

Relations Between Molecular Mixing State and Conductive Property in Blends Composed of Polyaniline and Aliphatic Copolymer Having Acid Groups

Kenji Yamada,¹ Hirokazu Yamane,¹ Teruki Haishi,¹ Katsuhiko Yamamoto,¹
Toshihide Haraguchi,¹ Tisato Kajiyama²

¹Department of Materials Science and Chemical Engineering, Kitakyushu National College of Technology, Kitakyushu 802-0985, Japan

²Department of Materials Physics and Chemistry, Graduate School of Engineering, Kyushu University, Fukuoka 812-8581, Japan

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ABSTRACT: Blend films composed of polyaniline and aliphatic copolymer having carboxylic acid groups were prepared by vaporizing a solvent from a solution of both polymers. Poly(methyl methacrylate-co-methacrylic acid) and poly(1-vinylpyrrolidone-co-acrylic acid) were used as the copolymers in this work. Conductivity of the blend film increased with decreasing concentration of polyaniline and then decreased in the region of low concentration. The N_{1s} peak in the ESCA spectrum of the blend film was shifted to higher binding energy with decreasing concentration of polyaniline and then was done to lower the binding energy in the region of low concentration. Polyaniline chains in the blend films become conductive by being oxidized with the

carboxylic acid groups, which are the constituents of the copolymers. Through strong intermolecular interactions such as ionic bonding and hydrogen bonding between polyaniline and the copolymer, densities of the blend films are always higher than those predicted on the basis of the additive law. Blend films with higher density and higher conductivity are able to be prepared with a higher vaporizing rate, given that phase separation occurring during vaporizing process can be depressed. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1113–1117, 2002

Key words: blends; conducting polymers; density; ESCA; structure–property relations

INTRODUCTION

How to generate prominent properties by blending two kinds of polymers has been the subject of investigation for some time.¹ For example, polystyrene and poly(2,6-dimethyl-1,4-phenylene ether) are soluble with each other, and an additive property cannot be applied to density of the composite composed of these polymers. It is because of the formation of intermolecular interaction that elasticity and yield strength of the composite are higher than those predicted by an additive law.² Poly(*p*-phenylene-3,4'-oxydiphenylene terephthalamide) and poly(4,4'-oxydiphenylene-4-carbonamidephthalimide-*N*-yl) are compatible.³ Intermolecular interactions between the two components are increased by hydrogen bonds formed between the amide linkages of the component polymers. The elastic modulus of the composite was always higher than the modulus predicted on the basis of the additivity. Similar deviations from additivity were observed for the bulk density. It was elucidated that polymer-containing sulfonic groups and polymer-containing pyri-

dine groups become compatible as the result of ionic interaction.^{4–7} It was shown that polymer-containing electron donors and polymer-containing electron acceptors become compatible because of the formation of complexing.^{8,9}

In this work, blend films composed of reduced polyaniline and aliphatic copolymers having carboxylic acid groups were prepared by vaporizing a solvent from a solution of both polymers. It will be expected that the reduced polyaniline is oxidized with carboxylic acid groups of the copolymer in the film and then ionic interaction is formed between the two polymers. Mixing states of the two components in the blend films are elucidated and the relationships between electric conductivity and molecular mixing state are investigated in the blend film.

EXPERIMENTAL

Synthesis of polyaniline

An aniline solution (concentration 18.7 g/L) was prepared by dissolving purified aniline with 2M HCl. To polymerize aniline, 1.8M ammonium peroxodisulfate solution (50 mL) was added dropwise over 80 min to the aniline solution, which was kept at 273 K with

Correspondence to: K. Yamada (kyamada@kct.ac.jp).

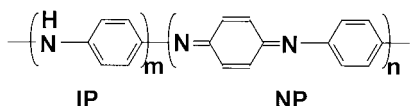


Figure 1 Chemical structure of the reduced polyaniline containing IP and NP structures.

stirring, and then the solution was further stirred at 273 K for 3 h. The product composed of oxidized polyaniline was washed successively with distilled water and acetonitrile, and then was dried at 353 K in vacuum. After the product was immersed in boiled 2M NaOH solution for 8 h to be reduced, it was washed successively with distilled water, ethanol, and acetonitrile. The product composed of reduced polyaniline (PA) was dried at 353 K in vacuum. The fractions of imino-1,4-phenylene (IP) and nitrilo-2,5-cyclohexadiene-1,4-diylidene-nitrilo-1,4-phenylene (NP) structures in the reduced polyaniline were evaluated from the infrared absorptions of 1500 and 1590 cm^{-1} by using *N,N'*-diphenyl-1,4-benzenediamine and *N,N'*-diphenyl-1,4-diylidenebis(benzenamine) as model compounds of IP and NP structures, respectively.¹⁰ Figure 1 shows the chemical structure of the reduced polyaniline containing IP and NP structures. It becomes apparent that the reduced polyaniline is composed of 64 mol % IP and 36 mol % NP structures.

