

Solvent-Induced Crystallization in Polyetheretherketone Exposed to Methylene Chloride—During Solvent Sorption or During Solvent Desorption?

MING QIU ZHANG,¹ KAI JUN NING,¹ TIE QI LI,^{2*} HAN MIN ZENG²

¹ Materials Science Institute, Zhongshan University, Guangzhou 510275, People's Republic of China

² Laboratory of Polymeric Composite and Functional Materials, the State Educational Commission of China, Zhongshan University, Guangzhou 510275, People's Republic of China

Received 13 October 1998; accepted 16 April 1999

ABSTRACT: The phenomenon of solvent-induced crystallization observed in some polymer–solvent pair was well documented. It is generally believed that solvent-induced crystallization occurs during sorption of the solvent. However, this is actually a hypothesis and needs to be proven. To clarify the true situation, the present article investigates crystalline structural variation of polyetheretherketone before and after treatment of methylene chloride. The results indicate that crystallization of the polymer was induced by the solvent mainly when the solvent was desorbed. The possible mechanism is discussed in the light of molecular motion. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 3376–3379, 1999

Key words: solvent-induced crystallization; polyetheretherketone; reorganization

INTRODUCTION

Transport of a solvent in a crystallizable polymer may usually cause a rise in crystallinity, which is attributed to the mechanism of solvent-induced crystallization (SIC), as well as a decrease in stiffness resulting from the effect of plasticization. Both of the two processes exert opposite influences on material's mechanical properties. Therefore, study on SIC becomes important for failure prediction and performance monitoring of polymers serving in environment containing solvents.

With respect to polyetheretherketone (PEEK), a high-performance crystalline thermoplastic

polymer, SIC in its swelled version has aroused significant research interests.^{1–4} A survey of the related reports reveals that SIC is generally considered to be present during sorption of solvent; however, the employed methodology, which compares the difference in crystallinity, determined by means of density measurement, differential scanning calorimetry (DSC), and wide-angle X-ray scattering (WAXS), between original specimen and solvent-desorbed specimen, seem to be not enough to evidence the conclusion, because the latter specimen had actually experienced sorption and desorption of the solvent. To find out in which process (i.e., solvent sorption, or desorption, or both of them) SIC occurs, the current article investigates morphological variation of PEEK exposed to methylene chloride (CH₂Cl₂).

EXPERIMENTAL

PEEK produced by ICI and CH₂Cl₂ were employed here as experimental materials. PEEK

Correspondence to: M. Q. Zhang.

Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 59725307.

* On leave from Department of Materials Science and Engineering, Guangdong University of Technology, Guangzhou 510090, P.R. China.

Journal of Applied Polymer Science, Vol. 74, 3376–3379 (1999)

© 1999 John Wiley & Sons, Inc.

CCC 0021-8995/99/143376-04

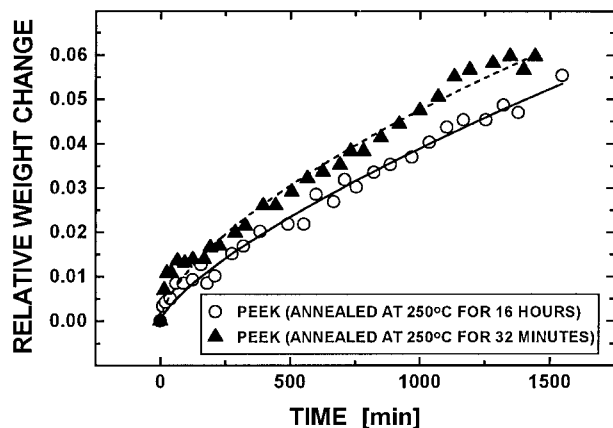


Figure 1 Typical absorption of CH_2Cl_2 in PEEK at 35°C .

films ($50 \times 20 \times 0.16 \text{ mm}^3$), were first annealed at 250°C for 16 h, 2 h, and 32 min to achieve different crystallinities and then immersed in CH_2Cl_2 at 35°C . Typical time dependence of the absorption is illustrated in Figure 1. When the specimens were saturated with the solvent, characterized by constant weights within finite observation time, WAXS measurements were carried out on them by using a Rigaku D/MAX-III A X-ray diffractometer with $\text{CuK}\alpha$ radiation. About 25 min were needed for each specimen to obtain a complete WAXS spectrum. Although CH_2Cl_2 kept on being desorbed during the measurement, there were still 80 wt % of the equilibrium amount of solvent sorbed in the specimens as revealed by the kinetics investigation,⁵ indicating the recorded WAXS spectra can be taken as those of saturated specimens for purposes of comparison. When the scattering originated by the solvent (a

