Rheological characterization for the gelation process of polyaniline-emeraldine base/NMP solution by oscillatory test

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(Received May 6, 2010; final revision received July 27, 2010; accepted July 29, 2010)

Abstract

The gelation process of the 4 wt.% PAni-EB/NMP solution was characterized by measuring the viscoelastic property in oscillatory test. The solution showed a weak gel state in which the storage modulus decreased rapidly even at low strain in the constant angular frequency test, and the damping factor increased rapidly to a state of typical viscous liquid at a specific angular frequency in the early stage of the constant strain test. It was supposed that the weak bonding of dipole force between polymer molecules was broken by the external deformation. The angular frequency of the sudden change in the damping factor was defined as a critical angular frequency. The PAni solutions with a prior shear deformation resulted in the lower critical angular frequency, showing the delay of gelation process by the prior shear deformation. The PAni solution with the metal-organic framework (MOF) resulted in the lower critical angular frequency proving the anti-gel effect of the MOF.

Keywords: polyaniline, gelation, weak gel, critical angular frequency, gel inhibitor, MOF

1. Introduction

Many researches have been conducted on the Conducting Electroactive Polymer (CEP) as a metal substitute for electric conductance since it was discovered in the 1970s. Especially many researches have focused on polyaniline (PAni) because it can be easily synthesized and has a high electric conductivity. It has already been used for several applications in industry. However, one of the major drawbacks in the industrial applications of PAni is the fast gelation. It makes long-term storage difficult and restricts processing capability in the industrial applications.

Gel inhibitor is an additive to keep the liquidity of the PAni solutions for long-term storage purpose while it keeps solubility and conductivity. It is necessary to process the PAni solutions for the industrial applications. In order to develop gel inhibitor of the PAni solution, it is necessary to characterize rheologically the structural change in the solution by the inhibitor. In the gelation process, the connected structure between polymer molecules in the sol state grows until the material shows elastic behavior. The transition between gel and sol is called gel point by Winter (1986). Researches have been focusing on gelation kinetics by characterizing the gel point. Gel point was estimated theoretically with empirical equations derived from the chemical bonding characterization by Adolf et al. (1990). Experimentally gel point was detected by characterizing the viscoelastic property, the storage and the loss moduli by Winter and Chambon (1986) and Matsuhiro and Shibayama (2007).

In order to examine the gelation behavior of the PAni solution, rheological studies have been carried out. Jain et al. (1995) determined stability of PAni solutions with various solvents by the viscosity change. The solution viscosity increased rapidly as the PAni concentration increased. Yang and Mattes (1999) examined the gelation behavior by the viscosity change at the constant shear rate, and proved the effect of the gel inhibitor suppressing the hydrogen bonding between polymer chains.

Deformation under the constant shear rate may disturb the weak bonding in a physical gel so that it may change the gelation behavior. Therefore, it would not be an appropriate way to examine the structural change of solutions. After the constant shear deformation was applied to the PAni solutions to characterize the gelation behavior in the beginning of this study, it was realized that the constant shear deformation affected the gelation behavior by agitating the fluid structure too much. Therefore, oscillatory test was applied to examine the gelation behavior of a PAni solution to minimize the external disturbance.

The purpose of this study was to develop a rheological method to characterize the gelation behavior of PAni solution. Many concentrations of the PAni solutions were tested

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by applying the oscillatory test in the preliminary experiments. The experiments showed a consistent result. In order to present the feasibility of the rheological characterization in this study, 4 wt.% PANi-EB/NMP solution was chosen in this article for providing the details of the experimental result. Environmental conditions such as temperature and humidity would affect the gelation behavior, but a few research result of the effect has been reported. Therefore, the experimental atmosphere was precisely controlled in a constant temperature and humidity chamber in this study.

