

## Complex-Forming Polyoxyethylene: Poly(acrylic acid) Interpenetrating Polymer Networks<sup>1</sup> III. Swelling and Mechanochemical Behavior

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**ABSTRACT:** Potentiometric titration, swelling and mechanochemical behavior were studied on complex-forming polyoxyethylene (POE):poly(acrylic acid) (PAA) interpenetrating polymer network (IPN) having equimolar composition. In the IPN, POE associates with PAA at low pH through hydrogen bonding between acidic hydrogens and ether oxygens, but dissociates at high pH. The value of  $pK$  is lowest for PAA homopolymer, and increases in the order: equimolar POE:PAA complex, the semi-IPN in which only PAA is crosslinked, and the full-IPN in which both components are crosslinked, reflecting difference in their interpenetrating network structures. The degree of swelling of the full-IPN is dependent on pH with a maximum at  $pH=9$  and decreases with increasing ionic strength. The swelling-deswelling and mechanochemical reactions proceed reversibly for the full-IPN, but irreversibly for the semi-IPN upon changing pH. The mechanochemical reaction of the full-IPN involves at least two distinct processes: One related to reversible association and dissociation of the POE:PAA complex, and the other to viscoelastic creep and recovery of the IPN structure.

**KEY WORDS** Interpenetrating Polymer Network / Polymer Complex / Complex-Forming IPN / Swelling / Titration / Mechanochemical Reaction / Creep and Recovery /

Interpolymer complexes<sup>1,2</sup> belong to a class of polymer blends, which have unique structures and properties resulting from specific polymer:polymer interactions such as hydrogen bonding between ether and carboxyl groups of polyoxyethylene (POE):poly(acrylic acid) complex.<sup>3,4</sup> However, interpolymer complexes reported so far were often hard and brittle, and inferior in mechanical properties. A film made from interpolymer complex was disintegrated upon complex dissociation, and was not reformed even after its environment was readjusted to allow complex reformation.

Interpenetrating polymer networks (IPNs)<sup>1,2</sup> also belong to another class of polymer blends, in which two different polymers are forced to mix with each other through chemical cross-links within each component but not necessarily between different components.<sup>5-7</sup> For IPNs, synergistic effects may result from two homopolymer components which are often immiscible and thus incompatible without cross-links. A number of studies have been reported on the degree of interpenetration, morphologies and physical properties of various IPNs.<sup>5-14</sup>

To combine these advantageous features of

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the interpolymer complex and IPN, we tailored POE:PAA complex *via* matrix polymerization<sup>15,16</sup> into an IPN so that reversible complex formation and dissociation would take place within the IPN. We explored potential properties of the complex forming POE:PAA IPN.<sup>8-11</sup>

Studies on potentiometric titration and pH dependent swelling behavior of homopolyelectrolytes and their networks have been carried out by many investigators.<sup>17-20</sup> However, similar studies on binary or multicomponent systems, especially on interpolymer complex, are rather sparse. Analyses of such behavior of interpolymer complex should give information not only on the type and number of the dissociable groups but also on the nature of the interactions between complex forming species. Specifically, the number of effective charges and interactions between the dissociated groups and counter ions can be analyzed through these studies. Such knowledge should provide understanding on the mechanism of the mechanochemical reactions that complex-forming IPN exhibits.

The viscosity of a polyelectrolyte solution changes remarkably on varying pH, ionic strength, and the dielectric constant of the medium, reflecting conformational change of the polyelectrolyte chains. If this conformational change in the molecular scale could be converted to a change in the volume and/or length of the specimen in the macroscopic scale, the chemical energy may be converted to the mechanical energy. Such a system may thus be called a *mechanochemical* system.<sup>21-23</sup> The present POE:PAA IPN should exhibit reversible mechanochemical response, because the complex formation and dissociation may be controlled reversibly within the IPN. We examined the potentiometric titration, swelling and mechanochemical behavior of POE:PAA blend (complex), semi- and full-IPN samples of equimolar composition. We report the results here.

