Physical Aging Study of 6F-PEEK and m-TPEEK by MDSC

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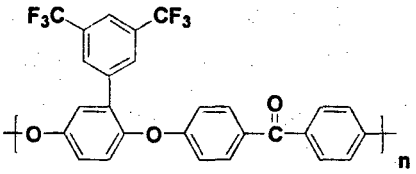
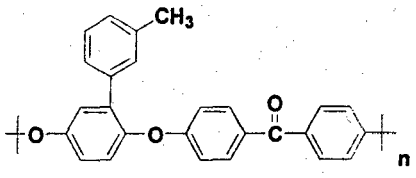
Introduction

Aromatic poly(ether ether ketone) (PEEK™), is a kind of high performance engineering thermoplastics known for its excellent combination of chemical, physical and mechanical properties.[1] We have successfully synthesized two amorphous PEEKs, 6F-PEEK and m-TPEEK . They had high thermal stability, low dielectric constant and good solubility. The glass transition temperatures of 6F-PEEK and m-TPEEK were 149°C and 148°C, respectively.[2,3]



6F-PEEK



m-TPEEK

It is well known, changes in structure and material properties, such as specific volume, enthalpy, and entropy, occur in amorphous polymers upon annealing below and close to the glass transition temperature through the configurational rearrangement of polymer segments. This time-dependent behavior has been attributed to the nonequilibrium nature of the glassy state, which is often referred to as physical aging.[4] DSC and modulated DSC (MDSC) has been extensively used to study the enthalpy relaxation process associated with the physical aging of polymers because they are convenient, sensitive and highly reproducible.[5-8]

In this paper, the physical aging behaviors of 6F-PEEK and m-TPEEK were studied by MDSC. The effect of aging time on the parameters such as total heat flows and other parameters are illustrated. At the same time, we tried to study the aging phenomenon of these two kinds of materials from the view of molecular activity.

Experimental

6F-PEEK and m-TPEEK were synthesized by our lab. The powder of 6F-PEEK and m-TPEEK were pressed into films at 300°C using a thermal compression machine, followed by quenching into films at room temperature in order to erase their previous thermal history. All the films were then removed to a temperature-controlled oven, annealed at 128°C and 129°C, which is 20°C below their own glass transition temperature.

The MDSC measurements were performed with a TA 2920 MDSC instrument. The conditions of the experiments utilized in MDSC were heating rate of 1°C/min with a modulation amplitude of 1°C and a period of 60s. A N_2 purge was used for all the measurements. The signal processing software was provided by the manufacturers. Careful baseline calibration is critical for these films and was performed regularly using indium.

Results and Discussions

To both of the two kinds of materials, the experimental results are well agreed with the predictions of an earlier theoretical model. [9]

Figure 1 shows the two families of curves of the total heat flow as function of temperature for 6F-PEEK and m-TPEEK for different aging times, separately. It is obvious that the glass transition of the two kinds of materials, which was at the same temperature difference to their own glass transition

temperatures is characterized by marked endothermic peaks. The endothermic peaks indicate the familiar overshoot at the glass transition temperature, which grow in magnitude and move to higher temperature as the aging time increases. This phenomenon is associated with and characteristic of physical aging in heat flow, as observed from the DSC trace when heating through their glass transition. It is a well-know effect displayed in conventional DSC scans.

Figure 2 showed the variation of total enthalpy (the area under the total heat flow curve) with aging time of 6F-PEEK and m-TPEEK separately. It is obvious that the enthalpies, in other word, the extents of their endothermic process, of 6F-PEEK and m-TPEEK increase as a linear function of $\ln t_a$ with different slope.

The excess enthalpy developed at aging time t, ΔH_t, could be obtained from the difference between the standard quenched glass and the aged glass between two fixed temperatures as outlined by others[9]. From scheme 1, we could get the maximum enthalpy change, ΔH_{max}, which is corresponding to the equilibrium state that has been achieved at the aging temperature T_a.

$$\Delta H_{max} = \Delta C_p (T_g - T_a) = \Delta C_p \cdot \Delta T \quad (1)$$

When the equilibrium amorphous glass is looked as the reference state, the extent of physical aging at aging time t could be deduced as $\Delta H_t/(\Delta C_p \cdot \Delta T)$ and the extent of the unaged part is $[1-\Delta H_t/(\Delta C_p \cdot \Delta T)]$. The semi-logrithmic plots of the unaged extents with time of 6F-PEEK and m-TPEEK are shown in Figure 3, which shows the kinetic parameters of physical aging.

