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Crosslinked hydroxypropyl cellulose films retaining cholesteric liquid crystalline order

Part III *Tensile creep behaviour in vacuo*

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The crosslinked and uncrosslinked hydroxypropyl cellulose solid films retaining the cholesteric liquid crystalline order were cast from the liquid crystalline solutions in methanol. The tensile creep behaviour of the films was determined and the deformability of the films and the size of the liquid crystalline domains in the films were discussed. There was a great difference in the creep behaviour between the crosslinked and uncrosslinked films; both kinds of the films exhibited a linear increase in strain with time, however, only the crosslinked films exhibited a constant region of strain after a given time. The constant strain depended on the crosslinking conditions: The strain decreased with increasing crosslinking agent concentration. The Eyring activation volume (V) could be evaluated. V for the crosslinked films was smaller than that for the uncrosslinked films; V decreased exponentially with increasing crosslinking agent concentration. Our data suggested that the inter-domain crosslinking occurred more or less. There was a critical stress where V changed; V in the lower stress region was greater than that in the higher stress region.

1. Introduction

In our previous papers, we have reported the preparation method of the crosslinked hydroxypropyl cellulose (HPC) solid films retaining cholesteric liquid crystalline order [1] and those swelling behaviour in water [2]. We intended to apply such films to filters of gas, liquid, or small materials [3, 4]. From the industrial viewpoint, the data on the mechanical behavior, in particular, small deformation behaviour of the films are needed to make clear the possibility of such a filter application. Furthermore, from the engineering viewpoint, we need to know the mechanism of deformation for the liquid crystalline domains of which the films are consisted; it is widely known that the HPC liquid crystalline solutions and solid films form the piled polydomain texture at rest state [5].

We have determined the tensile creep behaviour of the ethyl cellulose and HPC solid films in vacuo [6–8]. When an Eyring activation theory can be applied to the tensile creep behaviour of the films, the Eyring activation volume (V) can be estimated. The applicability of the theory to the cellulosic films noted above was valid [7]. V is possibly related to the size of domain of liquid crystalline order. Furthermore, the creep behaviour provides directly the deformability of the films.

In this study, we prepared the crosslinked HPC films retaining cholesteric liquid crystalline order (CLCO) and determined the effects of crosslinking conditions (crosslinking agent type and concentration) and of stress on the tensile creep behaviour and V of the CLCO films. The difference in the creep behaviour between the crosslinked and uncrosslinked films was also determined. We discussed the deformability and the domain size of the CLCO films.

2. Experimental

2.1. Samples and preparation of sample films

All samples used in this study were the same as those used in our previous papers [1, 2]: HPC (Tokyo Kasei Kogyo Co. Ltd.) as solute, methanol (Pure Chemical Co. Ltd.) as solvent, glyoxal and glutaraldehyde (Tokyo Kasei Kogyo Co. Ltd.) as crosslinking agent, and hydrochloric acid (Wako Pure Chemical Industry Ltd.) as catalyzer. The preparation of the crosslinked HPC films was also shown in detail in our previous papers [1, 2]. The retainment of the CLCO in the crosslinked and uncrosslinked films was confirmed by circular dichloism study [1]. The thickness of the cast films was ca. 85 μm.

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2.2. Tensile creep determination

The creep apparatus used was the same as that in our previous papers [6–8]. The main point is a measurement in vaccum state; the effect of moisture on the creep behaviour of the HPC films can be eliminated. The creep strain was determined with a travelling micrometer as a function of time at a given temperature (90 °C) and at given loads.

2.3. Analysis of *V*

On the basis of the Eyring activated process [9], the following relation has been able to apply to the creep behaviour [10, 11].

$$\log \dot{\varepsilon}_{\mathrm{p}} = \log(\dot{\varepsilon}_{\mathrm{p}}/2) - \Delta U/2.3\kappa T + \sigma V/2.3\kappa T \quad (1)$$

where $\dot{\varepsilon}_{\mathrm{p}}$ is a constant plateau strain rate, $\dot{\varepsilon}_0$ is a constant, ΔU is the activated energy, κ is the Balzmann constant, σ is an applied stress, T is the absolute temperature. When the plot of $\log \dot{\varepsilon}_{\mathrm{p}}$ against σ at a given temperature is a straight line of a slope of $V/2.3\ \kappa T$, the value of V can be evaluated. The more details were described elsewhere [7].