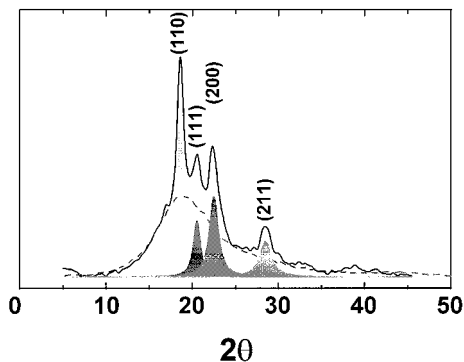


Figure 2 Typical WAXS spectrum of PEEK and corresponding spectrum deconvolution. The dashed line represent the amorphous halo of PEEK.

Table I Nonisothermal DSC Analysis of Original PEEK and the Solvent Treated Versions

Annealing Time at 250°C	Solvent Treatment	T_m ($^\circ\text{C}$)	ΔH_m (J/g)
16 hours	No	342.31	35.24
16 hours	Yes	336.13	36.45
2 hours	No	339.17	33.90
2 hours	Yes	337.53	34.52
32 minutes	No	339.74	32.56
32 minutes	Yes	338.46	37.06

* T_m and ΔH_m stand for the melting peak temperature and heat of fusion, respectively. In the case of double melting, these two parameters give the values of the upper endotherms.

straight line in parallel with the horizontal axis) had been subtracted from the raw WAXS spectra, the structure parameters of PEEK were analyzed as usual (Fig. 2). Desorption was conducted by laying the above-saturated specimens under vacuum at 40°C until constant weights were achieved, and then the specimens were examined by the X-ray diffractometer.

DSC scans of original and solvent-treated PEEK specimens were performed by a Perkin-Elmer DSC 7C in N_2 at a heating rate of $10^\circ\text{C}/\text{min}$.

RESULTS AND DISCUSSION

The effect of the solvent treatment is shown in Table I. It is seen that the melting enthalpy of the specimens treated by a cycle of CH_2Cl_2 sorption/desorption is higher than those of the original. This is typically indicative of SIC, as demonstrated by other researchers.⁶ Another evidence for SIC can be found from the DSC curves (Fig. 3).

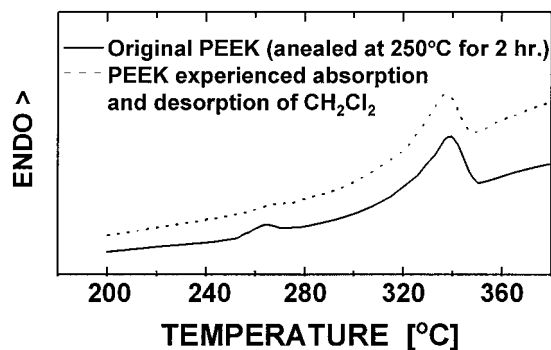


Figure 3 Typical DSC heating traces of PEEK.

Table II Effect of Solvent Treatment on Interplanar Spacing, d_{hkl} , of Crystalline Planes (hkl) of PEEK

Annealing Time at 250°C	Solvent Treatment	d_{110} (nm)	d_{111} (nm)	d_{200} (nm)	d_{211} (nm)
16 hours	No	0.4639	0.4199	0.3850	0.3036
16 hours	Saturated	0.4615	0.4161	0.3792	0.3016
16 hours	After desorption	0.4615	0.4167	0.3822	0.3022
2 hours	No	0.4654	0.4217	0.3864	0.3046
2 hours	Saturated	0.4603	0.4171	0.3794	0.3008
2 hours	After desorption	0.4647	0.4199	0.3832	0.3036
32 minutes	No	0.4644	0.4217	0.3854	0.3049
32 minutes	Saturated	0.4659	0.4193	0.3840	0.3029
32 minutes	After desorption	0.4661	0.4213	0.3844	0.3037

In analogue to some other crystalline polymers, double melting behavior can be observed on the DSC heating trace of the original PEEK specimen. Although the interpretation of this phenomenon is still very controversy, the authors of the present article believe that the reorganization model, i.e., melting of the less perfect crystals caused by annealing followed by their recrystallization and remelting, proposed by Lee and Porter,⁷ is acceptable. Returning to the DSC curve of the solvent-treated PEEK, only a single endotherm appears at around 340°C, exhibiting different melting characteristic in comparison with the untreated one. Evidently, imperfect crystals had reorganized to the higher melting forms during solvent treatment.