## EXPERIMENTAL

### Materials

Experiments were carried out on five different types of films: Cross-linked poly(oxyethylene) (cr-POE), cross-linked poly(acrylic acid) (cr-PAA), equimolar POE:PAA blend (complex), and equimolar POE:PAA semi- and full-IPNs. Preparation and characterization of these samples were reported previously.<sup>8,9</sup> We thus describe here the procedures only briefly.

For preparing an equimolar blend film, a prescribed amount of hydroxyl terminated POE (the catalogue molecular weight of 7800 to 9000) was dissolved in an equimolar amount of AA monomer containing 1 wt% benzoyl peroxide (BPO). Then, the AA monomer was allowed to polymerize. For preparing semi-IPN, the POE precursor was dissolved in a mixture of AA monomer (equimolar to POE) containing 1 mol% divinylbenzene (DVB) and 1 wt% BPO. Then, the monomer was allowed to polymerize and crosslink. For preparing full-IPN, the POE prepolymer was first end-crosslinked with 17 mol% trimethylolpropane (TMP) and 4,4'-diphenylmethane diisocyanate (MDI). Then, the cross-linked POE (cr-POE) obtained was swollen with the same AA/DVB/BPO mixture used for the semi-IPN preparation. The absorbed AA mixture was allowed to react *in situ*, yielding PAA second network of the full-IPN. As a reference, cr-POE and cross-linked PAA (cr-PAA) films were used. The latter was prepared from the same AA/DVB/BPO mixture.<sup>8</sup>

In a previous paper,<sup>9</sup> we described use of a trifunctional isocyanate, (2-isocyanato)ethyl-(2,6-di-isocyanato) hexanoate to obtain cr-POE for the first network. However, we did not use this crosslinking agent in this study, because it is rather unstable, particularly, in a highly alkaline medium.

### Methods

Potentiometric titration was carried out

using a micro-hand burette (E457 Micro-Hand Burette, Metrohm AG., CH-9100 Herisau) with 0.5 *N* sodium hydroxide aqueous solution (NaOHaq) and with or without supporting electrolyte, NaCl. To prepare sample solutions, we used water purified by passing through ion-exchange columns and then distilling twice just before use. The conductivity was less than  $10^{-6} \Omega^{-1} \text{cm}^{-1}$ . For the titration, each IPN specimen was crushed into pieces, a few ten milligrams of them were dispersed in the purified water or an adequate buffer solution, and then subjected to the test under a nitrogen stream passed through saturated NaOHaq to remove  $\text{CO}_2$ . To obtain one data point, we consumed 50 to 60  $\mu\text{l}$  standard NaOHaq solution, and it took from about 30 min to several hours to ensure equilibrium.

A swelling experiment was conducted on full-INP, cr-POE, and cr-PAA films at 20°C. In one series of tests, the specimens were swollen in 0.01  $[\text{Na}^+]$  sodium phosphate buffer at various pH, while in another series of tests, the specimens were swollen in NaCl aqueous solution of pH=7.0 at varying ionic strength. The degree of swelling  $Q$  was determined as,

$$Q = (W_{\text{sw}} - W_{\text{p}}) / W_{\text{p}} \quad (1)$$

where  $W_{\text{p}}$  and  $W_{\text{sw}}$  are the weights of the dry

and swollen specimens, respectively.

Observation of mechanochemical reactions was made on semi- and full-IPNs. Figure 1 shows a schematic picture of the apparatus. An IPN film of typically  $20 \times 4 \times 0.2 \text{ mm}^3$  size was first swollen with distilled water to reach equilibrium under a constant load of 2.4 g. Then, either 0.5 *N* NaOHaq or aqueous hydrochloric acid solution (HClaq) was added alternately to the medium at 25°C. Another method was a pH jump method. A full-IPN film was first suspended in sodium phosphate buffer of pH=4.0 under a given load until equilibrium. Then, the pH of the medium was changed from 4.0 to 7.0 by adding sodium phosphate buffer with 0.012 M  $[\text{Na}^+]$ . The change in the film length was read with a cathetometer (Shimadzu model HV-100). The temperature were 25, 40, and 55°C.