2. Various Types of Gel

Polymer gels are classified into three types; covalently crosslinked materials, entanglement networks, and physical gels according to Kavanagh and Ross-Murphy (1998). Molecules of covalently crosslinked materials make covalent bonding between polymer molecules to form interconnected network, which is a huge single molecule. The storage modulus, \(G'\), of the covalently crosslinked materials shows little change with angular frequency, which is a typical behavior of elastic body. Entanglement networks are topological interaction of polymer chains. It appears at the concentration and the relative molecular weight higher than a critical entanglement molecular weight. In the dynamic mechanical analysis, it shows a high viscosity liquid \((G'' > G')\) at the terminal zone of low frequency. As the frequency increases the storage modulus grows proportionally until it reaches to the state in which the damping factor \(G''/G' = \tan\delta\), is less than 1.0, and shows little change with the frequency.

Physical gel is formed by the dipole force between polymer molecules such as dipole-dipole or hydrogen bonding interactions. Therefore, it is likely to be affected easily by heat and external deformation. Physical gels are classified into the weak and the strong gels by the bonding strength. If the linear strain of a physical gel is larger than 20% which is the upper bound of the linear viscoelasticity, it is classified into the strong gel. If the linear strain is at the level of 1/1000, it is classified into the weak gel by Kavanagh and Ross-Murphy (1998).

It has been known by many researchers of Yang and Mattes (1999), Pan et al. (2005), Jeon et al. (1999) and Yang et al. (2006) that the PANi solution forms a physical gel by making a hydrogen bonding between the amine and imine groups. The hydrogen bond formation of PANi-EB molecules is shown in Fig. 1. Yang and Mattes (1999) explained that the viscosity decreasing at an early gelation stage is a phenomenon caused by breakage of hydrogen bonding. Yang et al. (2006) found that moisture affects the solubility and stability of the PANi solution by adding moisture intentionally to the PANi solution during the dissolving process. Therefore, it is desirable to keep the moisture content as regular as possible during the characterizing experiment. In this study, all experiments were done in a constant temperature and humidity chamber.

3. Experiments

3.1. Preparation of the 4 wt.% PANi-EB/NMP solution

PANi was prepared by the oxidative polymerization of aniline using a self-dispersing method as reported by Lee et al. (2005). In a typical experiment, 20 ml aniline was dissolved in a mixture containing 300 ml HCl and 200 ml chloroform. The dispersed colloidal solution was placed in a reactor equipped with mechanical stirring and 11.44 g ammonium peroxydisulfate in a 100 ml HCl was added in portions and stirred at 200 rpm at 10°C until they became green. The resulting green precipitate (emeraldine hydrochloride) was collected at room temperature on a paper filter placed in a Buchner funnel and washed repeatedly by distilled water and methanol. The filtered powder was put and stirred in 0.1 M ammonia water solution for 20 hours at 100 rpm. Again it was filtered and washed by distilled water and methanol. PANi powder in the Emeraldine base (EB) form was finally produced by drying the filtrate in an oven at 50°C for one day. The 4 wt.% PANi-EB solution was made by putting the EB powder into N-Methyl-2-pyrrolidone (NMP) slowly with stirring by homogenizer, and filtering the solution by 2.7 micrometer syringe filter.

3.2. Rheological characterization

Rheological characterization of the PANi-EB solution with respect to gelation was done by a rotational rheometer UM by Physica Co. Due to the low viscosity of the PANi-EB solution, a double-wall concentric cylinder type device was chosen for a proper magnitude of measuring torque. The rotating device has 111 mm of length, 23.5 mm of outer radius, 22.75 mm of inner radius, and 0.5 mm of gap between the wall of the device and the wall of the stationary cup, as shown in Fig. 2. All experiments were done in a constant temperature and humidity chamber by JEIO Tech. Co. (TH-GA-300). Environmental condition in the chamber was set to 20°C(±0.4°C) and 50%(±1%) relative humidity. To protect fast air flow around the sample, air protector covered the rheometer.

Fig. 1. Schematics showing the hydrogen bond formation of PANi-EB molecules.
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Viscosity measurement at steady state shear condition is widely used to measure the viscosity of a fluid in the industrial processing applications. However, steady state shear deformation may influence much the structure of the PAni-EB solution during gelation process. In the preliminary tests, it was found that a major structural change began in several hours. It was also difficult to keep the steady state shear deformation for such a long time. Instead of the steady state shear deformation, oscillatory test has a benefit that it applies less energy to the solution under a structural change.

