The Influence of Cross-Linking Reaction on the Mechanical and Thermal Properties of Polyarylene Ether Nitrile

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ABSTRACT: The processing of cross-linked polyarylene ether nitrile (PEN), which has a triazine rings structure, has been investigated under different reaction times and temperatures. In this study, the PEN films prepared by the tape-casting formed the thermally stable triazine rings by catalytic cross-linking reaction gradually, which was characterized by Fourier transform infrared spectroscopy. The chemical cross-linking reaction occurred as the CN group absorption of PEN at 2221 cm^{-1} decreased and a new absorption peak, at 1682 cm^{-1}, was observed, and the absorption peak intensity would be progressively larger, with the extension of the processing time. After the formation of cross-linking networks, the cross-linking degree and thermal and mechanical properties of the processed films were improved substantially, compared with the untreated films. The film with added $ZnCl_2$ as the catalyst was more rapidly cross-linked, and its properties were better than that without catalyst at the same treatment conditions. The glass-transition temperature (T_g) of PEN films processed at 350°C for 4 h (213.65°C) was higher than that of PEN films before the treatment (161°C), and the tensile strength was also improved significantly. The PEN was processed at 350°C for 2 h, whose initial decomposition temperature increases by about 10°C, compared with that of untreated film, at one time. The rheology behavior of the cross-linked films was processed on dynamic rheometer to monitor and track the process of polymer cross-linking reaction. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 1822–1828, 2011

Key words: films; high performance polymers; cross-linking; mechanical properties; thermal properties

INTRODUCTION

Polyarylene ether nitriles (PENs) are well known for their outstanding properties such as radiation resistance, high thermal and thermo-oxidative stability, and good mechanical properties. They also have good chemical inertia, which makes them very attractive to develop composites used at elevated temperatures and aggressive chemical environments encountered in aerospace, industry, and automobile applications.[1–7] The presence of CN groups in PEN endow the polymers with stronger polarizability than that of polyarylether, which seems to promote the adhesion of the polymers to many substrates, possibly through polar interactions with functional groups on the substrate.[8] Moreover, the CN groups also serve as potential sites for the cross-linking reaction of PEN because the groups are likely to form thermally stable triazine rings.[9–11]

Lots of polymers with nitriles or as end or pendant groups have been proved to be cross-linked by triazine rings resulted from the catalytic cross-linking reaction between the nitriles.[12] For example, Haddad et al.[13] first proved that the cross-linking of poly (arylene sulfides) by the triazine rings resulted from their pendent cyano groups. Verborgt and Marvel[14] prepared a series of polyethers with terminal nitrile groups and intensively studied their cross-linking reactions. Anderson and John[15] prepared aromatic *S*-triazine polymers through the thermal trimerization of aromatic nitriles by using chlorosulfonic acid as the catalyst and heat.[16] The thermal stability of the cross-linked polymers are enhanced because the resonance energy of the triazine (82.5 kcal/mol) is much higher than that of benzene (36 kcal/mol).[17,18] In fact, cross-linking of polymers generally improves their physical properties, such as dimensional stability, resistance to thermal deformation and stress cracking, etc., particularly at high temperature.

In this study, cross-linking reaction of PEN was carried out. The influences of catalyst, reaction temperature, and the time of treatment on the reaction were studied. The thermal properties and mechanical properties of the cross-linked PEN were characterized. A physical explanation of the remarkably improved mechanical behaviors of PEN was proposed according to the rheological analysis.

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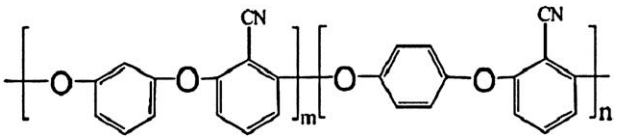

Figure 1 Repeating units of PEN.