The pH measurement was made with an ion analyzer (Selection 5000 Ion Analyzer, Beckman Instruments) and a combination electrode (Beckman Instruments Futura Combination Electrode #39504 for the potentiometry and #39501 for the swelling and mechanochemical reaction).

## RESULTS AND DISCUSSION

### Potentiometric Titration

Figure 2 shows potentiometric titration curves for the semi- and full-IPNs and the blends with and without adding NaCl. In this figure,  $\text{p}K = \text{pH} + \log[(1-x)/x]$  are plotted against the degree of dissociation  $\alpha$ . For all samples,  $\text{p}K$  increased with  $\alpha$ . This behavior is similar to that of a common polymeric acid. At the same  $\alpha$ , the  $\text{p}K$  value of the full-IPN is the largest of the three, and that of the blend, the smallest. In the IPN films, carboxylate anions cannot diffuse out of the film and thus the Donnan equilibrium<sup>24</sup> can be established between the IPN phase and the exterior solution, because hydroxyl anions may not readily penetrate the IPN phase. The interpenetration and complex formation between

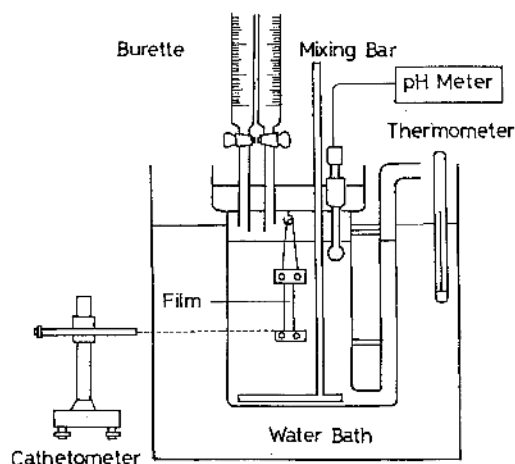


Figure 1. A schematic illustration of the apparatus used for observation of mechanochemical reaction.

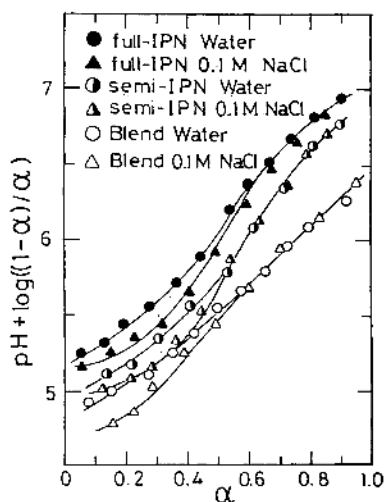


Figure 2. Potentiometric titration curves for equimolar POE:PAA blend (complex), semi- and full-IPN at 25°C.

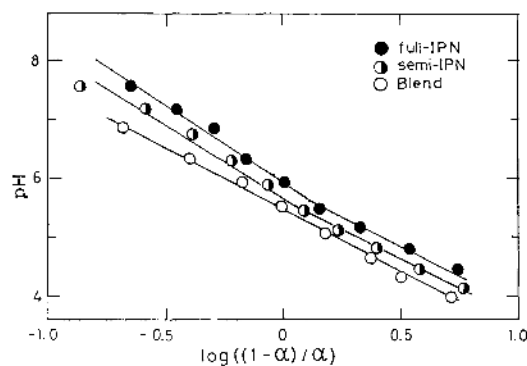


Figure 3. Henderson-Hasselbalch plots for POE:PAA blend, semi- and full-IPN at 25°C without added NaCl.

POE and PAA segments may also prevent the carboxyl groups from releasing protons. The difference in  $pK$  between the semi- and full-IPNs must have resulted from the difference in the cross-link density in the POE first component.

