Studies on Saponification of Acrylonitrile Terpolymer for Suspending Particles of Electrorheological Fluids*

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Abstract In order to prepare suspending particles for electrorheological fluids, hetergeneous hydrolysis of acrylonitrile terpolymer is conducted in presence of saponifying agent(sodium hydroxide) in this paper. The effects of the saponification conditions such as the amount of added sodium hydroxide, time duration and temperature on the degree of saponification are studied in detail. Meanwhile, the conversion of nitrile groups is discussed with the result that the saponification of nitrile groups of the terpolymer initially yields amide groups, then slows down to carboxylic groups. The research sets a way for the preparation of dispersing particles of water-free electrorheological fluids tentatively used for controlling light transmittance.

Key words saponification; acrylonitrile terpolymer; electrorheological fluids; suspending particles

Electrorheological fluids (ERF) are typical suspension whose rheological properties can obviously and reversibly change under an external electric field. One of the promising applications of ERF is as a working fluid in automotive suspension systems, such as dampers of motor vehicles, electric clutches and robotics control systems. The current ERF devices, however, are unable to meet the industrial needs mostly due to the narrow operating temperature range : 0～70℃, in which case water is often used as the activating and enhancing agent for ER response[1]. Due to the recent improvements on polymeric and water-free ERF, ERF have again attracted people′s attention. Finely powdered polymethacrylic acid is typically acted as dispersing particles[2]. In this paper, as a proceeding work for fabrication of water-free ERF, hetergeneous saponification of acrylonitrile terpolymer was conducted to yield saponification product particles with different ionization, which is carried out under alkaline conditions[3]. In addition, the influence of the alkali concentration, the time duration and the temperature of hydrolysis on the degree of saponification were systematically studied.

1 Experiment

1.1 Saponification and Products Separation

The terpolymer fibers containing acrylonitrile 90.0%, methylacrylate 9.0%, acrylic acid 1.0% and saponifying agent (aqueous sodium hydroxide) of given amount were introduced to a three-necked flask placed in a thermostat, which was equipped with a magnetic stirrer, a condenser and a nitrogen inlet. At a specified temperature, the saponification was conducted for planned time duration (t) with continuous stirring. The amount of added sodium hydroxide can be determined by using the Saponification Index ($S.I.$) defined as follows, $S.I.= \frac{W_s}{W_p}$, where, W_s is the weight of the saponifying agent and W_p is the

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(*S.I.*) defined as follows, $S.I.=\frac{W_s}{W_p}$, where, W_s is the weight of the saponifying agent and W_p is the weight of the terpolymer, respectively.

At the end of saponification, the saponified polymer solution was cooled. The unsaponified terpolymer fibers were extracted with vacuum filtration and the filtrate was precipitated with methanol. The precipitate was then dissolved with deionized water, followed by precipitation with methanol. The precipitate was repeatedly washed with methanol, which was then dried to constant in vacuum at 50℃ after soaked in methanol for 12 hrs.

1.2 Determination of the Degree of Saponification

As we known, the nitrile groups are hydrolyzed to the amide groups under mild conditions. Otherwise, the conversion from amides to carboxylic groups process occurs under intense conditions, i.e., in presence of strong acid or strong alkali[4]. The content of -(-CH_2-CH-)- (COOK) was determined by conductivity titration[5], which characterized the degree of saponification.

1.3 Determination of the Nitrile Groups and the Amide Groups

The content of nitrile groups and amide groups in saponification products were determined with IR spectra on the Nicolet 208XB spectrophotometer[6]. Using the intensity of the -CH2- groups absorption at 2 920 cm^{-1} *A*(CN) as inner reference, the quotient of the intensity of -CN- groups absorption *A*(CN) to *A*(CH_2) is as the content of the nitrile groups. Similarly, *A*($CONH_2$)/*A*(CH_2) (Q_A) is as the content of the amide groups.

1.4 ERF Preparation and Performance Evaluation

Without any water added, ERF with particle concentration of 2.5%(*m/m*) were prepared by dispersing the ready-made spherical particles of saponification products with an average diameter of 2.5 μm in silicone oil. The property of the ERF for controlling transmittance was evaluated according to the previous work[7].