Preparation of polymer blends

Figure 2 shows chemical structures of the two kinds of copolymers used in this work. The copolymers are poly(methyl methacrylate-*co*-methacrylic acid) (PMCM) and poly(1-vinylpyrrolidone-*co*-acrylic acid) (PVCA). Weight-average and number-average molecular weights in PMCM were about 34,000 and 15,000, respectively, whereas those in PVCA were about 96,000 and 20,000, respectively. The reduced polyaniline and the copolymer were dissolved with 1-methyl-2-pyrrolidone (NMP) to prepare the polymer solution. In the solution the total weight of the polyaniline and the copolymer was 0.5 g and the volume of NMP was 40 mL. The solution was vaporized in vacuum at 363 K on standing to prepared blend films. Weight ratios of polyaniline to copolymer were 90/10, 70/30, 60/40, 50/50, 30/70, and 10/90 in the PA/PMCM and PA/PVCA blend films.

Analyses of mixing structure and conductive property of the polymer blends

X-ray photoelectron spectroscopy measurement of the polymer blends was carried out with a Shimadzu ESCA3400 (Shimadzu, Kyoto, Japan) to clarify the oxidation state of polyaniline in the blends. The value of binding energy was corrected with $\text{Au}_{4f7/2}$ of fine gold particles, which were attached on a surface of the

blends by the sputtering method. The density of the polymer blends was measured at 303 K by a flotation method using a methanol/tetrachloromethane mixture. Infrared spectra of the polymer blends were measured with a Magna 550 Fourier transform infrared spectroscopy (Nicolet Analytical Instruments, Madison WI) equipped with a Barnes analytical diffuse reflectance accessory to clarify the mixing structure in the blends. The conductivity of the polymer blends was measured at 298 K with an HP4339B high-resistance meter (Hewlett-Packard, Palo Alto, CA).

RESULTS AND DISCUSSION

Conductivity of polymer blends

Figure 3(a) and (b) show conductivities of PA/PMCM and PA/PVCA blend films, respectively, as a function of PA concentration. Conductivities of PA/PVCA blend films could not be measured when the concentration of polyaniline was lower than 50 wt %, given that the films were very brittle and were broken in measuring. Maximum values of conductivity were given around 90 and 70 wt % of PA concentration in PA/PMCM blends and PA/PVCA blends, respectively. It is therefore confirmed from Figure 3 that the blends composed of polyaniline and the copolymer become conductive.

Figure 4 shows the ESCA N_{1s} spectrum and four N_{1s} peaks separated from the spectrum in PA/PMCM(60/40) blend film. The concentration of polyaniline is 60 wt % in the PA/PMCM(60/40) blend film. According to Kumar et al.,¹¹ the ESCA N_{1s} peak is attributed to the neutral imine nitrogen atom of the NP structure,

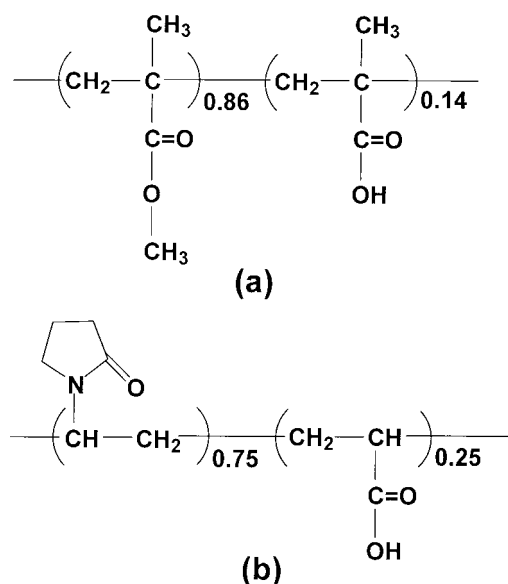
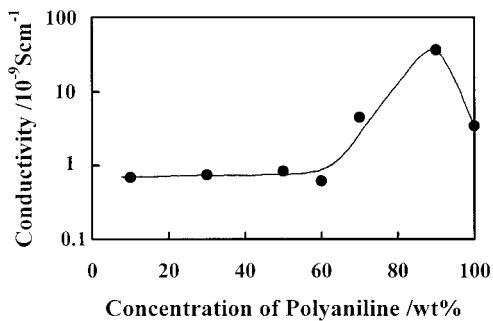
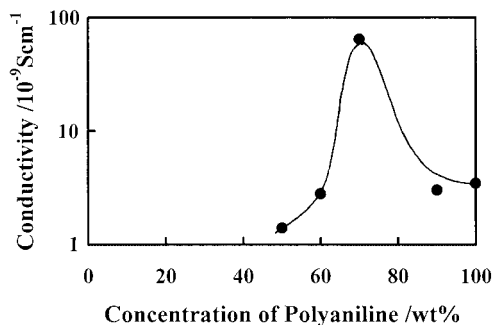