3. Results and discussion

3.1. Characteristics of creep for uncrosslinked and crosslinked films

Fig. 1 shows the dependence of the typical creep curves on time at each applied stress. Strain increased with time and with applied stress. Within the experimental conditions, the films did not break down. For the uncrosslinked films, strain increased linearly after a given initial time, whereas for the crosslinked films, strain became finally constant through a linear increase. Fig. 2 shows the schematic curves for each film. In our experimental range, the uncrosslinked films exhibited no constant strain. The constant strain (hereafter equilibrium strain) was characteristic for the crosslinked films and was dependent on the crosslinking agent concentration and applied load. Fig. 3 shows the dependence of the equilibrium strain on the crosslinking agent concentration (the number of moles of crosslinking agent per 1 g of HPC) at each applied load. The equilibrium strain decreased exponentially with increasing crosslinking agent concentration. Comparison of data in Fig. 3 showed that the crosslinked films with glyoxal exhibit

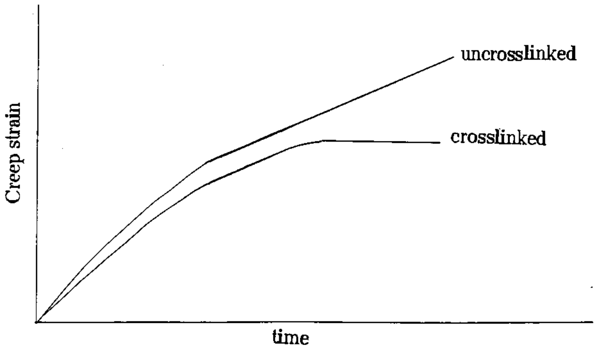


Figure 2 Schematic creep curves for the uncrosslinked and crosslinked HPC films.

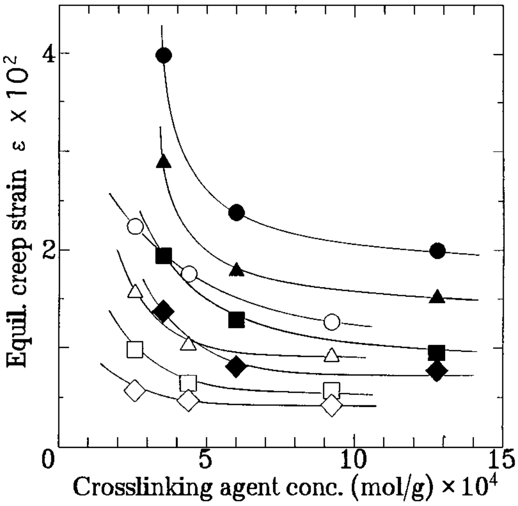
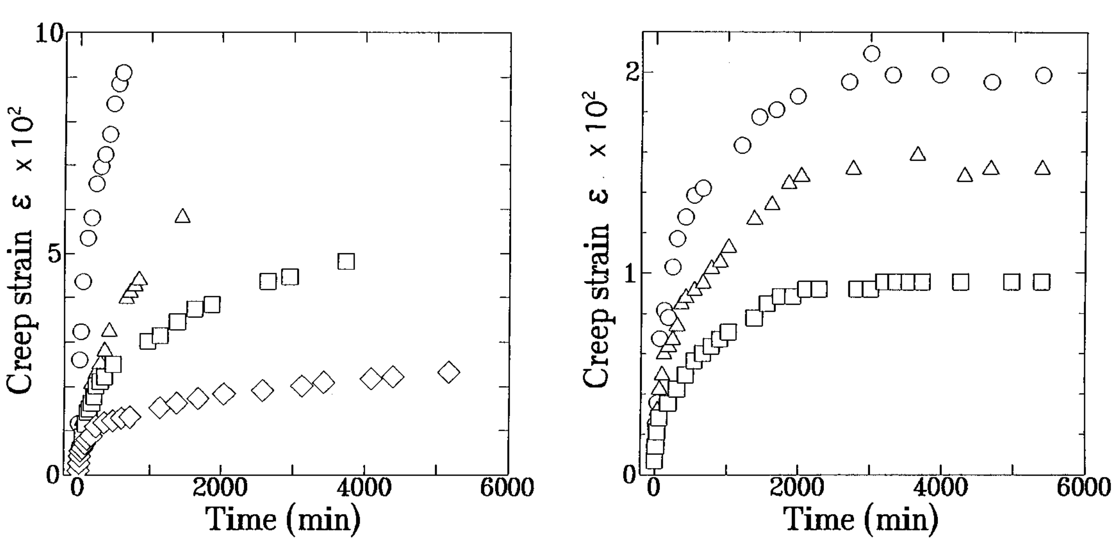