In this study, the storage and the loss moduli were measured by applying sinusoidal shear deformation in the oscillatory test. In order not to disturb the structural change of the PAni-EB solution during the rheological test, it is desirable to keep the deformation energy in the oscillatory test as small as possible. It was difficult to detect sufficient amount of torque at low level of strain and low angular frequency. In preliminary tests, the strain smaller than 600% did not generate a sufficient torque level at an angular frequency of 1 radian/s because of the limit of the torque measuring capability of the rotational rheometer used in this study. The highest limit of angular frequency of the rheometer used in this work was 100 radian/s. The angular frequency range in the test was from 1 radian/s to 100 radian/s, and the proper strain level was determined with respect to the torque level providing a stable data. Because the gelation process takes a long time, the oscillatory test was done every two hours. Between tests, the solution was kept undisturbed in the measuring jig. The time reference in the measurement was based on the time of the solution prepared. For example, the measuring time of a solution was 1 hour if one hour passed after the solution was just made.

4. Results and Discussions

It was reported by Lee et al. (2000) that the covalently crosslinked gel is formed at a high temperature over 100°C in the PAni-EB solution. The gel formed at room temperature is regarded as a physical gel with hydrogen bonding in the case of the PAni-EB solution. The physical gel with the hydrogen bonding between the amine and imine groups is considered to go through gelation process from the weak gel having sparse hydrogen bonding to the strong gel with a high density of hydrogen bonding. The weak gel is supposed to show non-linear viscoelasticity even at low strain. As the number of hydrogen bonding becomes larger, the gel is supposed to show a behavior close to elastic body. A major structural change in the gelation process would be detected by the change of the rheological behavior.

Fig. 3 shows the storage modulus of the 4 wt.% PAni-EB solution with increasing strain at the constant angular frequency of 50 radian/s. The angular frequency of 50 radian/s for the test was chosen to have stable and reproducible data in preliminary tests. In the early stage, the storage modulus showed a sudden decrease as strain increased. The strain showing the sudden decrease of the storage modulus increased as the measuring time increased. After 21 hours, the storage modulus showed little change with increasing strain. The result can be interpreted as the hydrogen bonding in the weak gel state at an early stage collapses by the external deformation energy with increasing strain. However, as the number of hydrogen bonding becomes larger after 9 hours the solution becomes a state withstanding the external deformation energy with little breakage of bond-
With the result, it is supposed that the PAni-EB solution is in the weak gel state before 9 hours, but the density of hydrogen bonding increases rapidly in the 9 to 17 hours period until it becomes the strong gel state after 21 hours. With respect to the non-linear regime at the early stage, Wang and Chang (2008) and Tariq et al. (1998) proposed a characterization method for non-linear viscoelastic materials that the rheological characteristics were analyzed by searching a range of strain showing the linear viscoelastic behavior. However, the linearity range of strain changed with time in our test so that characterization of gelation process was focused instead of characterizing the non-linearity of the material.

The changes of viscoelastic moduli after 19 hours since the experiment began are shown in Fig. 4. The storage modulus showed a small change with increasing angular frequency. The angular frequency at which the storage modulus is equal to the loss modulus (\(\tan \delta = 1\)) increases as the measuring time increases. It explains the property change of the solution resulted from elasticity increase during the gelation progress. However, the PAni solution already showed a highly elastic behavior at 19 hours of measuring time. It did not have sufficient fluidity for manufacturing processes such as ink jet or printing processes. Therefore, the characterization method of searching the interception point of the storage and loss moduli could not be used to detect the gelation behavior as early as possible. Another way was needed to early detect the gelation behavior change.