Figure 2 Chemical structures of aliphatic copolymers used in this work: (a) poly(methyl methacrylate-*co*-methacrylic acid) and (b) poly(1-vinylpyrrolidone-*co*-acrylic acid).



(a)



(b)

Figure 3 Conductivities of (a) PA/PMCM blend films and (b) PA/PVCA blend films as a function of concentration of PA.

the neutral amine nitrogen atom of the IP structure, the positively charged nitrogen atom of the IP radical cation, and the positively charged nitrogen atom of the proton-added NP structure. Binding energies of N_{1s} in NP structure, IP structure, IP radical cation, and proton-added NP structure are 398.5, 399.5, 400.8, and 402.2 eV, respectively, and their peak intensities are able to evaluate as N_1 , N_2 , N_3 , and N_4 , respectively, by

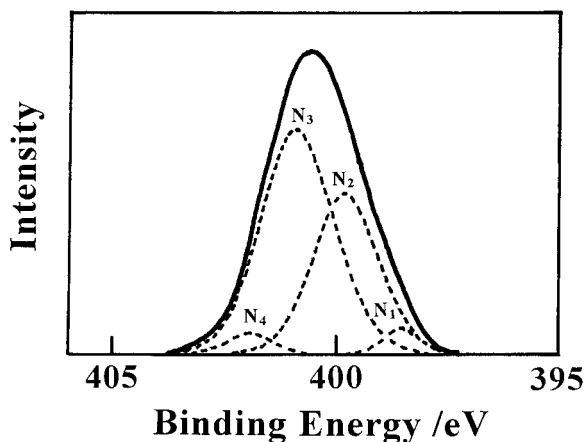


Figure 4 ESCA N_{1s} spectrum and four N_{1s} peaks separated from the spectrum in PA/PMCM(60/40) blend film.

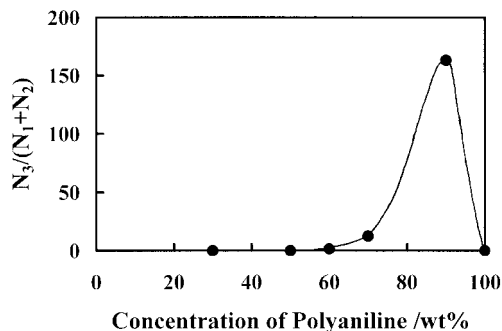
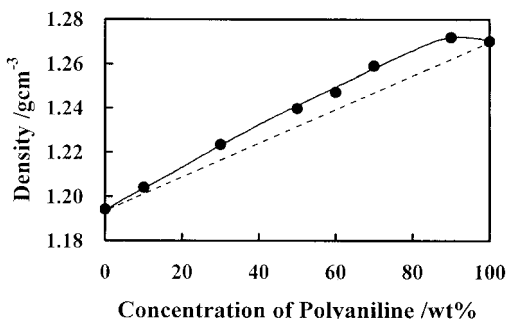


Figure 5 $N_3/(N_1 + N_2)$ ratio as a function of PA concentration in PA/PMCM blend films.

separation of the N_{1s} peaks shown in Figure 4. However, N_{1s} peaks in PA/PMCM(10/90) blend film was too small to separate accurately into the four components. Figure 5 shows $N_3/(N_1 + N_2)$ ratio as a function of PA concentration in PA/PMCM blend films. The ratio shows a maximum around PA concentration of 90 wt %. This result shows that the degree of oxidation of PA by which IP radical cations are formed takes place more predominantly around a PA concentration of 90 wt % and the polymers of PA and PMCM are mixed at the molecular level. Therefore it becomes apparent that oxidized polyaniline chains become conductive.



