spherical shape as samples of PAPVA30, PAPVA40 and PAPVA50. They was very irregular. Generally, as stabilizer concentration decreases, the shape changes from sphere to irregular shape with diameters of several tens micrometers indicating some aggregation of the primary particles. The conductivities of dried PAPVA series measured by the four probe method was about 10^{-1} S/cm after washing, filtering and drying of PAPVA series solution.

Figure 1 shows SEM micrographs of the surfaces for PAPVB composite series. The size range of the particles is approximately 1~200 μm, showing that the characteristic morphology depends on the weight percent of aniline/(aniline+PVA) content. The more the PANI content of the PAPVB composites increase, the higher the electrical conductivity of room temperature is from 10^{-11} S/cm to 10^{-2} S/cm.

PAPVB composite particles are used to the dispersed phase in ER fluids. Compared to other ER fluids, the PANI particle has relatively lower density, better thermal stability, and a more controllable conductivity. ER fluids were then prepared by dispersing the dried PAPVB40

particles in silicone oil (30cS) by 20 vol%, 15 vol% and 10 vol %.
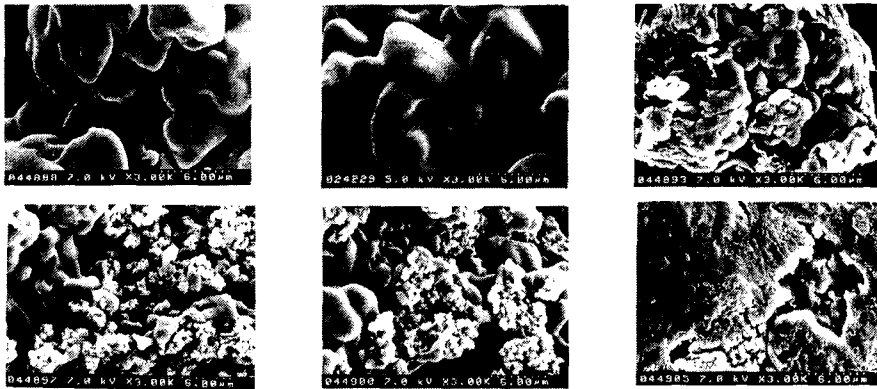

Fig. 1 SEM of PAPVB particles with various stabilizer weight fractions (a) PAPVB0.1 (b) PAPVB1 (c) PAPVB20 (d) PAPVB30 (e)PAPVB40 (f) PAPVB50

Fig. 2 (a) shows flow curves of shear stress vs. shear rate for PAPVB particle based ER fluid with various electric field strengths (Kim *et al.*, 2001;Lee *et al.*, 2001; Sim *et al*, 2001). In the absence of an electric field, the fluid is similar to that of a typical concentrated shear–thinning suspension. The slope of 0.87 in the shear stress - shear rate plot is less than 1 (which is the Newtonian fluid limit). Shear stresses for the ER fluid increased over the entire shear rate range with an increase of electric field strength. After the plateau region, shear stress increases with shear rate similar to Newtonian fluids, implying that the hydrodynamic force begins to dominate over the electrostatic force. The behavior which depends strongly on the electric field strength at a low shear rate is due to the deformation, reformation and destruction of chainlike or columnar structures as the shear rate increases below the critical shear rate. The fibril structure becomes slightly extended and the fibrils more sharply aligned as sharing takes place. This would lead to a more uniform distribution of the particles, thereby reducing the amount of overlap of the charged dipoles, and in turn yielding stronger average dipole strength per particle.
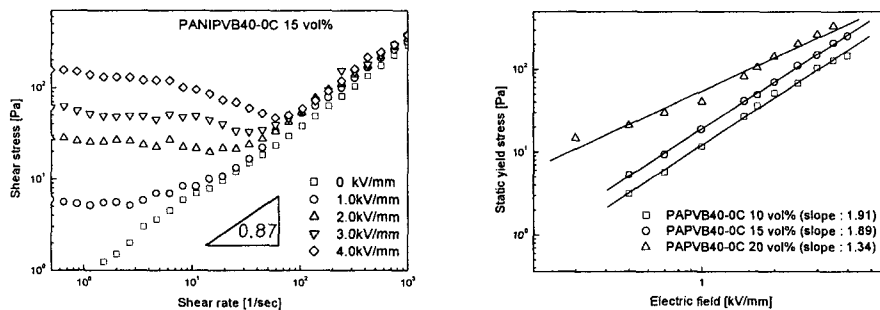

Fig. 2 (a) Shear stress vs. shear rate and (b) static yield stress for PAPVB 40 in 30 cS silicone oil

Fig. 2(b) shows change of static yield stress of PAPVB 40 composite measured by CSS

mode at various electric field strengths and volume fraction (Choi *et al.*, 2001). Contrary to a CSR mode in which a shear rate is applied to the ER fluid and the resulting shear stress is measured giving a dynamic yield stress, the ER fluid is stressed by an applied mechanical torque until the particle chain structure is perfectly broken so that the shear rate occurs. The ER effect of PAPVB series is only observed at the system of PAPVB30 and PAPVB 40. Because the insulating part with PVB of PAPVB composites increases the distance between the polarizable particles, it reduces the electrostatic forces between them. The occurrence of maximum yield stress may be attributed to surface polarization, which is determined by the electron movement within the polyaniline particles and electron hopping between the polyaniline particles under high voltage electric field. When the electron movement within the polyaniline particles plays an important role in the surface polarization of PANI, the yield stress increases. However, when the electron hopping between the polyaniline particles determines the surface polarization of the polyaniline particles, the yield stress decreases with the increase in the content of PVB.

Conclusion

In this study, PANI-PVB particles were synthesized and used as the dispersed phase in ER fluids. Size effects of PANI-PVB composites and PAPVA particle were examined by SEM, TEM and DLS. The particles were chemically characterized by FT-IR. Thermogravimetric analysis was performed on the particles to measure thermal properties. Effects of electric field strength, particle concentration and particle size on ER properties of PANI-PVB were also examined and then its viscoelastic properties were investigated under applied elastic fields using a rotational rheometer with high voltage generator in both controlled shear rate and shear stress modes.

Acknowledgement

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