EXPERIMENTAL

Materials

PEN was provided by Union Laboratory of Special Polymers of UESTC-FEIYA, Chengdu, China. It is a copolymer derived from 2,6-difluorobenzonitrile with hydroquinone, with an intrinsic viscosity of 1.22 dL/g (in *N*-methylpyrrolidone, 0.005 g/mL). Repeating units of PEN are shown in Figure 1. *N*,*N*-Dimethylformamide (DMF) (99.5%) and $ZnCl_2$ (98%) were obtained from TianJin BODI Chemicals, China.

Cross-linking reaction of PEN

$ZnCl_2$ 5 wt % was mixed with a certain amount of DMF in a round-bottomed flask. Good dispersion of $ZnCl_2$ in the solvent was achieved by half an hour's mechanical stirring. Then, PEN was added into the flask at a final concentration of 10 wt %. The mixture was subsequently heated at 160°C for 1.5 h, during which a vigorous stirring was also performed. After that, the mixture was filtrated and cast onto a clean glass plate to develop film. The film was placed in an oven and heated at 80, 100, 120, 160, and 200°C for 2 h, respectively, and then heated at 280, 300, 320, 340, 350, and 360°C for certain time to cure, and finally slowly cooled to room temperature.

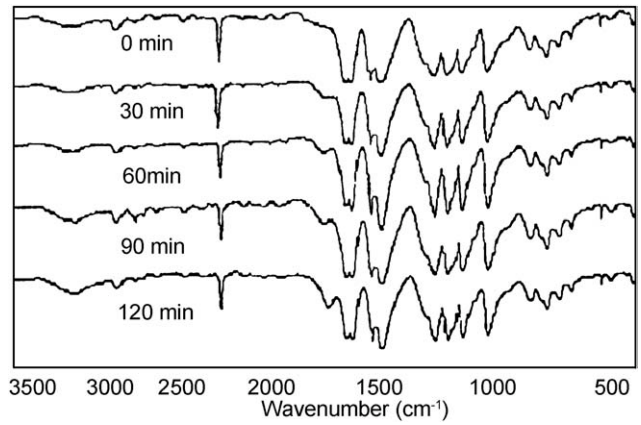

Figure 2 Fourier transform infrared spectra of films processed at different times at 320°C.

Characterization and apparatus

The chemical structure was analyzed by Fourier transform infrared (FTIR) spectra recorded on a Nicolet 200 SXV spectrophotometer in transmission mode. The cross-linking Degree (*J*) of PEN was measured with a weight difference method. Briefly, the films were placed in DMF and subjected to a heat treatment at 160°C. The undissolved debris was then filtered by a glass funnel and subjected to another heat and filtration cycle. These treatments were not ended until no more dissolution occurred. The final debris was dried in oven at 160°C. The cross-linking degree (*J*) was calculated according to the equation below.

$$J = G/G_0 \times 100\%$$

where G_0, and G present the initial weight of the film and the weight of the debris, respectively.

