Rheology, thermal and mechanical properties of polyether ether ketone with metal ions

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Abstract:We have studied the effect of manganese on PEEK. Rheology analysis indicated that the addition of Mn(VII) had significant influence on PEEK. Thermal analysis revealed that crosslinking occurred internally and thermal stability was worse. Mechanical properties and degree of crystallinity were also influenced by Mn(VII).
Keywords: Polyether ether ketone; manganese; rheology

1. INTRODUCTION

Polyether ether ketone(PEEK) [1-3] is a semi-crystalline thermoplastic polymer which has a extensive research with excellent performance. In the process of synthesis and production of PEEK, metal ions are inevitable. In this work, polyether ether ketone(PEEK) mixed with $KMnO_4$ was chosen to study. Research of rheology pointed out the melt mobility. Thermal stability and degree of crystallinity were explored by TGA and DSC. Mechanical properties was also applied to study the impact.

2. EXPERIMENTAL

2.1 Materials

PEEK was powder purchased from Changchun Jilin University SEP Co., Ltd (P.R.China). Potassium permanganate ($KMnO_4$) was purchased from Beijing Chemical Works(Beijing,China).

2.2 Sample preparation:

$KMnO_4$ was dissolved in the water and then sprayed respectively in the powder of PEEK, stirring with the high speed mixer for 2h. The mixture was heated at 120°C for 8 h. The content of the $KMnO_4$ was intended to be 0.01%, 0.04%, 0.07% and 0.10% of PEEK matrix in mass ratio and we marked them as PEEK, PEEK-1, PEEK-4, PEEK-7 and PEEK-10.

2.3 Methods

Melt flow rate (MFR) test was performed on a Melt Flow Rate Instrument (Jilin University Scientic And Teaching Instrument Factory μPXRZ-400A). The shear rates of capillary rheometer (Dynisco LCR7001) were ranged from 10 s^{-1} to 6000 s^{-1} at a temperature of 400°C. Parallel-plate rheometer (TA AR2000) test was was kept at 400°C for 1 h at a frequency of 1 Hz. Thermal stability was determined by TA 2050. DSC (TA Q100) test was carried out with the rate of 10°C/min to 400°C. Tensile tests were performed on a Shimadzu AG-1universal testing machine with the rates of 5 mm/min.

3. RESULTS AND DISCUSSION

3.1 Melt flow rate studies

Table 1 indicated that with the increase of the content, MFR constantly decreased and the mobility was getting worse. There was a similar relationship in time. In general, Mn(VII) produced a great impact on the mobility in PEEK even if it was a slight amount.

Table 1. MFR test results

Sample	5 min(g/10min)	30 min(g/10min)	60 min(g/10min)
PEEK	21.0±0.2	19.6±0.3	16.4±0.0
PEEK-1	15.9±0.1	9.88±0.65	7.09±0.77
PEEK-4	10.4±1.0	2.89±0.00	1.51±0.08
PEEK-7	8.49±0.13	1.06±0.08	0.528±0.019
PEEK-10	4.54±0.06	0.245±0.010	0.121±0.000

3.2 Rheological performance from capillary rheometer

Fig.1 indicated that content increasing of $KMnO_4$ made the apparent shear viscosity change obviously at the same apparent shear rate.

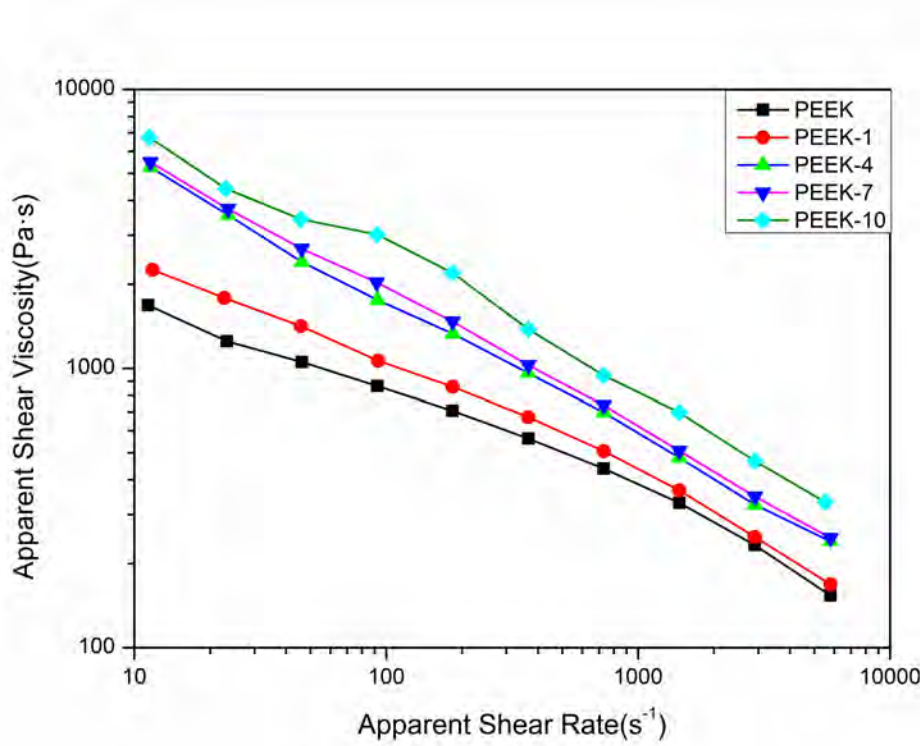

Figure 1. Apparent shear viscosity versus apparent shear rate curves

3.3 Rheological performance from parallel-plate rheometer

Fig. 2 indicated that the complex viscosity grew along with time and the addition of Mn(VII) had a great influence in PEEK.