(a)

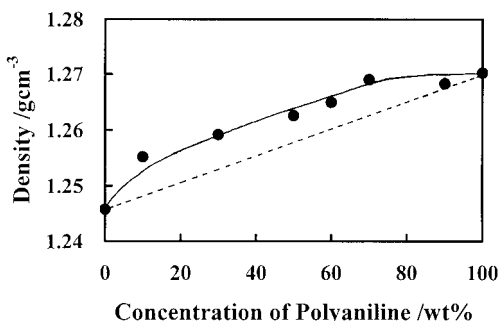


Figure 6 Density of (a) PA/PMCM blend films and (b) PA/PVCA blend films as a function of PA concentration. Dashed lines in the figures follow the additive law.

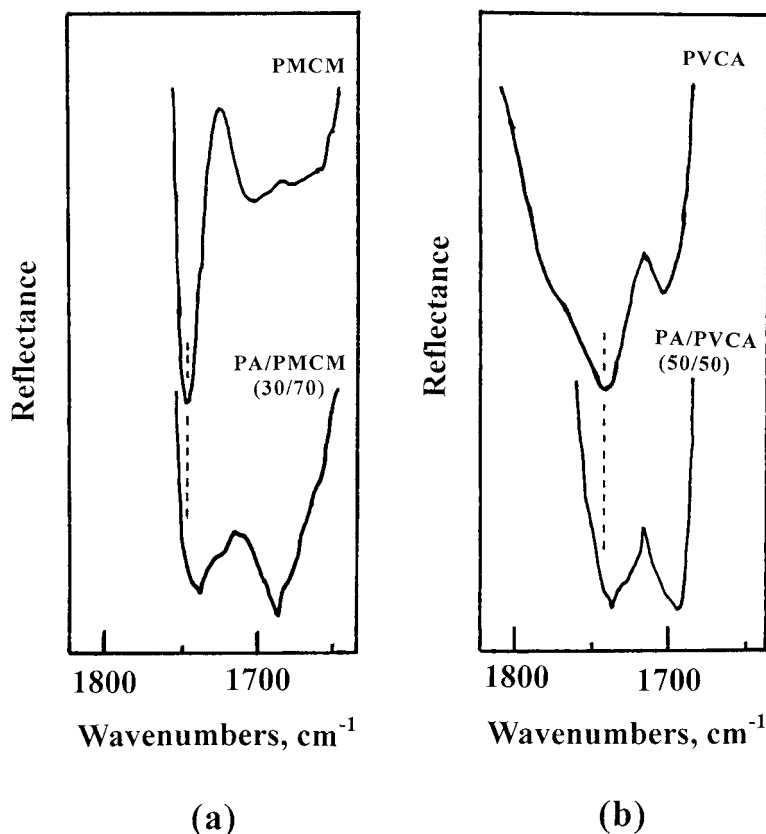


Figure 7 Infrared spectra (a) in PMCM film and PA/PMCM(30/70) blend film and (b) in PVCA film and PA/PVCA(50/50) film.

N_{1s} peaks measured in PA/PVCA blend films are difficult to separate into the four types of N_{1s} peaks of polyaniline because N atoms are also constituents of PVCA. As presumed from Figure 5, the oxidation of PA is generated by the transfer of H^+ from carboxylic acid of PMCM to the neutral imine nitrogen atom in the NP structure of polyaniline and thus polyaniline is positively charged. Given that a strength of 402.2 eV was very small, IP radical cations will be generated through the proton-added NP structure formed by the protonation of the neutral imine nitrogen atom. It will therefore be presumed that PA/PVCA blend films become conductive by the transfer of H^+ from carboxylic acid of PVCA to polyaniline. In PA/PVCA blend films PA and PVCA are mixed at the molecular level around a PA concentration of 70 wt %, given that it can be presumed from Figure 3(b) that the degree of oxidation of PA takes place more predominantly around the PA concentration of 70 wt %.