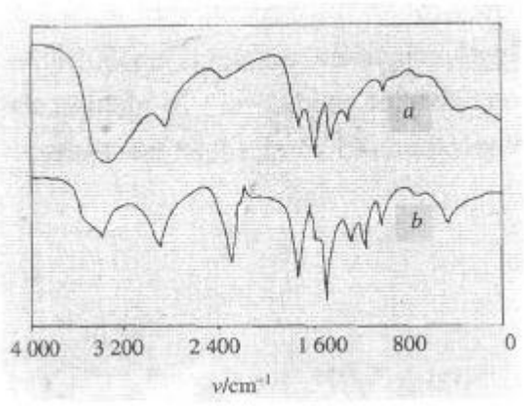

Fig.1. IR spectra of product and terpolymer

2 Results and Discussions

2.1 Saponification of Acrylonitrile Terpolymer

As saponification begins, the terpolymer fibers change remarkably in color from white to deep brown and the fibers are dissolved little by little until they turn to yellowish solution, which accompanied by the evolution of ammonia. The saponification process can be illustrated as follows[3]

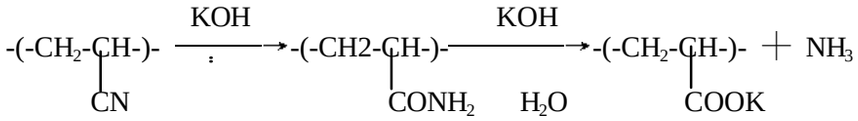

Fig.1 shows considerable changes in the IR spectra of saponification product (*a*) and acrylonitrile terpolymer (*b*). It indicates a decrease in the intensity of the absorption band at 2 245 cm^{-1} and a increase in the intensity of the absorption band at 1 675 cm^{-1} and 1 566 cm^{-1}, which attribute to the conversion of

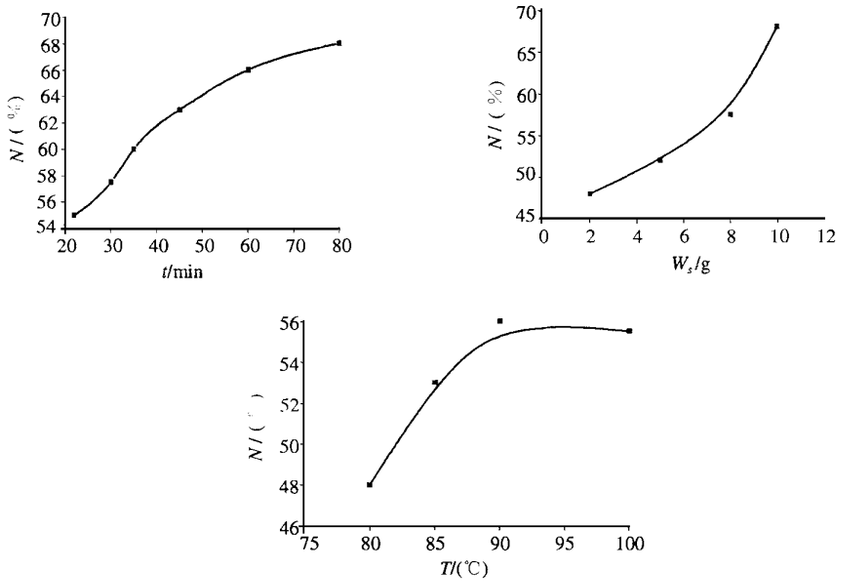

Fig 2　Effect of saponification conditions on $N\%$

the nitrile groups to the amide groups and the carboxylate groups. The product is terpolymer containing acrylonitrile, acrylamide and sodium acrylcaroxylate..

