전기유변유체를 기초한 폴리아닐린 알킬-치환체의 영향

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Effect of alkyl-substituted copolymer on polyaniline based electrorheolgical fluid

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Introduction

Electrorheological(ER) fluid have been widely used as smart and intelligent materials for various engineering applications such as stop valves, clutches, torque transducers, dampers, dengine mounts, shock absorbers, robotic arms, etc [1-5]. The ER fluid exhibit non-linear response on their rheological properties when exposed to external electric field[6]. Under the application of electric field, the ER fluids rapidly transform their structure from liquid-like to solid-like [6,7]. They are generally considered as field-induced Bingham fluid which can develope their yield stress with a certain amount of electric field [6]. ER fluids are consisted with the suspensions of dielectric or semiconducting particles in a nonconducting liquid such as silicone oil [2]. Polyaniline(PANI) has been considered as one of the most advantageous suspended particles for ER fluid [8]. PANI also known as a most promised semiconducting polymer because of its high conductivity, thermal stability. Furthermore, its conductivity can be continuously turned by varying the degree of doping [9].

However, PANI has difficulty for being processed through a traditional method because it is unstable at melt-processing temperature and insoluble in most organic solvents except for N-methylpyrrolidine(NMP), greatly limiting its further wide practical application. Thereby several method of modification have been developed to improve its solubility. Among them, alkyl, alkoxy, and amino ring-substituted and N-substituted PANIs have caught great interest because of their much better solubility in many common solvents [10].

In this study, PANI was polymerized in presence of methylaniline as a comonomer to overcome the lack of processibility. We controlled the functionality by copolymerization of methylaniline and aniline with various ratios. The mechanical properties of the fabricated polymer were analyzed with increase of alkyl functionality, in order to investigate the effect of alkyl-substituted PANI. The surface morphology was observered via Scanning Electron Microscope(SEM). Fouier Transform-Infrared Spectroscope(FT-IR) was used to investigate the chemical structures of product. The conductivity was measured by resistivity meter. ER fluid prepared by dispersing polyaniline, polymethylaniline particles in silicone oil, and their rheological properties were measured under the external electric field.

Experimental

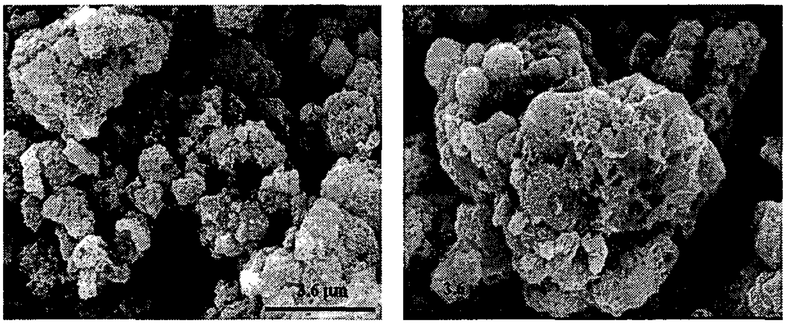
Aniline(AN)(Junsei Chemical, Japan, 99%), and methylaniline(MA)(Junsei Chemical, Japan, 98%), ammonium persulfate(APS)(Daejung chemicals, 98%), 1.0M HCl(DC

Chemical, Korea, 35%)aqueous solution and 1.0M NaOH(Daejung chemicals, Korea, 98%) aqueous solution were analytical grade and used. Each AN/MA monomer was added to the reactor with 1M HCl 400ml by mechanical stirring(250rpm). The APS as an initiator dissolved in 1M HCl 240ml was doped into the reactor for 2 h. After dropping initiator, the polymerization was maintained at 0℃ for 24 hrs. The products were washed using distilled water and methanol. Reacted polymers were full doping using enough 1M HCl for 24 h, and then we removed the HCl aqueous solution using the centrifuse and dried in a vaccum oven. Then AN/MA copolymers were dedoping with 1M NaOH until the pH of mixture to be 10.

Electrical conductivity in both doped and dedoped polymer which was pelletized by 13mm pelltizer was measured via resistivity meter (Hiresta-UP MCP-HT450, Mitsubishi Chemical, Japan). Chemical structure characterized via FT-IR spectroscopy (Perkin-Elemer System, USA). The mophology of the polymer was observed by SEM(S-4200, Hitachi, Japan). Density of the polymers were measured by gas pycnometer (AccuPyc 1330, Micromeritics, German). In addition, we prepared 15vol% ER fluid of which AN/MA copolymers were dispersed in silicone oil(viscosity:30cs, density:0.955g/ml). The electrorheological properties of the ER fluids were analysized by using rheometer (MCR300, Physica, German) with electric field controller.

Results and discussion

In Fig. 1, SEM images shows the morphology of doped and dedoped aniline/methylaniline copolymers are showed in Fig.1. The particle shape deviates from the sphere and some agglomerates are observed. Compared with pure polyaniline, the particles morphologies in the micro scales did not changed by copolymerization. Virtually no difference in particle surface mophology between doped state and dedoped state.