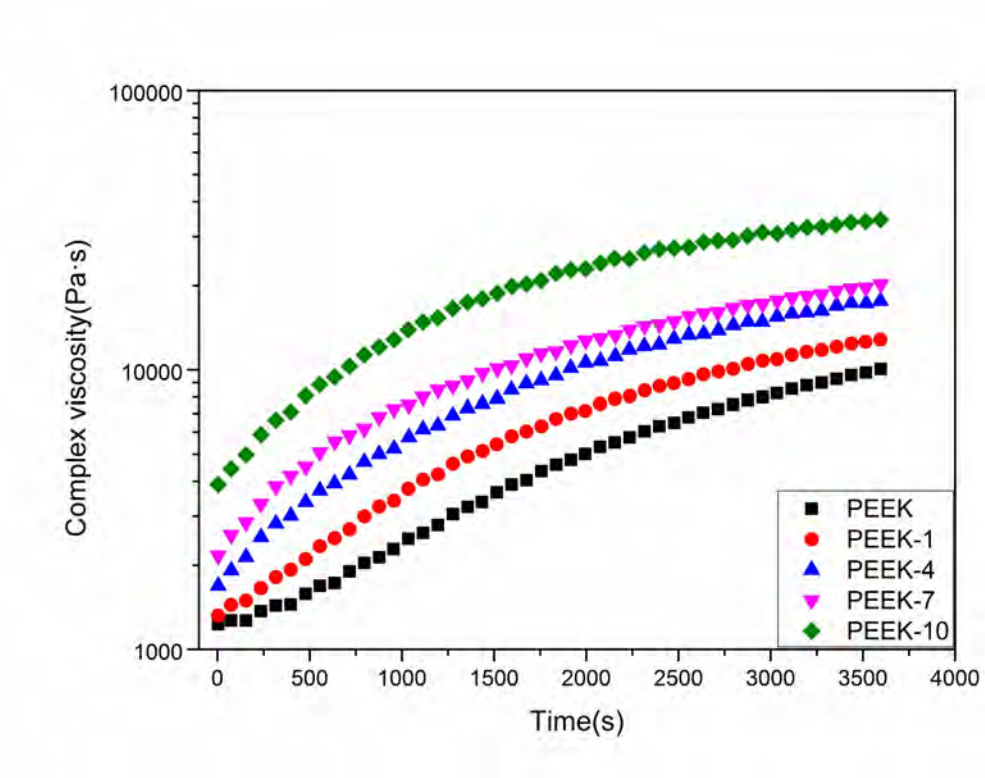

Figure 2. Complex viscosity versus time curves

3.4 Thermal analysis and degree of crystallinity

T_d^5 by TGA were presented in Table 2. Thermal stability of PEEK mixed with Mn(VII) was worse. Meanwhile, Tm by DSC decreased with the exist of Mn(VII) and degree of crystallinity(WDSC) decreased. These were more proof of crosslinking in PEEK.

Table 2. Thermal properties and crystallinity degree

Sample	T_d^5(°C)	Tm (°C)	ΔH (J/g)	W_{DSC} (%)
PEEK	572	341	41.9	32.2
PEEK-1	568	340	33.7	25.9
PEEK-4	558	339	32.8	25.2
PEEK-7	558	339	31.3	24.1
PEEK-10	541	338	31.6	24.3

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3.5 Mechanical properties

Table 3 shows that the max-strength increased when adding the Mn(VII) and the tendency of decline might be connected with the excessive crosslinking. Elongation at breaking increased in general with the increasing of Mn(VII) indicating that the regularity of PEEK were destroyed and the crystallinity decreased.

Table 3. Mechanical properties

Sample	Max-Strength (MPa)	Modulus (GPa)	Elongation at breaking (%)
PEEK	65.0	2.5	9.0

PEEK-1	70.3	2.5	9.4
PEEK-4	67.2	2.2	8.8
PEEK-7	54.9	2.2	11.8
PEEK-10	54.8	2.4	10.5

4. CONCLUSIONS

Rheometer measurements suggested that the addition of Mn(VII) could make the processability of PEEK worse mainly because of crosslinking. Thermal and mechanical analysis revealed the worse thermal stability and applicability. Therefore, avoiding manganese and manganese ions is of great importance during material process.

References

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