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Ductile–brittle transition induced by aging in poly(phenylene oxide) thin films

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The mechanical toughness of poly(phenylene oxide) (PPO) thin films was found to degrade remarkably from physical aging and the fracture mode transformed from ductile shear into a brittle type that involved no stable deformation zone growth. In the beginning, the fresh PPO films deformed almost uniformly upon stretching up to more than 20% strain. However, when the film was isothermally aged, diffuse shear deformation zones grew in response to the external deformation. The deformation zones could sustain extremely large strain (>20% elongation) without cracking, but their breadth narrowed and boundaries sharpened as the aging time increased. As the aging time further increased, the diffuse zones were gradually replaced by the sharp straight shear zones that nucleated at a much lower strain and could break down during the course of deformation. These deformation zones had a generally smooth interior surface but sometimes showed no fibrillated microstructure and their growth followed a micro-necking mechanism. Finally, at the very long aging times, the PPO films cracked catastrophically at small strains around 1% elongation without the evidence of stable deformation zones. Increasing the aging temperature sped up this degradation process. A separate experiment using *FT*i.r. to examine the films cast from deuterated toluene indicated that the degradation was not due to the effect of solvent. The degradation, possibly due to the enthalpic relaxation during aging, however, requires further study to reveal its origin. Copyright © 1996 Elsevier Science Ltd.

(Keywords: poly(phenylene oxide); shear deformation zone; aging)

Introduction

Poly(phenylene oxide) (PPO) is a widely used engineering polymer that demonstrates high ductility and fracture toughness. It was sometimes cited as a model system for ductile polymers because of the conspicuous shear deformation zones, rather than crazes, that grow exclusively during stretching[1–5]. Although, it had been suggested[1] that physical aging could slightly increase the degree of strain localization in response to the external deformation, the polymer has been firmly regarded as an intrinsically tough engineering plastic that brittle fracture is not a possible route for fracture. In this communication, however, we report a discovery that physical aging not only can reduce the scale of the shear deformation, but also will introduce a considerable embrittlement effect on the PPO films. The evolution of the microdeformation behaviour as a function of aging, and the temperature effect are examined here. Furthermore, the possible effect of solvent used in film casting was examined by *FT*i.r. The origin of the embrittlement is important for understanding the fundamental behaviour of polymer mechanical properties.

Experimental

Uniform thin film poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) of 0.5 μm thickness was cast from the toluene solution at around 70°C when the solution turned completely clear. The polymer was purchased from the Aldrich Chemical Company with a molecular weight of $M_w = 244\,000$ and $M_n = 32\,000$. After the solvent had escaped, the PPO thin film was floated off the substrate onto the water surface, and picked up on a supporting copper grid which was annealed and precoated with PPO to ensure good extensibility and strong adhesion to the polymer film[3].

To study the aging embrittlement effect at room temperature, different elapse times of 1 h, 18, 103, and 250 days between the specimen preparation and deformation were used. The specimen was stretched in a hand-operated strain jig while a polarized light microscope (Zeiss Axioplan) was used to monitor the nucleation and growth of the deformation in the film. The effect of aging temperature was also explored by aging the specimens at the various temperature of 5, 25, 120, and 210°C before testing.

In order to check the influence of film casting solvent, an *FT*i.r. instrument was used to detect the residual solvent content in the polymer film in an effort to relate it to the observed aging effect. In this experiment, the PPO thin films were prepared from deuterated toluene solution on double-polished clean silicon wafers. Those specimens were aged for various aging times at room temperature and 120°C.