When  $0.1 \text{ mol l}^{-1}$  NaCl was added,  $pK$  decreased in the region of small  $\alpha$  for all the systems. This result implies that the increased ionic strength of the solution favors dissociation of carboxyl groups and decreases

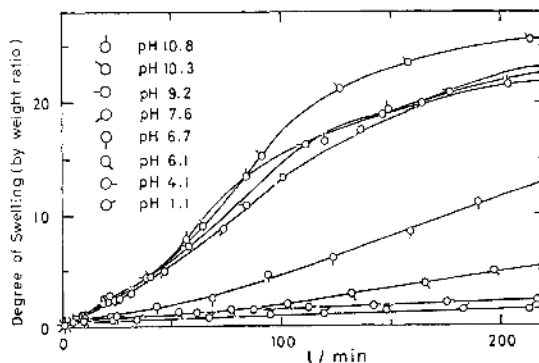


Figure 4. Dependence of the degree of swelling  $Q$  on time at 20°C for full-IPN in  $0.01 \text{ M} [\text{Na}^+]$  sodium phosphate buffer with different pH.

the pH of the solution.

Figure 3 shows Henderson-Hasselbalch plots of the titration curves without adding NaCl. For the blend, all data points fall on the generalized Henderson-Hasselbalch equation<sup>25</sup>

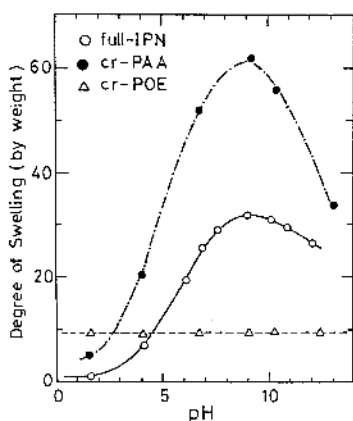
$$\text{pH} = \text{p}K - n \log[(1 - \alpha)/\alpha] \quad (2)$$

with  $n = 2.1$ . For the semi- and full-IPNs,  $n$  is equal to 2.1 in the region of small  $\alpha$ , but becomes 2.4 for the semi-IPN and 2.7 for the full-IPN as  $\alpha$  exceeds 0.5. The values of  $n$  may be compared with  $n = 2.0$  for PAA homopolymer<sup>26</sup> and  $n = 2.1$  for PAA crosslinked with 1 or 2 mol% DVB.<sup>27</sup>

The large values of  $n$  for the IPNs imply that the dissociation of protons from carboxyl groups in the IPN structure requires extra energy necessary for the complex dissociation before the proton release and also for the conformational change owing to electrostatic repulsion between the resulted carboxylate anions. Obviously, the free energy for the conformational change should be larger for the full-IPN than for the semi-IPN.

#### Swelling Behavior

Figure 4 shows the change in the degree of swelling  $Q$  (by weight) with time for the full-IPN at 20°C at various pH ranging from 10.8 to 1.1. The rate of swelling is rapid above pH

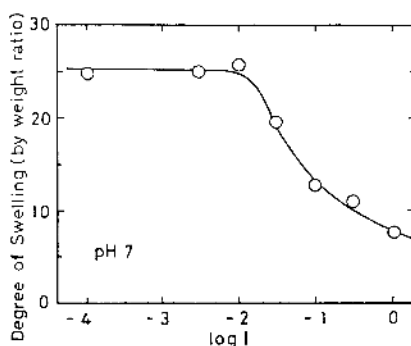


**Figure 5.** Dependence of the equilibrium degree of swelling  $Q_E$  at 20°C on pH for full-IPN, cr-POE, and cr-PAA.

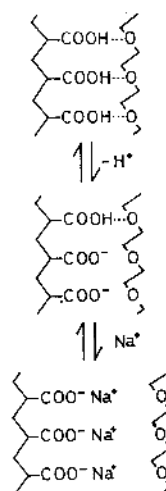
7, but is slow in the acidic medium. This may be explained by the fact that the complex is completely dissociated in an alkaline medium but only partly or not at all in an acidic medium.