Figure 3 Equilibrium creep strain against crosslinking agent concentration for crosslinked HPC films; applied load (g): (○) 100.69, (△) 87.15, (□) 75.71, (◇) 61.45. Closed mark: glyoxal; open mark: glutaraldehyde.



(a) (b)

Figure 1 Creep strain against time at 90 °C: a) uncrosslinked HPC films; applied stress (MPa): (○) 4.13, (△) 3.64, (□) 3.11, (◇) 2.72; b) crosslinked HPC films with glyoxal (10.0 wt %); applied stress (MPa): (○) 7.93, (△) 6.86, (□) 5.89.

the greater equilibrium strain than the films with glutaraldehyde at a given concentration and at a given applied load. The equilibrium strain is a measure of the crosslinking density. As the crosslinking density increases, the deformations of molecules are much more limited. Therefore, the trend in Fig. 3 was general for the crosslinked polymeric films. Furthermore, Fig. 3 clearly showed that glutaraldehyde had a greater efficiency of crosslinking than glyoxal: The crosslinking density for the crosslinked films with glutaraldehyde appears to be greater than that for the films with glyoxal.

We have reported the swelling behaviour in water, using the same crosslinked films [2]. The equilibrium swelling ratio should be correlated with the equilibrium strain. Fig. 4 shows the correlation between both data. The equilibrium strain correlated positively with the equilibrium swelling ratio, as expected. This confirmed that the equilibrium strain was the measure of crosslinking density.

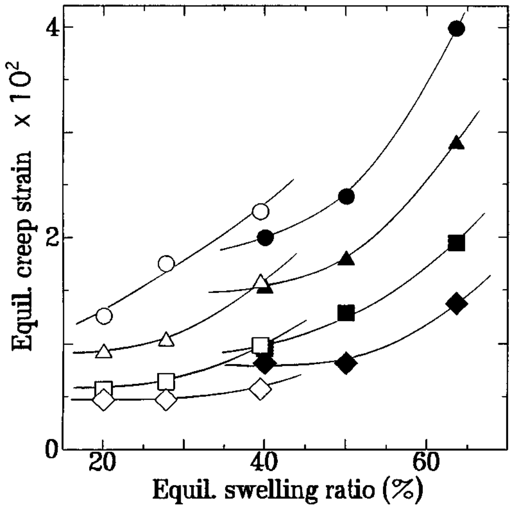


Figure 4 Equilibrium creep strain against equilibrium swelling ratio in water for crosslinked HPC films; applied load (g): (○) 100.69, (△) 87.15, (□) 75.71. Closed mark: glyoxal; open mark: glutaraldehyde.