Results and discussion

1. Effect of aging time at the ambient conditions.

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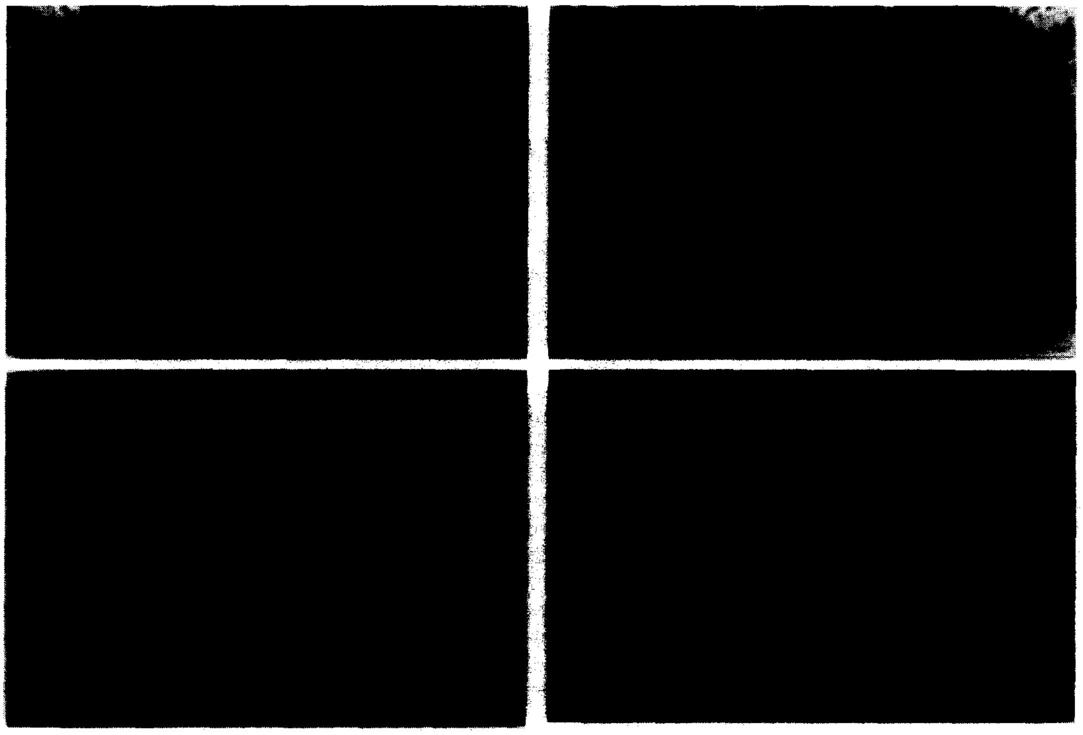

Figure 1 PPO films stretched after different aging time (t_a) at the room temperature: (a) t_a = 1 h, strain = 20%, (b) t_a = 18 days, strain = 20%, (c) t_a = 103 days, strain = 20%, and (d) t_a = 250 days, strain = 1%

Immediately after preparation, the PPO films can be stretched up to more than 20% elongation without the formation of any obvious local deformation zones, as shown in *Figure 1a*. As clearly shown in the optical micrograph, the whole film was uniformly deformed except for some isolated spots where dust particles and foreign inclusions induced very small scale local stress concentration and local deformation.

After being aged for 18 days at the ambient conditions, the PPO films developed diffuse microdeformation zones at large deformations. *Figure 1b* shows the aged PPO thin film stretched to 20% in which some local diffuse deformation zones were formed in the direction vertical to the stress. These diffuse deformation zones usually were connected with each other spreading over a large area in the specimen. The very tiny local spots of high strain concentration scattering around the whole film were due to dust particles and foreign inclusions.

Figure 1c shows the PPO film aged for 103 days followed by a 20% strain deformation. Straight and sharp deformation zones were apparent and grew independently all over the PPO film, indicating a higher degree of strain localization of the stretched polymer films.

As the aging time increased to 250 days, the PPO films became extremely brittle. The film broke catastrophically as soon as a small strain (less than 1%) was applied, as shown in *Figure 1d*. From the appearance of the sharp broken edges and the low breakdown strain, it appears that both the uniform global deformation of the film and the growth of the local deformation zones were highly suppressed during stretching.

From the sequence shown in *Figures 1a–d*, aging at room temperature obviously can cause a considerable embrittlement effect on the PPO thin films. The embrittlement process started with an increase of strain localization at the beginning of aging, that eventually evolved into a strong restriction of the growth of microdeformation zones that cause the film to crack in a very brittle fashion. It is important to note that signs of fibrillation were detected in the long aged PPO samples under a TEM, indicating that crazes might take place in the initially ductile films.

2. Effect of aging temperature. The effect of aging temperature was then studied. It was found that the aging temperature has a strong effect on the aging degradation of the PPO thin films. As shown in *Figure 2a*, the PPO films aged at 5°C for 25 days showed no obvious strain localization at a 20% elongation, in a sharp contrast to the room temperature aged ones for the same period of time in which local diffuse deformation zones grew readily at large deformations (*Figure 2b*).

On the other hand, when the aging temperature was raised, the degradation accelerated. For example, in the specimens aged at 120°C for 1 h (*Figure 2c*), tiny sharp shear deformation zones nucleated as early as a small external strain of 2% was applied. The deformation zones grew, thinned continuously, and eventually broke down to form cracks as the strain increased to 20%. Similarly, the 210°C aged samples, shown in *Figure 2d*, developed very tiny deformation zones all over the film at a critical strain of 1.5%. The deformation zones were so brittle that they broke down at a strain of 4.5%.

When the aging temperature was further increased to very close to or above the glass transition temperature (ca. 217°C for PPO), a retraction of the embrittlement was observed. That is, the critical strain for strain localization started to increase moderately after an initial sharp decrease during aging, and the morphology of deformation zones also showed a simultaneous decrease of localization.