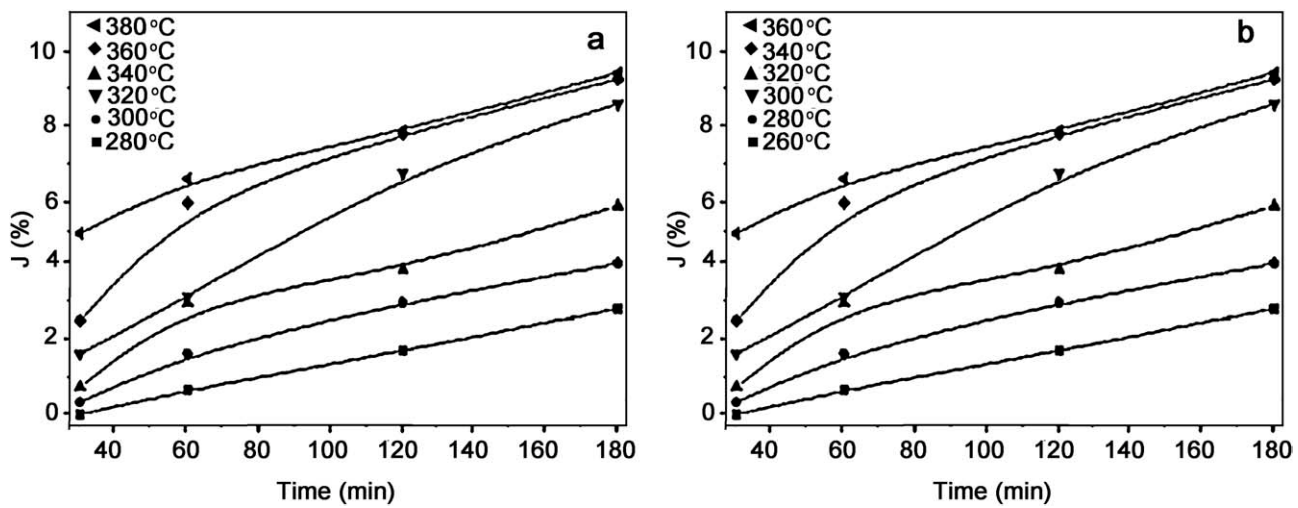

Figure 3 The cross-linking degree of films at different temperature. (a) Films without catalyst and (b) films containing catalyst.

TABLE I
Glass-Transition Temperature (*Tg*) of the Films at Different Times and Temperatures

	T_g (°C)				
Temperature °C	0 h	1 h	2 h	3 h	4 h
320	195	203.84	203.75	206.97	207.97
350	195	206.09	207.00	215.94	213.65

The tensile strength of the films was measured on SANS CMT6104 Series Desktop Electromechanical Universal Testing Machine, with sample size as 10 mm × 100 mm, and gained as average value for every three samples. DSC analysis was performed on a TA Instruments DSC-Q 100 modulated thermal analyzer under a nitrogen purge of 50 cm^3 min^{-1} at a heating rate of 10°C min^{-1} from room temperature to 350°C. Thermogravimetric analysis was performed on a TA Instruments TGA Q50 at a heating rate of 10°C min^{-1} under nitrogen purge of 50 cm^3 min^{-1}. Dynamical rheological measurements were carried out on a rheometer (TA Instruments Rheometer AR-G2) equipped with a parallel plate geometry (25 mm diameter). The dynamic frequency sweep measurements ranging from 0.1 to 100 rad/s at 300°C were carried out on samples prepared by compression molding, with a thickness of 1.0 mm and diameter of 25 mm. Time ramp sweep was measured at 10 Hz, and the temperature was fixed at 300°C.

RESULTS AND DISCUSSION

FTIR analysis of PEN films

The FTIR spectra of PEN films before and after the treatment with presence of $ZnCl_2$ at 320°C for different time intervals are shown in Figure 2. It can be seen that a peak at 2231 cm^{-1}, which was assigned to -CN group, presents in the spectrum of PEN films without any treatment. After 30 min treatment, the intensity of this peak diminished, and another peak at 1682 cm^{-1} emerges, which is assigned to triazine.[19,20] These results confirmed the cross-linking reaction between -CN groups in PEN chains. Moreover, the intensity at 1682 cm^{-1} increases over time, indicating that the cross-linking reaction is quite time dependent.

Influences of catalyst, temperature, and time on the cross-linking degree (*J*)

The influences of catalyst, temperature, and time on the cross-linking degree were investigated in this study. The results are summarized in Figure 3. As can be seen, the *J* value remains 0 even after a treatment at 280°C for 30 min. It was elevated to 2% with the addition of 5 wt % $ZnCl_2$ under the same condition. Similar phenomenon was also observed at other temperatures. Thus, it suggests that the addition of $ZnCl_2$ is an effective way to accelerate the cross-linking reaction.[21,22] On the other hand, it is quite evident that all the *J* values of PEN films treated at different temperatures with or without catalyst increased over time, in agreement with the results of FTIR (Fig. 1). Elevated *J* values are also observed with increase in temperature. Interestingly, the increase in *J* values is steady when the temperature was elevated from 280°C to 320°C, whereas that is marked from 320°C to 380°C. In brief, the addition and increase in temperature or time interval are effective ways to promote the cross-linking reaction.