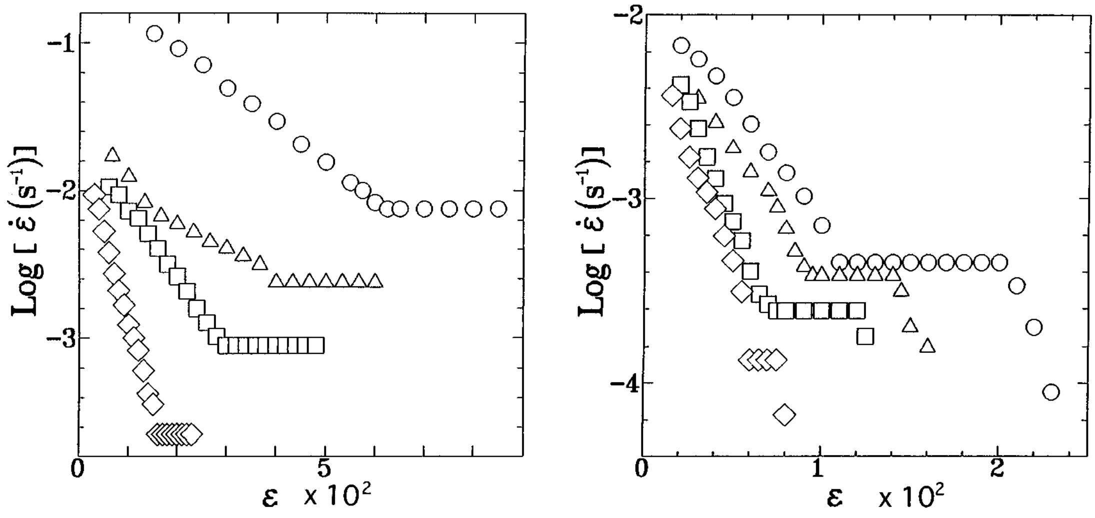
3.2. Estimation of V

Fig. 5 shows the typical Sherby-Dorn plot (logarithum of strain rate against strain). To estimate V on the basis of the Equation 1, we need to plot the strain rate against strain. The strain rate was obtained from the differential of the creep curves at each time. For the uncrosslinked films, the plots of strain rate vs. strain showed the final plautou strain rate as shown in Fig. 5a. When the plautou strain rate is plotted against the stress and the plots are linear, V can be obtained from the gradient of the lines. However, the plots for the crosslinked films were little different from those for the uncrosslinked ones. The strain rate decreased and became to constant and again decreased with increasing strain, as shown in Fig. 5b. The secondary decrease in strain rate was corresponded to the equilibrium strain shown in Fig. 1b. Interestingly, the region of the plautou strain rate shown in Fig. 5b depended on the crosslinking agent concentration and the stress. In this study, V for the crosslinked films was also estimated from those plautou strain.

Fig. 6 shows the plots of plautou strain rate vs. stress for the crosslinked films with glyoxal. The logarithum of the plautou strain rate was linear against stress in the range. Therefore, the Equation 1 could be applied to our creep data.

Fig. 7 shows the dependence of V on the crosslinking agent concentration. V decreased exponentially with increasing crosslinking agent concentration. At relatively higher crosslinking agent concentration, V tended to become constant and no difference between crosslinking agent type seemed to be observed. The order of V for our films was 1000 Å^3.

Nishio *et al.* [12] have reported the size of liquid crystalline HPC domain at a rest state. The domain size they reported was greater than the size of our V. This may be due to the difference between their measurement conditions and ours; their data were observed at no loads and ours were determined at given loads. The difference in the size of the domain and V suggests that V possibly depends on the range of stress. When the suggestion is true, the plot of the logarithum of the



(a)

(b)

Figure 5 Typical Sherby-Dorn plot: a) uncrosslinked HPC films; applied stress (MPa): (○) 4.13, (△) 3.64, (□) 3.11, (◇) 2.72; b) crosslinked HPC films with glyoxal (5.0 wt %); applied stress: (○) 8.22, (△) 7.12, (□) 6.18, (◇) 5.02.