Tables II and III further give the crystalline structure data of the specimens calculated from WAXS experiments. It can be found that the values of d_{hkl} ($hkl = 110, 111, 200, 211$) are the highest for the untreated specimens, but the smallest in the presence of solvent. Under the

present circumstances, a smaller d_{hkl} should be the result of (a) the perfection of crystals, and (b) the osmotic stress arising from swelling that is compressive in nature. When the solvent was desorbed, deformation due to the latter factor was recovered, as demonstrated by a slight rise in d_{hkl} . Therefore, Table II eventually suggest an improvement of crystal regularity owing to CH_2Cl_2 treatment, which coincides with the above DSC results. However, it cannot be distinguished yet whether SIC occurred in the course of sorption or desorption.

With respect to the results of stack height estimation (Table III), the specimens saturated with CH_2Cl_2 have higher values of L_{111} and L_{200} but lower values of L_{110} and L_{211} , as compared with the original specimens. After desorption, all the values of L_{110} , L_{111} , L_{200} , and L_{211} are higher than the saturated ones, or even the original PEEK. The increase in L_{hkl} ($hkl = 110, 111, 200, 211$) actually manifests that CH_2Cl_2 penetrated into the less perfect portion on the corresponding

Table III Effect of Solvent Treatment on Stack Height, L_{hkl} , of Crystalline Planes (hkl) of PEEK

Annealing Time at 250°C	Solvent Treatment	L_{110} (nm)	L_{111} (nm)	L_{200} (nm)	L_{211} (nm)
16 hours	No	13.9	10.9	6.8	6.8
16 hours	Saturated	12.1	14.7	8.3	4.6
16 hours	After desorption	13.1	15.9	9.4	8.8
2 hours	No	13.3	13.4	7.1	9.4
2 hours	Saturated	15.1	15.4	8.8	4.2
2 hours	After desorption	16.9	25.3	8.6	7.5
32 minutes	No	13.6	9.6	6.7	9.8
32 minutes	Saturated	10.4	13.0	7.5	4.8
32 minutes	After desorption	11.8	22.4	8.8	8.2

planes and induced reorganization to get more PEEK macromolecules involved in crystallization. Because a remarkable rise in L_{hkl} is observed after desorption of CH_2Cl_2 , one can conclude SIC took place mainly during the desorption process, and (111) is the most preferable direction.

On the other hand, the smaller L_{110} and L_{211} of the saturated specimens imply a rather low reorganization rate in the direction perpendicular to (110) and (211) planes in the presence of the solvent. Consequently, the swollen parts could not sufficiently crystallize within the finite observation time. The subsequent increase in L_{110} and L_{211} of the solvent-desorbed specimens gives another support for the consideration that solvent desorption facilitates SIC more efficiently.

Although additional experiments should be done to find out the mechanism involved, it can be roughly estimated in the light of molecular motion. That is, when CH_2Cl_2 transported into PEEK, the strong interaction between CH_2Cl_2 and PEEK resulted in viscoelastic response of PEEK molecules, and a rise in intersegmental spacing eventually. During the desorption of CH_2Cl_2 , the escape of the solvent molecules left much larger rooms among PEEK segments. Owing to the diminishing effect of solubilization, there were sufficient space provided to enable regulation of PEEK chain conformation. Therefore, the amorphous region originated in the presence of the solvent was able to crystallize as the solvent was desorbed.

CONCLUSION

By using WAXS technique to examine the crystalline structure of PEEK saturated with CH_2Cl_2 as well as of PEEK treated after a circle of sorption/desorption of CH_2Cl_2 separately, it was found that solvent-induced crystallization predominately accompanies the desorption of CH_2Cl_2 . A further investigation of the controlling mechanism might yield deeper understanding of solvent diffusion characteristics and polymer crystallization.

The financial support by the National Natural Science Foundation of China (Grant: 59725307), and the Talent Training Program Foundation of the Higher Education Department of Guangdong Province are gratefully acknowledged.

REFERENCES

1. Grayson, M. A.; Wolf, C. J. *J Polym Sci Part B Polym Phys* 1988, 26, 2145.
2. Hay, J. N.; Kemmish, D. J. *Polymer* 1988, 29, 613.
3. Mensitieri, G.; Del Nobile, M. A.; Apicella, A.; Nicolais, L.; Garbassi, F. *J Mater Sci* 1990, 25, 2963.
4. Arzak, A.; Eguiazabal, J. I.; Nazabal, J. *J Mater Sci* 1993, 28, 3272.
5. Ning, K. J. M.Sc. Thesis, Zhongshan University (1997).
6. Stober, E. J.; Seferis, J. C. *Polym Eng Sci* 1988, 28, 634.
7. Lee, Y.; Porter, R. S. *Macromolecules* 1987, 20, 1336.