Thermal analysis

Glass-transition temperature (T_g) of the PEN with added $ZnCl_2$ was calculated from the curves of DSC and is listed in Table I. It can be seen that T_g increases with the increase in time and temperature about heat treatment, respectively. As a general rule,

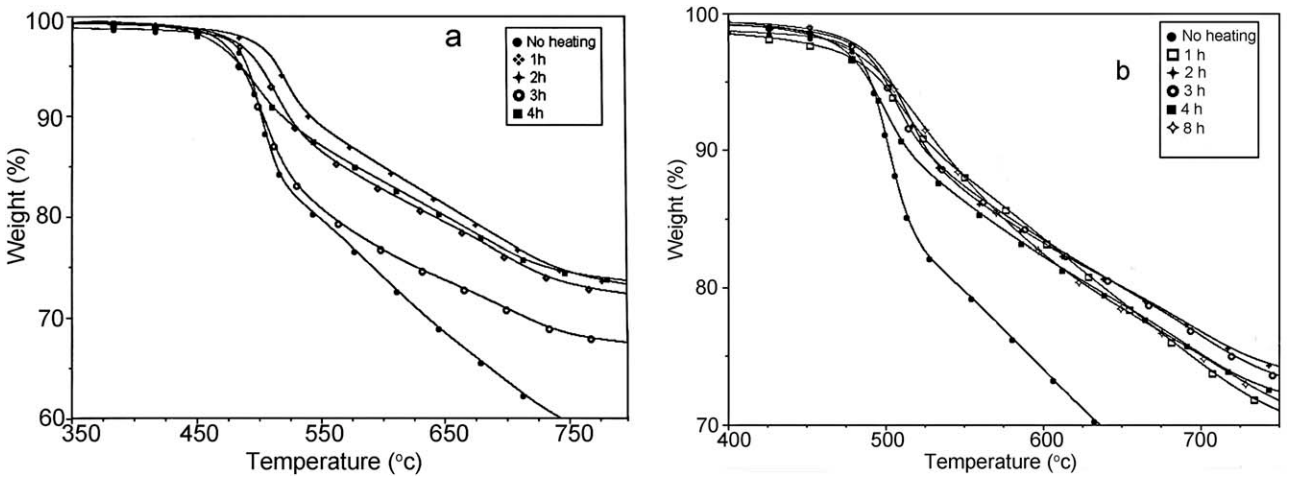

Figure 4 Thermogravimetric analysis traces of the films processed at (a) 320°C and (b) 350°C.

TABLE II
Mechanical Properties of the Films

	Tensile strength (MPa)				
Temperature °C	0 h	1 h	2 h	3 h	4 h
320	111	108	122	145	166
350	111	130	134	144	174

any structural features that reduce segmental mobility or free volume will increase the T_g. The cross-linking of PEN films restricts on segmental mobility and enhanced T_g. Thus, T_g of PEN films processed at 350°C for 4 h is higher than that of PEN films before the treatment (161°C). The thermogravimetric profiles of the samples containing $ZnCl_2$ are shown in Figure 4. We can see that there is a significant increase in the thermal stability of the films containing catalyst because of the increase in the cross-linking degree and the activation energy of thermal decomposition. The initial decomposition temperature of PEN films processed at 320°C for 2 h increases by about 10°C, and the char residue increases by about 10%, compared with that of untreated film. The results exhibited that the heat-resistance property was improved obviously after elevating-treated temperature and prolonging the reaction time because of the formation of cross-linking network. Interestingly, as shown in Figure 4(a), the initial decomposition temperature and the char residue of PEN films processed at 320°C for 2 h are even higher than that of PEN films processed at 320°C for 3 and 4 h. Furthermore, in Figure 4(b), PEN film processed at 350°C for 2 h also shows the most char residue. The results exhibited that the excess increment in processing time and heating temperature will make the PEN films processed in an oven oxidation and side reaction, leading to the thermal stability of PEN decreasing slightly. Thus, moderate cross-linking reaction is apt to improve the performance of PEN. The phenomenon attracted our interest very much, and further detailed investigations are going on.

