Improvement of Heat Resistance using Physical Aging in Polystyrene Injection Moldings

Kosaku Tao[1,2], Koji Yamada[1], Seiji Higashi[1], Keitaro Kago[1], Shiho Kuwashiro[1], Hiroshi Hirano[1], Hiroki Takeshita[2] and Katsuhisa Tokumitsu[2]

[1]Osaka Research Institute of Industrial Science and Technology, Japan
[2]Department of Material Science, School of Engineering, University of Shiga Prefecture, Japan

ABSTRACT

This work examined the effect of temperature during annealing below glass transition temperature (T_g) on relaxation behavior of amorphous structure and improvement of physical heat resistance in polystyrene injection moldings. The higher the annealing temperature, the faster the rate of the enthalpy relaxation, resulting in that the annealing time required to increase heat distortion temperature (HDT) was shortened. Meanwhile, when the annealing time was longer than 7 hours, it was not that the higher the annealing temperature, the higher the HDT. Then, we investigated the dependence of both the enthalpy relaxation and the increase in HDT on the annealing temperature, using polystyrene with different T_g. As the results, the optimum annealing temperature for the increase in HDT due to the enthalpy relaxation depended on the temperature difference from T_g.

Intorduction

Amorphous resins are widely used in designing components such as automobile parts because amorphous resins are easy to color owing to high transparency. In particular, polystyrene has a high production volume owing to its high versatility.

Injection moldings is a common industrial process because it allows mass production together with high dimensional accuracy. In the injection molding of an amorphous resins such as a polystyrene, the resin is rapidly cooled rom the molten state when it is injected into the mold, so the molecular motion freezes before the intermolecular distance becomes close. It is thought to solidify in an unstable enthalpy state[1)]. When the injection moldings is annealed below T_g, the amorphous structure relax to more enthalpy-stable structure. It is known as physical aging that the various physical properties change with the relaxation of the excess enthalpy[2)]. In our previous studies, we have shown that physical heat resistance [Heat distortion Temperature (HDT)] improves with the enthalpy relaxation in polystyrene injection moldings[3)]. In this study, the annealing temperature dependence of the enthalpy relaxation and HDT was investigated

using polystyrene with different T_g in order to obtain a guideline to annealing condition for increase in HDT of polystyrene injection moldings using physical aging.

Experiment

We used 679 (M_w=237000, M_w/M_N=3.49, T_g=94 °C, PS Japan corp) and HF77 (M_w=240000, M_w/M_N=2.53, T_g=102 °C, PS Japan corp) as general purpose polystyrene.

The test specimen was molded using an injection molding machine (Si-80IV, Toyo Machinery and Metal Co., Ltd.), under the condition included a cylinder temperature of 210 °C, cooling time of 10 s, holding time of 20 s, and overall cycle time of 40 s.

HDT was measured by flatwise method with reference to ISO Test Method 75. The test load was 1.8 MPa. Each specimen was thermally analyzed using differential scanning calorimetry (DSC; DSC 214 Polyma, Netzsch) in temperature-modulated mode, the extent of enthalpy relaxation (ΔH) was quantified on the basis of the area of the endothermic peak near T_g.

Results and Discussion

Fig.1 shows the resuls of the annealing temperature dependence of the enthalpy relaxation and HDT, arranged by the temperature difference (T_g-T_a) between T_g and annealing temperature (T_a), with the annealing time fixed at 336 hours. As shown in Fig. 1, the annealing temperature at which the HDT was maximized was almost the same as in the case of enthalpy relaxation for each polystyrene. Therefore, the increase in HDT and the enthalpy relaxation are considered to be closely related. Inaddition, regardless of the material grade, the enthalpy relaxation and HDT were maximum at the same T_g-T_a. Therefore, the optimum annealing temperature for increaseing HDT using physical aging is thought to depend on the temperature difference from T_g.

The higher the annealing temperaturem, the faster the relaxation rate. Meanwhile, the enthalpy in the equilibrium state is high (that is, the ΔH is small), when the annealing temperature is high. From those balance, it is considered that the optimum temperature for enthalpy relaxation and increase in HDT existed in the annealing for 336 hours.

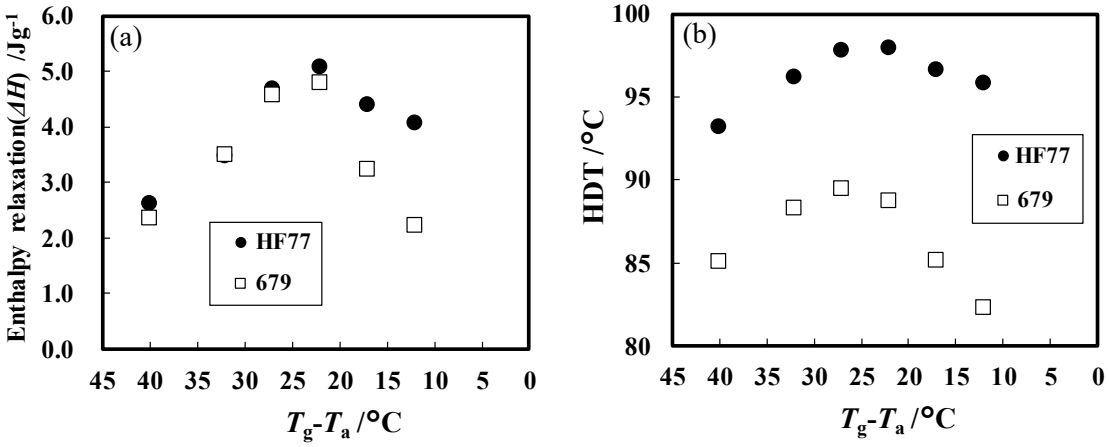

Figure 1: The enthalpy relaxation (a) and HDT (b) as a function of the annealing temperature.

Conclusion

The annealing temperature dependence of the enthalpy relaxation and HDT was investigated using polystyrene with different T_g in order to obtain a guideline for the annealing condition for the increase in HDT of polystyrene injection moldings using physical aging. As the result, the optimum annealing temperature for increasing HDT depends on the temperature difference from T_g. Although the optimum temperature is presumed to differ depending on the time scale, the optimum temperature is considered to be about T_g-25 °C in the heat treatment for 336 hours.

REFERENCES

1. Ho Huu, C.; Vu-Khanh, T. Effects of Physical Aging on Yielding Kinetics of Polycarbonate. *Theoretical and Applied Fracture Mechanics*, **40(1)**, 75-83., 2003. https://doi.org/10.1016/S0167-8442(03)00035-1.
2. Hutchinson, J., M.; Smith, S.; Home, B.; Gourlay, G., M. Physical Aging of Polycarbonate: Enthalpy Relaxation, Creep Response, and Yielding Behavior. *Macromolecules*, **32(15)**, 5046-5061., 1999. https://doi.org/10.1021/ma981391t
3. Tao, K.; Yamada, K.; Hatano, A.; Takeshita, H.; Higashi, S.; Kago, K.; Kuwashiro, S.; Hirano, H.; Tokumitsu, K. Relationship between dynamic viscoelasticity and amorphous structural changes associated with enthalpy relaxation in polystyrene injection moldings. *Journal of the Society of Rheology, Japan*, **50(2)**, 181-187., 2022. https://doi.org/10.1678/rheology.50.181