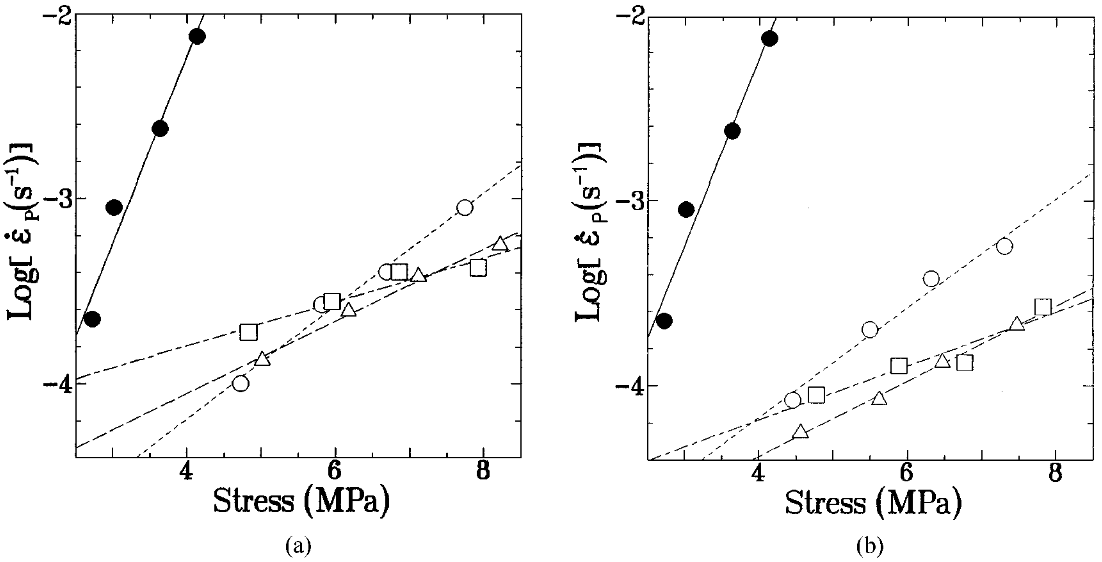


Figure 6 Logarithum of plautou strain rate against applied stress: a) crosslinked HPC films with glyoxal; concentration (wt %): (●) 0, (○) 3.0, (△) 5.0, (□) 10.0; (b) crosslinked HPC films with glutaraldehyde; concentration: (●) 0, (○) 3.0, (△) 5.0, (□) 10.0.

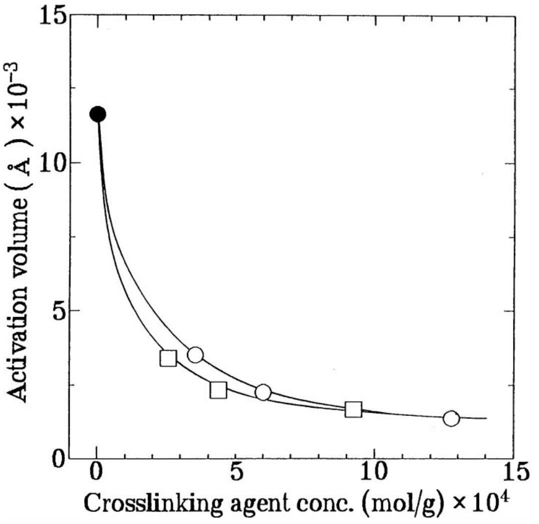


Figure 7 Eyring activation volume against crosslinking agent concentration for HPC films: (●) uncrosslinked, (○) crosslinked with glyoxal, (□) crosslinked with glutaraldehyde.

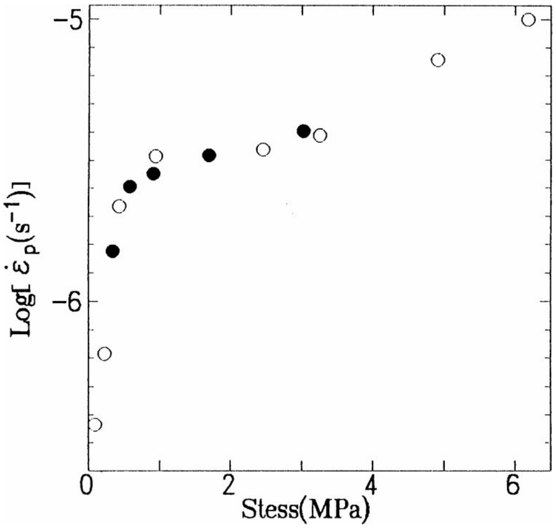


Figure 8 Logarithum of plautou strain rate against applied stress for HPC films: (●) uncrosslinked, (○) crosslinked with glutaraldehyde (5.0 wt %).

plautou strain rate vs. stress is not linear over the whole range of stress, but is broken at some critical stresses. As shown in Fig. 6, there was the linear relation within the experimental range of stress. However, we had no data at lower stress region, because of spending much time. We tried to obtain the data at lower stress region, in order to confirm whether or not V depends on the region of stress. Fig. 8 shows the plots of plautou strain rate vs. stress for the uncrosslinked film and the crosslinked film with glutaraldehyde. A critical stress was observed and at the stress (ca. 1 MPa) the slope of the straight line changed. This means that V obtained at lower stress region is greater than that at higher stress region. Furthermore, our data suggested that at further lower stress region the slope could change; V was greater. However, we could not obtain such data because of lacking reproducbility of very small creep measurement. Fig. 9 shows V against the stress on the average of stress region observed. As a reference, the liquid crystalline domain size reported by Nishio *et al.* [12] was shown in Fig. 9 at stress of zero. V decreased with increasing average stress subjected to the films. V clearly depended on the region of stress; the lower region of stress, the greater V.