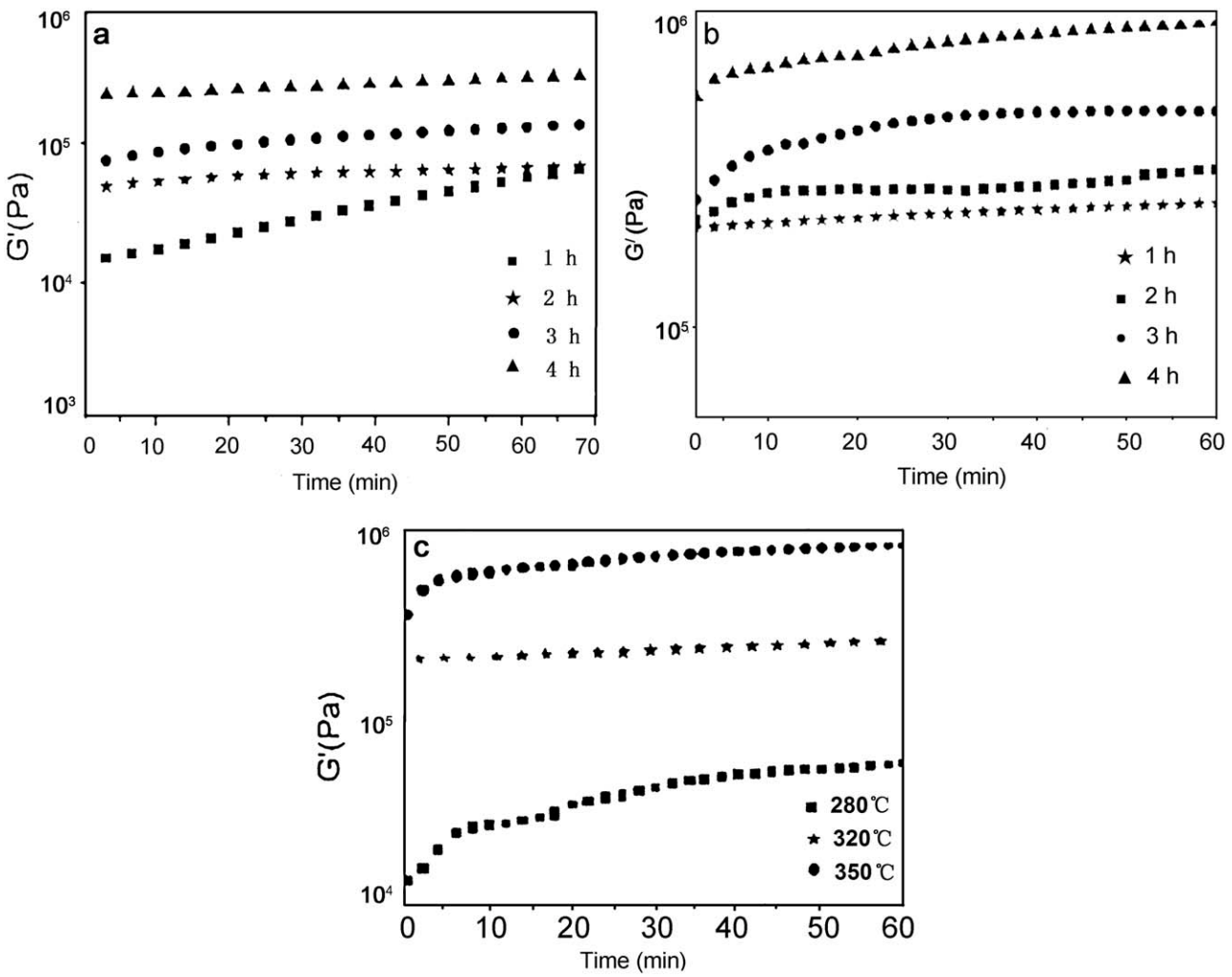

Figure 5 Temperature dependence of storage modulus of films processed at (a) 320°C and (b) 350°C, and (c) films processed 4 h.