Molecular aggregation state of the blends

Figure 6(a) and (b) show density as a function of PA concentration in PA/PMCM and PA/PVCA blend films. Densities of the blend films were always higher than those predicted on the basis of additive law. This result shows that PA and the copolymer will be finely

mixed over the whole range of PA concentrations and intermolecular interaction between the two polymers becomes strong. Therefore it will be considered that the continuous phase is changed from PMCM- or PVCA-rich phase to PA-rich phase, depending on PA concentration. The intermolecular interaction contains not only an ionic interaction between protonated PA chain and deprotonated carboxylic acid group of the copolymer, but also a hydrogen bond between the imino group of PA and the carbonyl group of the copolymer. Figure 7(a) shows infrared spectra in PMCM film and PA/PMCM(30/70) blend film and Figure 7(b) shows infrared spectra in PVCA film and PA/PVCA(50/50) blend film. Absorption associated with C=O stretching vibration appeared in the range of 1740 through 1750 cm^{-1} in infrared spectra of PMCM and PVCA copolymers, whereas it tended to shift to lower wavenumber by blending with PA. This result means that the hydrogen bonds will be easily formed in the blend films. As shown in Figure 3(a), conductivity of PA/PMCM blend films decreases by forming the PMCM-rich phase in the range of lower PA concentration, whereas it increases by forming the PA-rich phase in the range of higher PA concentration, given that PMCM is an insulator and oxidized PA is a conductor.

Formation process of blend film from polymer mixture solution

The molecular aggregation state and intermixing between the components of the blend film will be affected by vaporization rate of polymer solution. Polymer solutions in which the total weight of the polyaniline and PMCM was 0.5 g and the volume of NMP was 30, 40, and 50 mL were prepared to obtain PA/PMCM(60/40) blend films. Figure 8 shows density as a function of polymer concentration in PA/PMCM(60/40) blend films. Density of the blend films was increased with increasing polymer concentration. This result shows that the mixing state between PA and PMCM is enhanced with increasing polymer concentration.

Figure 9 shows conductivity as a function of polymer concentration in PA/PMCM(60/40) blend films. The conductivity of the blend films was increased with increasing polymer concentration. According to ESCA N_{1s} spectra of the films, the N_{1s} peak was shifted to higher binding energy with increasing polymer concentration, and thus $N_3/(N_1 + N_2)$ ratio was increased. It is elucidated from Figures 8 and 9 that the effects of relative polymer concentration on density and conductivity are the result of nonuniform phase separation. The blend film will be formed by using polymer solution at a higher polymer concentration before phase separation predominantly takes place during vaporizing, and thus a better mixing state will be obtained in the film.

CONCLUSIONS

In the blend films composed of reduced polyaniline and the aliphatic copolymer, which is poly(methyl methacrylate-*co*-methacrylic acid) or poly(1-vinylpyr-

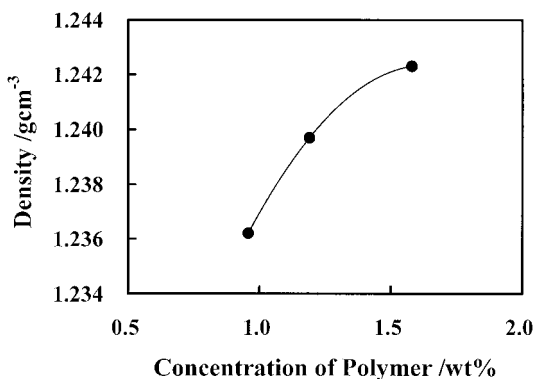


Figure 8 Density as a function of polymer concentration in PA/PMCM(60/40) blend films.

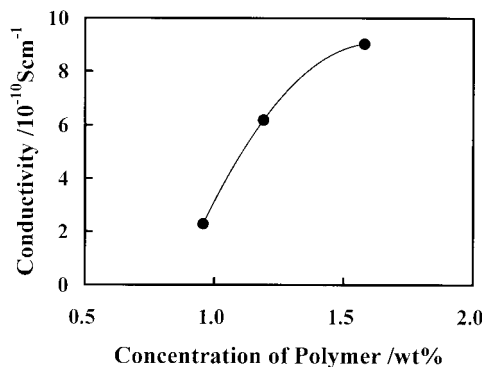


Figure 9 Conductivity as a function of polymer concentration in PA/PMCM(60/40) blend films.

olidone-*co*-acrylic acid), polyaniline chains in the film are protonated by carboxylic acid groups of the copolymer and thus the film becomes more conductive. Polyaniline oxidized in the blend films is charged positively and carboxylic acid group deprotonated is charged negatively, and therefore an ionic interaction is formed between polyaniline and the copolymer. Strong intermolecular interactions are formed by the above ionic interaction and hydrogen bonding between the imino group of polyaniline and the carbonyl group of the copolymer. It is generated by the formation of the strong intermolecular interactions, such that density of the blend film is always higher than that predicted on the basis of the additive law. Blend films with higher density and higher conductivity can be prepared with a higher formation rate of the blend film by which the phase separation will be depressed during vaporization of the solvent.

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