3.3. Mechanism of creep deformation

Nishio *et al.* [12] have proposed a model domain which is consisted of piled round particles. We assume to apply the model to our solid films. Furthermore, we assume the similar figure of the domain size as the Nishio's model [12], that is, the ratio of diameter to thickness is 10: Diameter is 1000–2000 Å, and thickness is 100–200 Å. Now, let the thickness of cylindrical domain be x, the volume V is presented by following;

$$(10/2x)^2 = V$$

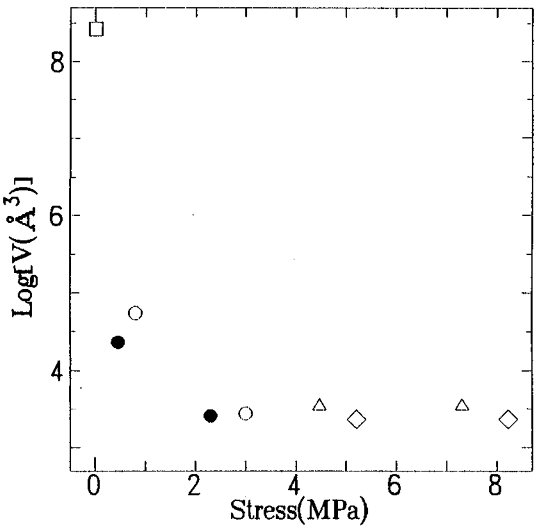


Figure 9 Eyring activation volume against averaged stress for crosslinked HPC films with glutaraldehyde. (□): Data by Nishio *et al.* [12]. Open mark: crosslinked films, closed mark: uncrosslinked films.

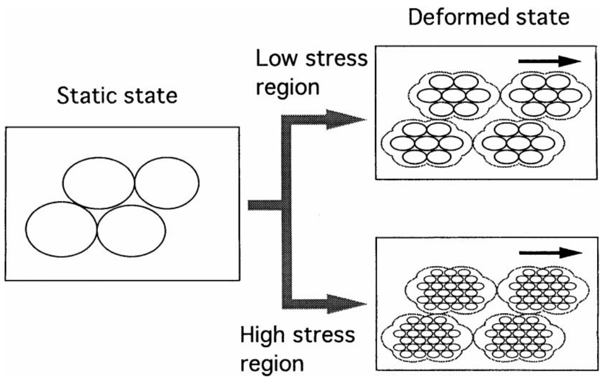


Figure 10 Deformation model of liquid crystalline domain during creep.

In this study, V for the uncrosslinked HPC films was ca. 11615 Å^3 at higher stress region. Consequently, we obtained x was 5.3 Å; diameter of the domain was 53 Å for uncrosslinked HPC solid films. On the other hand, V for the crosslinked HPC solid films was ca. 2000–3000 Å^3 at higher stress region. Then, in a similar manner, the diameter and thickness of the domain were 34 and 3.4 Å for the crosslinked HPC solid films, respectively. The domain size during creep deformation could be estimated, based on the Nishio's model; the domain size for the crosslinked films was smaller than that for the uncrosslinked one.

Ward and Wilding [13] have reported that V decreases with increasing crystal continuity for polyethylene films. We assume that the crystal continuity for the polyethylene films is analogious to the liquid crystalline domain continuity. Consequently, our results shown in Fig. 7 indicated that the crosslinking increased the liquid crystalline domain continuity. This was because not only the intra-domain crosslinking but also the inter-domain crosslinking occurred for our HPC crosslinked films at least.

Fig. 10 shows the schematic diagram of the liquid crystalline domain during creep deformation. The size of V during creep was smaller than the size of the domain at a rest state and the size of V depended on the region of stress subjected to the films.

4. Conclusions

There was a great different point in the creep behaviour between the crosslinked and uncrosslinked films: The crosslinked films exhibited a constant strain after a given time, whereas the uncrosslinked films did not. During creep deformation, V for the crosslinked HPC films was smaller than that for the uncrosslinked ones, and decreased with increasing crosslinking agent concentration. Our data suggested that the inter-domain crosslinking occurred more or less. V depended on the region of stress subjected to the films; around the critical stress of 1 MPa, the greater V, the lower region of stress.

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