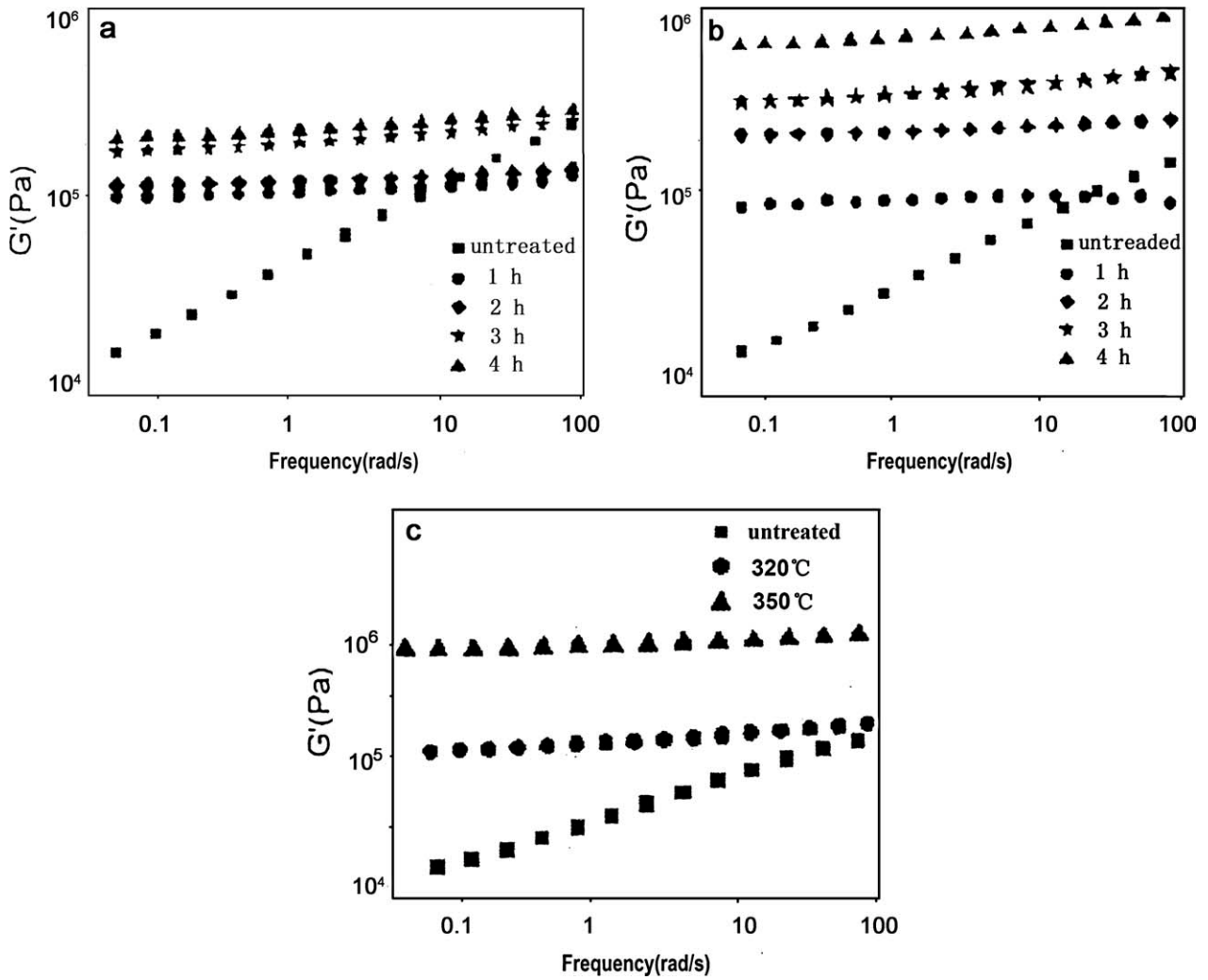

Figure 6 Frequency dependence of storage modulus of films processed at (a) 320°C and (b) 350°C, and (c) films processed for 4 h.