And the relaxation time, τ, was defined as:[10, 11]

$$1 - \Delta H_t / (\Delta C_p \cdot \Delta T) = A \ln (3t / 2\tau) \quad (2)$$

Therefore, we could get the relaxation time of 6F-PEEK and m-TPEEK during their aging process by the slope and the intercept of the semi-logarithmic curves of the unaged extents with aging time. After calculation, we got the $\ln(\tau/h)$ of m-TPEEK is 7.92 and that of 6F-PEEK is 8.64. The relaxation time of 6F-PEEK is longer than that of m-TPEEK, which might be explained by the structure of the materials. 6F-PEEK has a comparable larger bulky side-chain, (3, 5-ditrifluoromethy)phenyl side group, than that of m-TPEEK (3-methyl)phenyl side group, and it needs longer time to be relaxed.

Conclusion

We studied the physical aging behaviors of 6F-PEEK and m-TPEEK by MDSC. The total heat flow of MDSC was very similar to the conventional DSC. They both grew in magnitude and moved to higher temperature as the aging time increased, which is associated with and characteristic of physical aging in heat flow. The relaxation times of the two kinds of materials were calculated, and the relaxation time of 6F-PEEK is much longer than that of m-TPEEK. It means m-TPEEK is quicker to rearrange into local ordered phase than 6F-PEEK. This conclusion is well agreed with their structure. 6F-PEEK with bigger bulky pendant group is a little difficult to be relaxed than m-TPEEK.

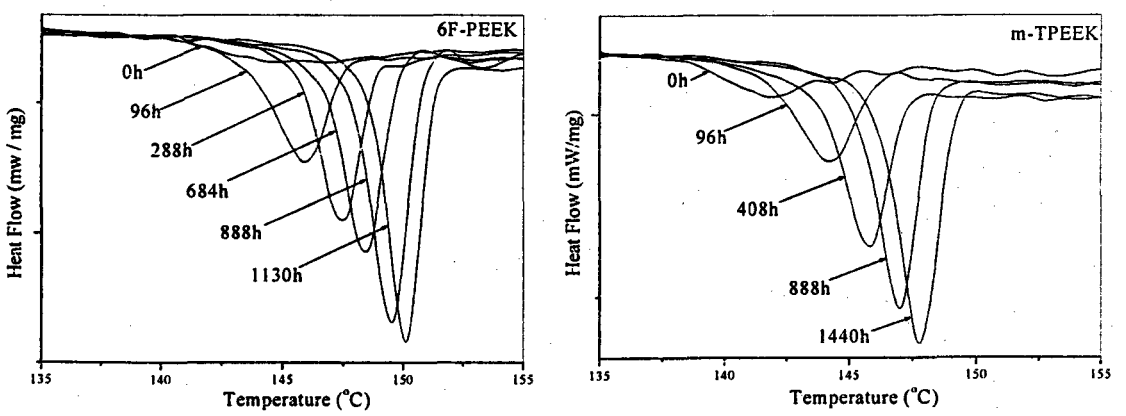


Figure 1. Total heat flow versus temperature for 6F-PEEK and m-TPEEK annealed at 129°C and 128°C for the times indicated against each curve.

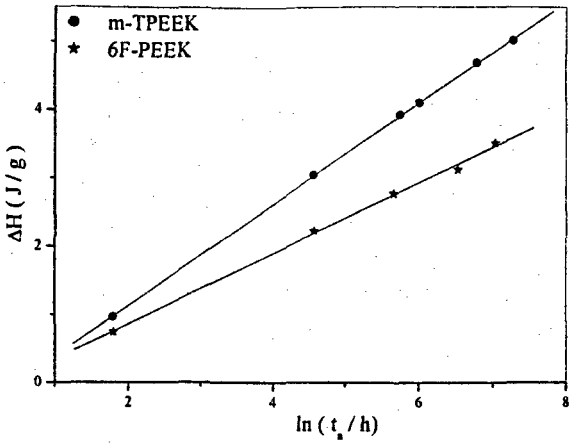


Figure 2. Semi-logarithmic plot of the total enthalpy of 6F-PEEK and m-TPEEK with time.

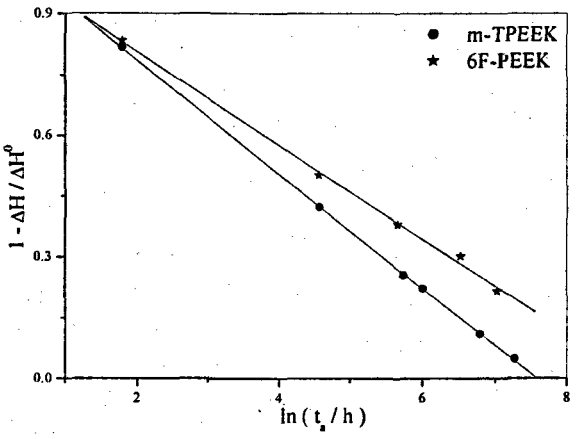


Figure 3. Semi-logarithmic plot of the unaged extent of 6F-PEEK and m-TPEEK with time separately.

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