2.1.1　Effect of Saponification Conditions on -(-CH_2-CH-)- (COOK) Content($N\%$) of Saponification Products

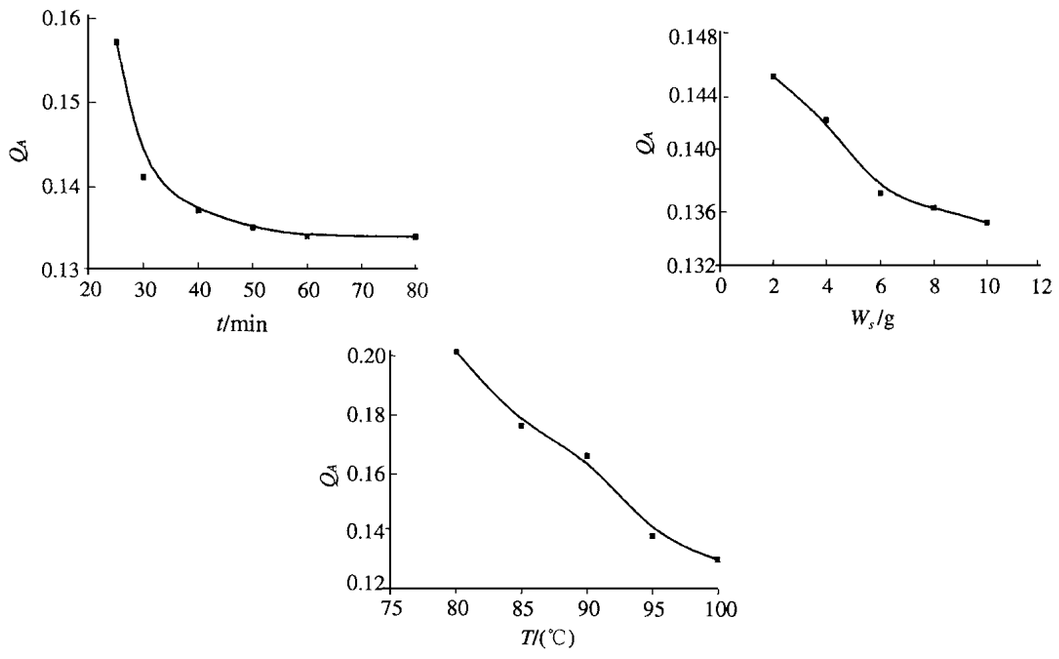

Fig 3　Effect of saponification conditions on Q_A

Fig.2 shows that $N\%$ increases with saponification tnime duration(t), added alkali(W_s) and saponification temperature(T), respectively. The increase of $N\%$ at the temperature from 80℃ to 90℃ is

much more than that at the temperature from 90℃ to 100℃, which results in the choice of saponification temperature of 90℃.

2.1.2 Effect of Saponification Conditions on -CN- Content

Fig.3 shows that the -CN- content decreases with the increase of saponification time duration, the amount of added alkali and the temperature, respectively. It is evident that there is initially a rapid loss in -CN- content but the rate slows down progressively with saponification time duration. It is further noted that it is of little effect of the amount of added alkali on -CN- content even after the saponification time duration of 45 min with *S.I.*=0.5.

2.1.3 Effect of Saponification Conditions on Amide Content of Saponification Products

Tab.1 and Tab.2 indicate the effect of the saponification conditions, i.e., saponification time duration and the amount of added alkali on amide groups content that is characterized by $A(CONH_2)/A(CH_2)$. The amide groups are in the intermediate state in the process of saponification of the nitrile groups, which is effected by the conversion ersion rate for nitrile groups to amide groups and the conversion rate for amide groups to carboxylate groups. At the beginning of saponification, the conversion of nitrile groups to amide groups mostly occurs. The amide groups content decreases with the elimination of ammonia groups, which is catalyzed by saponifiedly formed carboxylate groups. With the increase of the carboxylate groups of products, the second step slows down, leading to the increase of amide groups content again. The effect of increase in the amount of added alkali in the second step is marked than that in the first step.

Tab. 1 Effect of saponification time duration on $A(CONH_2)/A(CH_2)$

t/min	$\frac{A(CONH_2)}{A(CH_2)}$
20	1.45
30	1.30
40	1.40
75	1.48

Tab.2 Effect of the amount of added KOH on $A(CONH_2)/A(CH_2)$

W_s/g	$\frac{A(CONH_2)}{A(CH_2)}$
2.5	1.45
5.0	1.18
7.5	1.21
10.0	1.26

2.2 The Property for Controlling Transmittance

The ERF with saponification products used as suspending particles were measured in the presence and absence of the DC electric field of 500 $V \cdot mm^{-1}$ with the result that the solar transmittance change as much as 39.4% was obtained with the wavelength of 500 nm at the maximum.

3 Conclusions

In conclusion, the saponification of nitrile groups of acrylonitrile terpolymer initially yields amide groups, then slows down to yield carboxylic groups. The degree of saponification or ionization of saponification products increases with saponification time duration, the amount of added sodium hydroxide and saponification temperature. At the optimal saponification temperature of 90℃, suspending particles for water-free electrorheological fluids with different ionization can be prepared by means of controlling saponification time duration and the amount of added sodium hydroxide. The tentative investigation to the ERF with saponification product particles was successful.

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腈纶皂化制备电流变液悬浮粒子的研究*

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【摘要】为了制备无水电流变液用悬浮粒子，研究了腈纶在碱性条件下的多相水解。详细考察了皂化试剂氢氧化钾的用量，皂化时间和温度等皂化条件对皂化程度的影响；讨论了氰基转化过程。研究结果表明，在皂化初期，腈纶分子链上的氰基转化为酰胺基，然后缓慢转化为羧基。给出了一条制备无水电流变液用悬浮粒子的方法，并初步考察了该类电流变液的控光特性。

关　键　词　**皂化**；　**腈纶**；　**悬浮粒子**；　**电流变液**

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