

Analysis of the Relationship Between Solvent Diffusion and Polymer Chain Relaxation in the Chemical Resistance of Automotive Interior Decorative Films

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PMMA-based decorative films are widely used for automotive interior parts because they provide high design quality and various surface appearances. However, their appearance quality may deteriorate when exposed to organic solvents contained in cosmetics, disinfectant sheets, and other products used in vehicle interiors. In particular, whitening caused by limonene, the main component of citrus-based air fresheners, is one of the major concerns affecting the appearance quality of decorative films. In this study, three PMMA films with different glass transition temperatures (T_g), namely No.1 (98.2°C), No.2 (104.9°C), and No.3 (109.6°C), were investigated to clarify the mechanism of chemical resistance to limonene-induced whitening. Solvent absorption behavior, polymer-chain relaxation behavior, and void formation behavior were evaluated.

The limonene absorption behavior was analyzed using the Ritger–Peppas model. Higher- T_g films exhibited lower absorption rate constants (k) and higher diffusion exponents (n). In addition, higher- T_g films tended to retain Case II diffusion behavior even at elevated temperatures, whereas lower- T_g films tended to approach Fickian diffusion behavior as temperature increased. Because Case II diffusion is generally known to be strongly influenced by polymer-chain relaxation, rapid swelling induced by solvent absorption was suggested to be suppressed in the higher- T_g films.

As shown in Fig. 1, void growth and coalescence were significantly suppressed in the higher- T_g films. Although little difference was observed among the samples at the initial stage of immersion, void growth and coalescence became more pronounced in the lower- T_g films with increasing immersion time, resulting in a larger area-weighted mean void diameter. Because the formed voids scatter visible light, differences in whitening behavior among the films were attributed to differences in void growth and coalescence.

Dynamic mechanical analysis revealed that the relaxation temperatures of E' , E'' , and $\tan \delta$ shifted to higher temperatures with increasing T_g , indicating that polymer-chain relaxation occurred at higher temperatures in the higher- T_g films. Furthermore, as shown in Fig. 2, among the activation energies calculated from frequency-dependent measurements, only the activation energy derived from E'' showed a tendency to correspond to void formation behavior. The E'' -derived activation energy increased in the order of No.1, No.2, and No.3, whereas the area-weighted mean void diameter decreased. E'' reflects energy-dissipative polymer-chain motion, and a higher E'' -derived activation energy suggests that such polymer-chain relaxation occurs less readily. As a result, void growth and coalescence after limonene absorption are considered to be suppressed.

Based on these findings, whitening of PMMA decorative films is considered to progress through void formation, growth, and coalescence induced by limonene absorption. In addition, differences in the polymer-chain relaxation behavior reflected in E'' are suggested to influence whitening behavior through void growth and coalescence, thereby contributing to the resistance of PMMA decorative films to limonene. These findings provide useful guidelines for designing highly chemical-resistant decorative films for automotive interior applications.

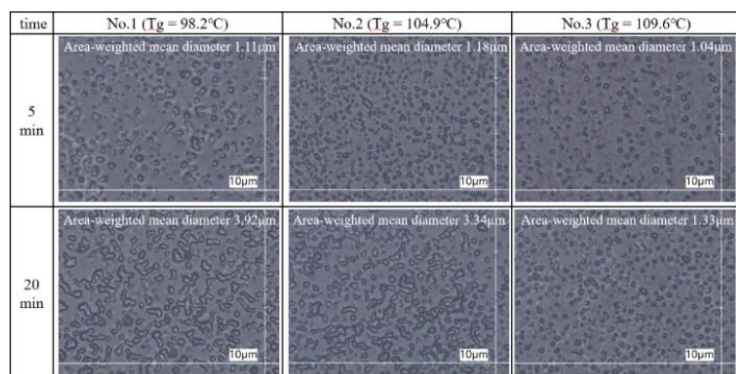


Fig. 1 Void growth and coalescence during limonene immersion.

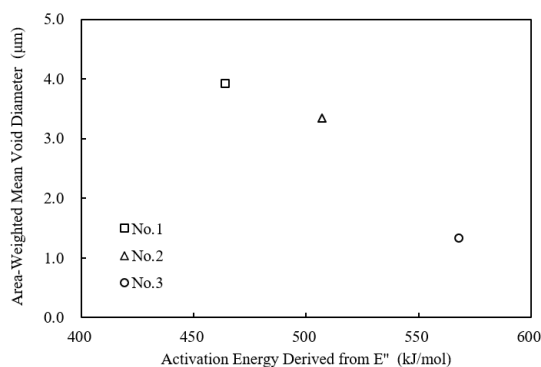


Fig. 2 E'' Activation Energy vs. Void Diameter.