Fig. 5 shows the damping factor of the 4 wt.% PAni-EB solution with increasing angular frequency from 1 to 100 radian/s at a constant strain of 600% of the gap. It shows that the solution behaves like a typical viscous liquid (\(\tan \delta \geq 1000\)) at angular frequencies higher than a certain frequency in the early stage. The behavior disappears after 10 hours. It is supposed that the hydrogen bonding or Coulombic bonding in the PAni solution is not broken any more by the external deformation energy as the angular frequency increases after 10 hours. In this study, the angular frequency for the sudden change of the damping factor to a typical viscous liquid was defined as the critical angular frequency. The critical angular frequency was used to analyze the gelation process of the PAni-EB solution.

The weak bonding of dipole force between polymer molecules in a physical gel can be easily broken by the external shear deformation, resulting in the delay of gelation process.
process. Fig. 6 shows the critical angular frequency of the PANi-EB solutions with different shear deformation history. The critical angular frequency of a sample was measured after the sample was deformed at a constant shear rate of 50 1/s for the steady-state-viscosity measurement while the critical angular frequency of the other sample was measured without the prior deformation. As shown in the figure, the critical angular frequencies of the solution with the prior shear deformation are always lower than the solution without the prior deformation. The result explains that the steady state shear deformation breaks the hydrogen bonding in the PANi-EB solution, resulting in the delay of the gelation process. It is difficult for hydrogen bonding with a specific bonding direction to restore the bonding after breakage while it is easy for ionic bonding without a specific bonding direction.

According to the experimental result, it was supposed that the gelation process largely depended upon the number of hydrogen bonding of the PANi-EB solution. As the number of hydrogen bonding increases, external deformation energy cannot change the structure of the solution, resulting in an elastic behavior. In order to check the supposition, a gel inhibitor of a metal-organic framework (MOF), shown in Fig. 7, was tested. The MOF interferes the hydrogen bonding in the PANi-EB solution to reduce the chance of making hydrogen bonding. It has been observed that the MOF has the better anti-gel effect for EB even at low concentration than the one proposed by the previous research of Yang and Mattes (1999).
Fig. 8 shows the critical angular frequencies of the PAni-EB solutions with and without the 2 wt.% MOF to EB. As expected, the critical angular frequency of the PAni-EB solution with the MOF showed lower values. The critical angular frequency of the solution with the MOF showed little change until 6 hours. The result confirmed that the gelation process of the PAni-EB solution tested in this work was governed by the hydrogen bonding, and the rheological characterization in this work was effective to characterize the gelation process.

5. Conclusions

In this work, the gelation process of the 4 wt.% PAni-EB/NMP solution was analyzed by the rheological characterization of oscillatory test. The early state of the PAni-EB/NMP solution showed a weak gel state consisting of weak bonding of dipole force such as Coulombic bonding or hydrogen bonding. It showed a non-linear viscoelastic behavior even at low strain. It also showed a non-linear regime that as strain increased at a constant angular frequency the storage modulus decreased rapidly at low strain. However, as the measuring time increased it approached to an elastic behavior at which the storage modulus changed little with strain. It was supposed that the hydrogen bonding in the solution increased with time withstand the external deformation. In the angular frequency test, a sudden change of the damping factor to the typical viscous liquid with angular frequency increase appeared. It was supposed that the sudden change was caused by the breakage of weak bonding of dipole force by external deformation energy. The angular frequency of the sudden change to a typical viscous liquid was defined as the critical angular frequency. The gelation process was analyzed by the critical angular frequency. When the critical angular frequencies of two solutions with and without prior steady state shear deformation were compared, the gelation process in the solution was delayed by the breakage of weak bonding caused by the prior shear deformation. The anti-gel effect of the MOF in the 4 wt.% PAni-EB/NMP solution was also analyzed by the critical angular frequency. The gelation of the solution with the MOF was delayed by 3 hours.

Acknowledgement

This research was financially supported by the Ministry of Knowledge Economy (MKE) and Korea Institute for Advancement of Technology (KIAT) through the Human Resource Training Project for Strategic Technology

List of Symbols

\[ G' \] : The storage modulus of oscillatory test
\[ G'' \] : The loss modulus of oscillatory test
\[ \tan\delta \] : The damping factor (=\( G''/G' \))

References