Mechanical properties

The mechanical properties of the films are listed in Table II. At the same processing temperature, the tensile strength improved gradually with the increase in processing time. For the films processed at 320°C for 4 h, the value of the tensile strength attained 166 MPa. The tensile strength of the films processed at 350°C was higher than that processed at 320°C, under the same reaction time. Thus, the increase in processing temperature and reaction time can accelerate the cross-linking reaction and improve the cross-linking degree; as a result, the mechanical properties are improved obviously.

Rheological measurements

The storage modulus (G') obtained from time scan measurements is shown in Figure 5. Obviously, the magnitude of G' of PEN films processed at 320°C and 350°C, respectively, increased with an increase in the processing time. With the increase in processing time, the dependency of G' on time increased slowly, and the G' curves exhibited a plateau distinctly. Moreover, as the processing temperature was increased, higher storage modulus values were obtained. Similar phenomenon was also observed in Figure 5(c). It indicated that cross-linking network structure formed gradually, and the cross-linking degree increased because of the long processing time and high heat-treated temperature. The storage modulus (G') obtained from the dynamic frequency scan measurements for the films processed is shown in Figure 6. Obviously, the G' of the sample with added $ZnCl_2$ but not heat-treated ascend with the increase in frequency, whereas the G' of the sample processed at high temperature changes indistinctly with the frequency. The results demonstrated that the cross-linking network was generated, and the movement of the molecular chain had changed greatly, in agreement with the results in Figure 5. The same results are shown in Figure 6. In Figure