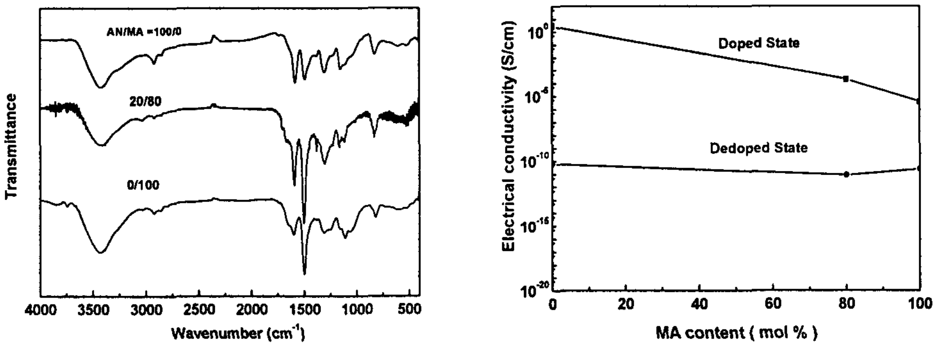


(a) (b)

Figure 1. SEM image of (a)Doped aniline/methylaniline copolymer (b)De-doped aniline/methylaniline copolymer

Fig. 2.(a) shows the FT-IR spectra of the copolymer bases with three aniline/methylaniline ratios of 100/0, 20/80 and 0/100 from KBr pellets. A broad band centerd at 3400-3430cm^{-1} is assigned to the N-H streching vibration of an aromatic amine. The bands at 2800-3000cm^{-1}are C-H streching vibrations[11-14]. The bands at 1600cm^{-1} are C=C stretching quinoid rings and the bands at 1500cm^{-1} are C=C stretching of benzenoid rings [10, 11]. The point that the peak around 1500cm^{-1} always has higher intensity than that around 1600cm^{-1} with increasing MA content as shown in the figure 2.(a). These

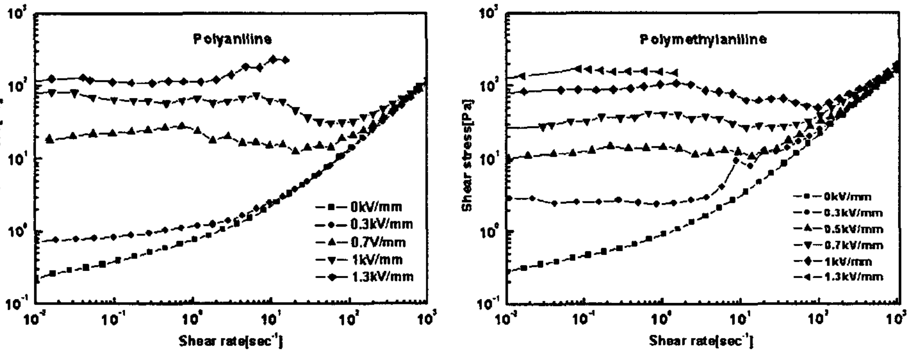
intensity difference of the C=C stretching with the different copolymer ratio indicated that the ratio of benzenoid group and quinoid group was affected by MA contents [10]. The band at 825cm^{-1} is out-if-plane H deformation of aromatic C-H bond [13]



(a) (b)

Figure 2. (a)FT-IR spectra of the AN/MA copolymer ratios(100/0, 20/80, 0/100). (b)Electrical conductivity of doped and dedoped polymer.

Fig.2. (b) presents the doped and dedoped electrical conductivities. In the doped state, electrical conductivity are deceased as increasing MA content. But Dedoped state electrical conductivity are almost regular in spite of changing MA content. This trend is seem to similarly ethyl-substituted PANI [10].



(a) (b)

Figure 3. Flow curve of (a)Polyaniline(PANI) (b)Polymethylaniline(PMA)

Fig. 3(a) and (b) show the ER behavior of shear stress as a function of the shear rate for 15vol% PANI and PMA paticles suspensions in silicone oil under the various electric field strengths. As the applied voltage is increased, the shear stress increases with the shear rate. Short circuiting was observed at voltages higher than 1.3 kV/mm both PANI and PMA. Consequently, the electrorheological behavior of PANI and PMA particles suspensions could not be measured above 1.3 kV/mm[5]. The yield stress of both PANI and PMA at 1 kV/mm and 1.3 kV/mm was similar from each other in log scales. However, the yield stress of PMA at lower voltages was higher that those of PANI.

Conclusions

PANI and its derivatives were synthesized via oxidation polymerization in order to investigate the influence of methyl functional group on the electrorheological properties of PANI. From the FT-IR spectra of AN/MA copolymer, we found that the peak around 1500cm^{-1} showed higher intensity than that of the peak appeared around 1600cm^{-1} when the content of MA was increased. This intensity difference was attributed to the inceased content of MA.

In doped state, the electrical conductivity was deceased from 2.6 to 3.7×10^{-6} S/cm as the MA content was increased. However, in the dedoped state, the electrical conductivity indicated no apparent change in spite of changing MA content.

Both PANI and PMA particles based ER fluids showed that the shear stress got enhanced when the applied electric field strength was increased.

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