Figure 5 shows the equilibrium degree of swelling  $Q_E$  at 20°C as a function of pH for the full-IPN, cr-POE, and cr-PAA films in 0.01 M  $[\text{Na}^+]$  sodium phosphate buffer. The  $Q_E$  for cr-POE is constant at any pH, while  $Q_E$  for the full-IPN increases with pH, passes a maximum at about pH=9, and decreases again with further increase in pH above 9. The  $Q_E$  versus pH curves are reversible and show no hysteresis against pH change as long as the ionic strength of the medium is kept constant.

Because of the Donnan equilibrium<sup>24</sup> between the IPN membrane which carries fixed  $\text{COO}^-$  anions at high pH and the exterior solution phase, the difference in the total ion concentration between the two phases becomes maximum at pH=9 and decreases with further increase in pH. This in turn induces deswelling of the IPN film in the region of pH above 9. This behavior resembles roughly that of cr-PAA at high pH. However, in the region of low pH, the  $Q_E$  for the full-IPN is smaller than that for the cr-PAA and is even much smaller than that for the cr-POE. Thus, the



**Figure 6.** Dependence of the equilibrium degree of swelling  $Q_E$  at 20°C on ionic strength  $I$  for full-IPN at pH=7.



**Figure 7.** A scheme for POE:PAA complex formation and dissociation.

IPN structure provides crosslinks at high pH, while the hydrogen bonds in POE:PAA complex act as strong physical crosslinks to suppress the swelling of the IPN at low pH.

Figure 6 shows plots of  $Q_E$  vs. ionic strength  $I$  at 20°C for the full-IPN in pH=7 NaClaq solution. For the full-IPN, the  $Q_E$  stays constant until the ionic strength reaches 0.01, and then decreases with further increase in ionic strength. Again, in the medium of high ionic strength, the Donnan equilibrium tends to decrease the difference in the ion concentrations between the membrane and exterior

solution phases. This induces deswelling of the IPN membrane in a medium of high ionic strength.

Figure 7 schematically depicts the process of complex formation and dissociation. Below a critical pH, PAA associates with POE through hydrogen bonding. Above the critical pH, PAA dissociates from POE and also releases protons from the carboxyl groups. As the number of carboxylate anions in the PAA network increases with pH,  $Q_E$  also increases. When sodium cations are present in the medium, the repulsive force between the carbox-

ylate anions is screened. These processes are reversible.

#### Reversible Elongation and Contraction

It was reported that a crosslinked poly(methacrylic acid) (cr-PMAA) film suspended in an aqueous medium elongated at high pH and contracted at low pH due to the swelling-deswelling of the charged-hydrogenated network balanced by the entropic forces of the network.<sup>28,29</sup> When POE was added in the medium at a neutral pH in which a cr-PMAA film was suspended, the film contracted, but when the added POE was washed out by raising the pH of the medium, it resumed its original length.<sup>29</sup>

Figure 8 shows changes in the film length induced by adding NaOH aq and HCl aq alternately to the medium in which a full-IPN or a semi-IPN film was suspended under a small load. Here, the original length  $l_0$  refers to the length of the film at low pH, where POE:PAA complex has presumably been formed. In the typical run, we suspended a full-IPN specimen of  $15 \times 3 \times 0.3 \text{ mm}^3$  size with a 2.14 g load in about  $100 \text{ cm}^3$  pure water, and first added  $0.5 \text{ cm}^3$  of  $1 \text{ M NaOH}_{\text{aq}}$  thus making the medium  $\text{pH}=11.7$  and the ionic strength  $I=0.005$ . Then, we added  $1 \text{ cm}^3$  of  $1 \text{ M HCl}_{\text{aq}}$ ,