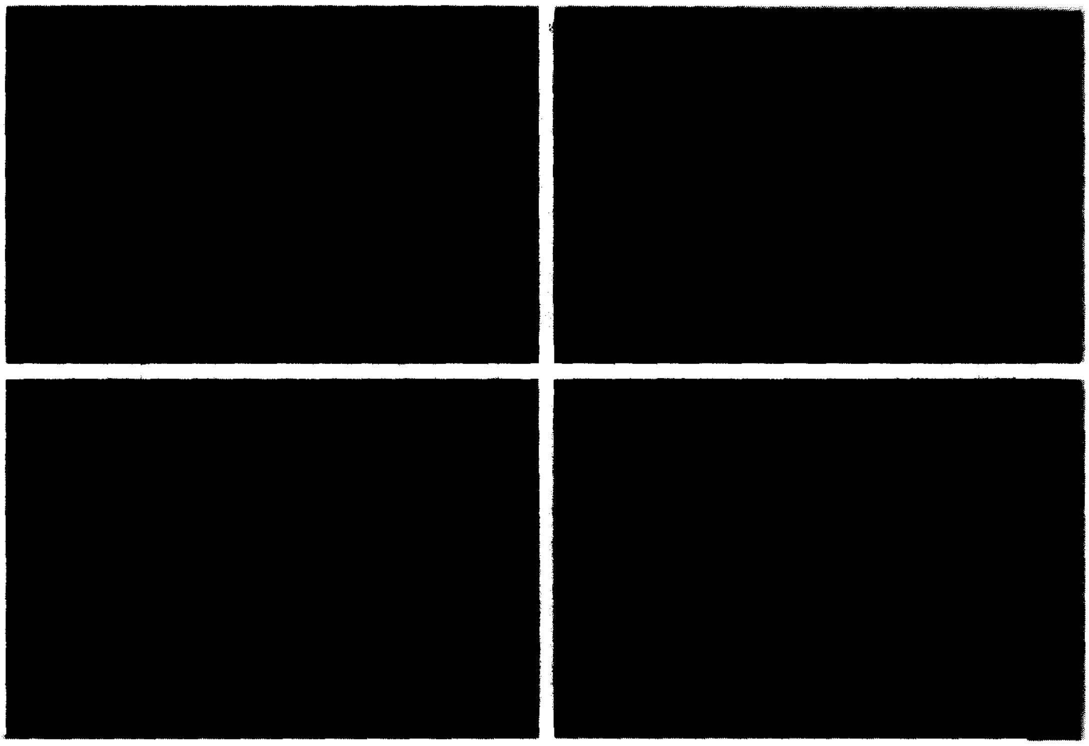

Figure 2 PPO films stretched after being aged at different temperature: (a) 5°C for 25 days with 20% strain, (b) 25°C for 25 days with 20% strain, (c) 120°C for 1 h with 20% strain, and (d) 210°C for 1 h with 5% strain