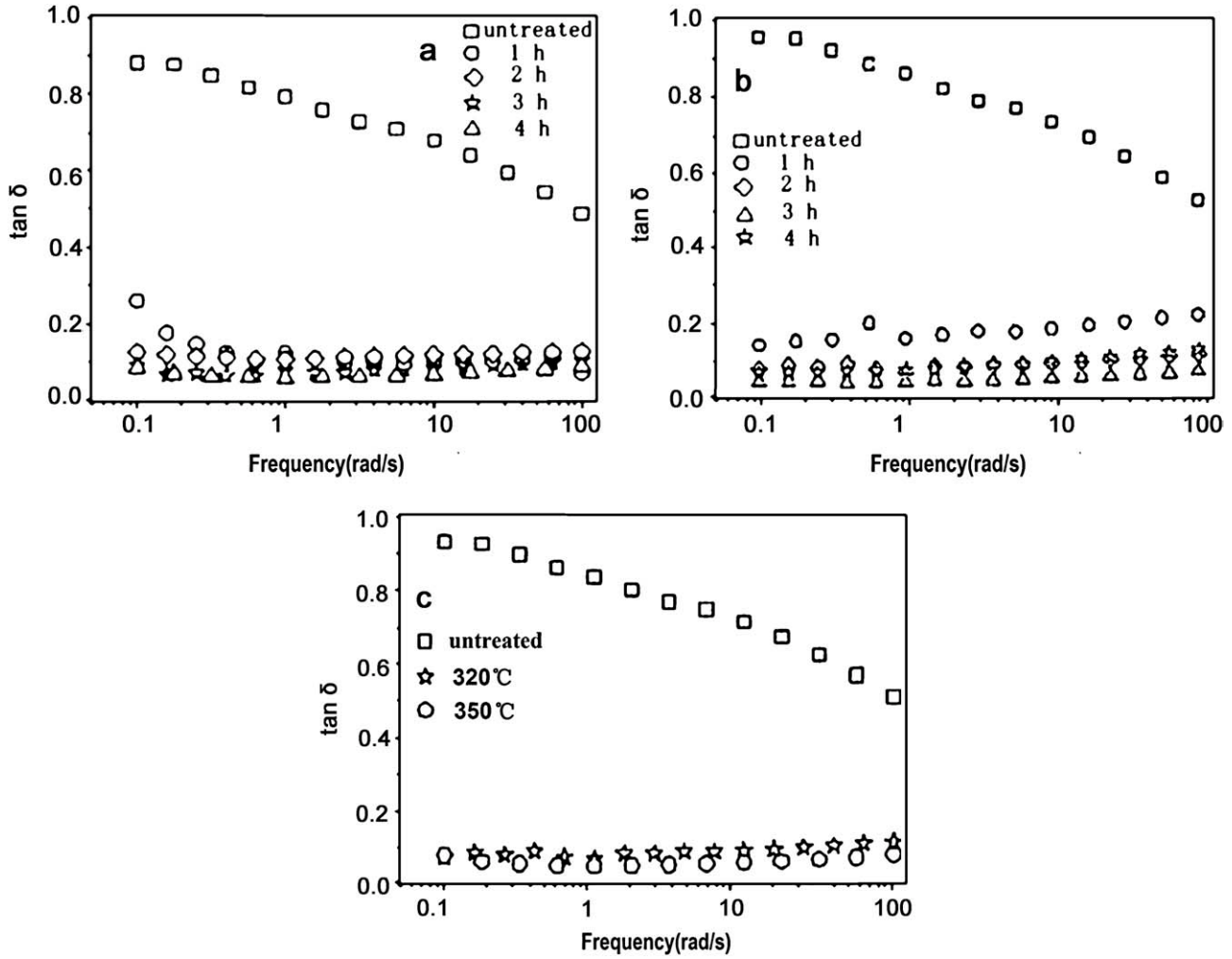

Figure 7 Frequency dependence of loss factor of films processed at (a) 320°C and (b) 350°C, and (c) films processed 4 h.

6(c), the G' of the sample processed 4 h, at 350°C (10^6 Pa) was higher than that at 320°C. Thus, raising the temperature could increase the cross-linking degree. A dynamic frequency scan of the loss factor (tan δ) is shown in Figure 7. It showed that the value of tan δ was close to 1 at low frequency, for the untreated film, and decreased with increasing frequency. It was noted that as a result of the formation of cross-linking network, restrictions on the molecular motions of the chain[23] and the frictional drag increased and high elastic deformation lagged behind the stress changes significantly. Then, the molecular structure of PEN shifted gradually from clutter into order, and the movement of molecular chain could keep pace with stress changes with the increase in shear frequency. But tan δ of the heat-treated samples was only 0.1 initially and increased slowly with the increase in frequency. It was worth noting that the cross-linking networks had been generated, and its movement fall behind stress changes; thus, the tan δ was small. As the frequency increases, cross-linking network made some response to the external force changes, showing that the tan δ increased slightly, but tan δ reduced with the increases in processing time, indicating that the more stable cross-linked networks were formed by prolonging processing time and increasing reaction temperature.

CONCLUSIONS

In this article, the catalytic cross-linking of PENs have been studied in the catalytic action of $ZnCl_2$ and the heat conditions. The cross-linking degree becomes good with the increase in processing time and reaction temperature. Furthermore, the heat-resistance property and mechanical strength can get improved obviously after catalytic cross-link. The glass-transition temperature, initial decomposition rate, residual rate, and the tensile strength have been improved significantly. A real time sweep of the rheology behavior of the cross-linked films was processed on dynamic rheometer. The result shows that the storage modulus (G') increased with the increase in reaction time and temperature, whereas the loss factor (tan δ) decreased conversely. The

relationship between rheology behavior of the cross-linked films and the sweep frequency has changed a lot, and this phenomenon demonstrated that the cross-link of cyano groups happened.

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