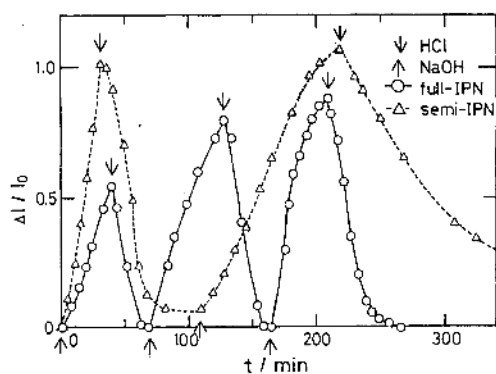


Figure 8. Mechanochemical elongation and contraction of semi-IPN (the dashed line with triangles) and full-IPN (the solid line with circles) induced at  $25^\circ\text{C}$  on addition of NaOH aq and HCl aq alternately.

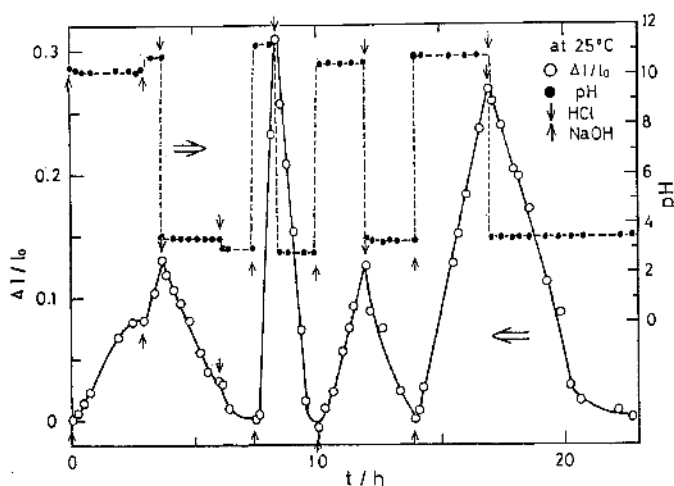


Figure 9. Reversible mechanochemical process for full-IPN induced upon pH change at  $25^\circ\text{C}$ .

making the medium pH=2.3 and  $I=0.015$ ; and further added  $1.0\text{ cm}^3$  of  $1\text{ M NaOH}_{\text{aq}}$  to make pH=11.7 and  $I=0.025$ ;  $1.5\text{ cm}^3$  of  $1\text{ M HCl}_{\text{aq}}$  to make pH=2 and  $I=0.04$ ;  $2.0\text{ cm}^3$  of  $1\text{ M NaOH}_{\text{aq}}$  to make pH=12 and  $I=0.06$ ; and  $2.5\text{ cm}^3$  of  $1\text{ M HCl}_{\text{aq}}$  to make pH=1.8 and  $I=0.085$ ; and so on.

For the full-IPN, the process is completely reversible, although the rates of contraction and elongation become gradually delayed as titration is repeated. On the other hand, the semi-IPN film elongates at high pH more than the full-IPN film, but does not contract to its original length when the pH is lowered again. In fact, the length of the semi-IPN film gradually increases by repeating the titration. This irreversibility implies that the uncrosslinked POE chains in the semi-IPN have been gradually lost during the alkaline cycles of titration. Consequently the elongation-contraction range of the semi-IPN changes from that of the full-IPN to that of cr-PAA by repeating the alternate titration. In the acidic region, the full-IPN film is shorter than the cr-PAA film because of the IPN structure and the complex formation between POE and PAA chains. On the other hand, the cross-links in the POE first network prevent, to some extent, elongation of the full-IPN film in the alkaline region. The situation is the same with swelling behavior. Similar elongation-contraction behavior by repeating titration was reported for water-insoluble poly(L-glutamic acid)<sup>30</sup> and for polyelectrolyte complex membrane composed of poly(vinyl alcohol) derivatives.<sup>31</sup>

Figure 9 shows the reversible mechanochemical response of the full-IPN film in detail. The film elongates and contracts as the pH of the medium is raised or lowered, respectively. The extent of elongation of the film increases with pH. The rates of elongation and contraction increase with the width of pH jump. The rates, however, decrease gradually as the titration is repeated. This is presumably due to gradual increase in the ionic strength of the system during repeated titration. These

results also correspond to those of the swelling behavior mentioned above.