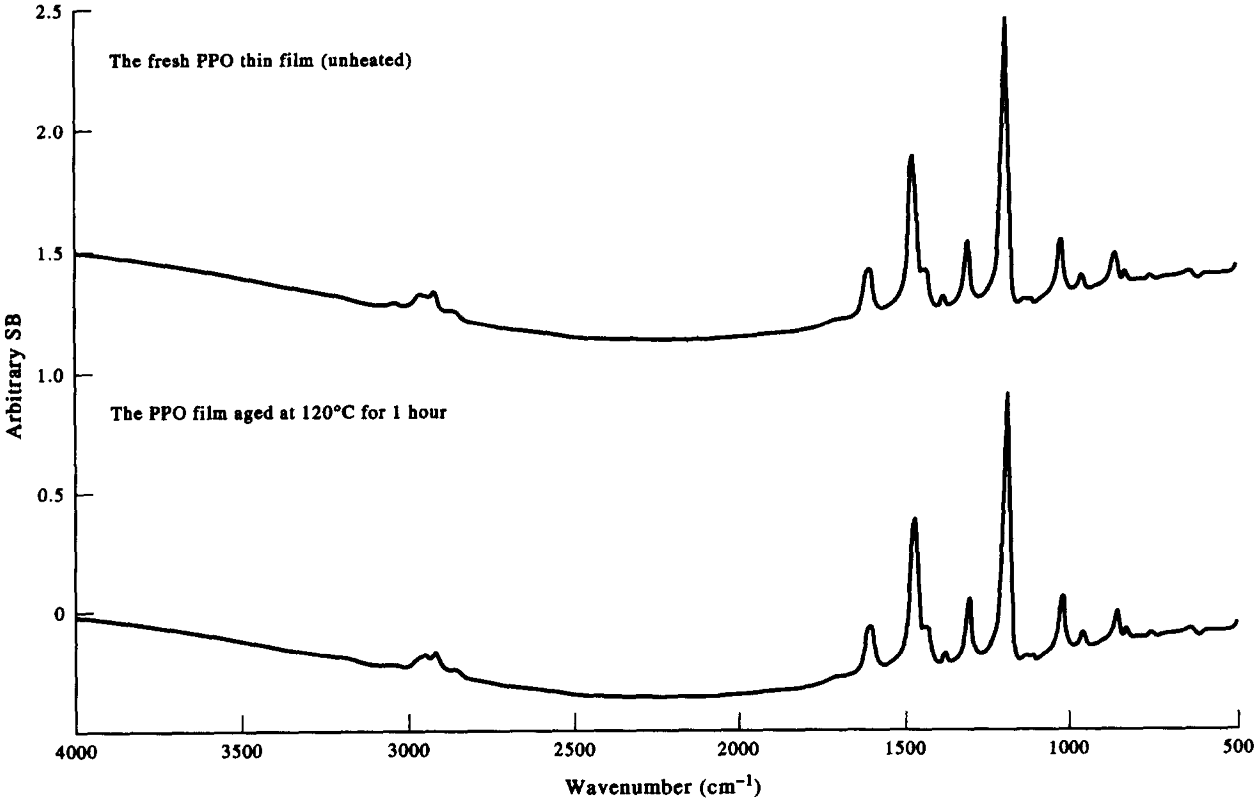

Figure 3 *FT*i.r. spectra of two 0.5 μm PPO films, one aged at the room temperature for 1 h and the other aged at 120°C also for 1 h

In summary, increasing aging temperature clearly resulted in stronger embrittlement that could eventually cause the PPO films to break catastrophically at low strains comparable to those observed in the very brittle polymers. The observation of retraction of embrittlement at higher aging temperature seems to indicate that the embrittlement is closely related to the sub-T_g chain relaxation.

3. FT *i.r. experiment.* To examine whether the aging embrittlement was related to the film casting solvent, thin film specimens were prepared using deuterated toluene which, if it remained in the films, could be easily detected in a *FT*i.r. spectrum. *Figure 3* shows the *FT*i.r. spectra of two specimens demonstrating very different microdeformation behaviour: one being annealed at 120°C for 1 h and the other always kept at room temperature. Despite the very different mechanical behaviour, it can be seen that the spectra of the two specimens are almost identical and the c–d vibration around 2100 cm^{-1} for the residual toluene is absent in both cases. These results indicate that the residual solvent in the film is very low and is not the cause of the observed aging degradation effect.

As suggested by Wellinghoff and Baer[1] for their discovery of the increase of strain localization in PPO from physical aging, improvement of chain packing in the glassy state during physical aging that causes the decrease of the conformational energy of the polymer chains may give rise to this ductile-to-brittle transition. It seems perplexing, however, as how the sub-T_g chain relaxation can lead to the striking transition from shear yielding to crazing, which was originally taken to be controlled only by the chain entanglement density[2]. Therefore, it seems to indicate that chain mobility and packing probably also have equally important roles in dictating the microdeformation behaviour of glassy polymers. While it may hint at problems in using PPO for structural applications due to the strong embrittlement effect under conditions of extensive physical aging, it should be noted, however, that the specimens used in this study were thin polymer films at which plane-stress condition was operating and the effect of strong in-plane chain orientation may further complicate the embrittlement process. However, much more work including density and T_g overshoot peak study obviously is required for a clear understanding of this aging embrittlement on this and possibly other originally tough engineering polymers.

Conclusions

Physical aging can remarkably change the mechanical behaviour of poly(phenylene oxide) films, causing the originally tough polymer to break catastrophically at very low strains. Both aging time and aging temperature have a strong effect on this ductile-to-brittle transition. As indicated by the *FT*i.r. experiment, the residual solvent in the films is negligible and is not the cause of the degradation. A retraction of this embrittlement was observed when the aging temperature was further increased to above T_g, indicating that the aging embrittlement is possibly related to the sub-T_g chain relaxation.

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References

1 Wellinghoff, S. T. and Baer, E. B. *J. Appl. Polym. Sci.* 1978, **22**, 2025
2 Kramer, E. J. *Adv. Polym. Sci.* 1983, **52/53**, 1
3 Lauterwasser, B. D. Ph.D. Thesis, Cornell University, 1979, p. 111
4 Yang, A. C.-M., Kunz, M. S. and Logan, J. A. *Macromolecules* 1993, **26**, 1767
5 Donald, A. M. and Kramer, E. J. *J. Mater. Sci.* 1981, **16**, 2977