When the temperature of the system was raised, the full-IPN film under a constant load elongated, unlike a crosslinked rubber film. This thermal elongation of the full-IPN film may have been caused through increase in the degree of dissociation of the carboxyl groups accompanying the partial dissociation of the complex with increasing temperature.

#### Mechanochemical Creep

The mechanochemical elongation-contraction of a full-IPN film under a constant load upon changing pH is a retardation process. We define the mechanochemical compliance  $J$  as,

$$J = (\Delta l / l_0) / \sigma \quad (2)$$

where  $\Delta l$  is the change in the film length with a pH jump, and  $\sigma$ , the applied load per unit cross-sectional area of the film before the pH jump. Figure 10 shows the  $J$  vs. time  $t$  curves at 25, 40, and 55°C induced on changing the pH from 4 to 7 for the full-IPN film under four different loads: The  $\sigma$  values were 177, 2110, 5570, and 10200 Pa. In all the cases,  $J$  increased with temperature.  $J$  was also dependent on the load  $\sigma$ . That is, the mechanochemi-

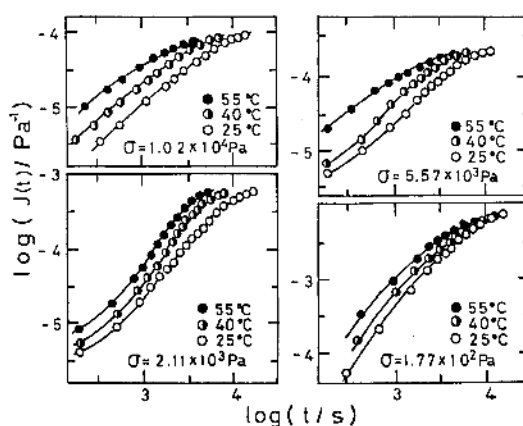


Figure 10. Double logarithmic plots of the mechanochemical creep compliance  $J$  vs. time  $t$  for full-IPN induced upon pH jump from 4 to 7 at 25, 40, and 55°C.

cal creep was non-linear.

Examining the mechanochemical creep curves closely, we noticed the following. When  $\sigma$  is 10200 Pa, the largest among the tests conducted here, the mechanochemical creep appears to be approximately a single retardation-

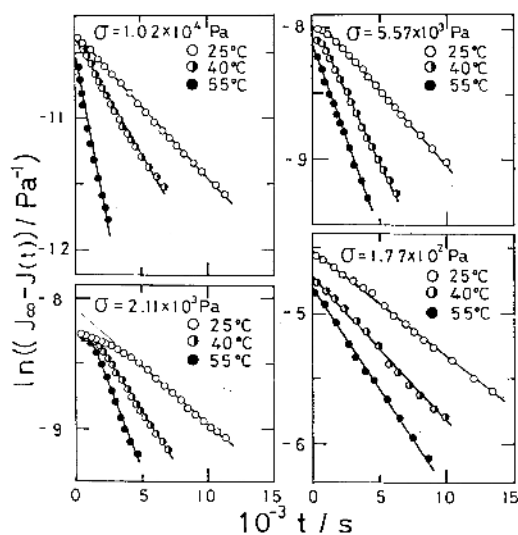


Figure 11. Plots of  $\ln\{J_\infty - J(t)\}$  vs. time  $t$  for full-IPN reproduced from the data shown in Figure 10.

Table I. The retardation time  $\tau^a$  and apparent activation energy  $E_a$  for the mechanochemical process of full-IPN induced upon pH jump from 4 to 7

$\sigma/\text{Pa}$	$T/^\circ\text{C}$	$10^{-3} \tau/\text{s}$
10200	25	9.1
10200	40	5.3
10200	55	2.6
		$(E_a \approx 36 \text{ kJ mol}^{-1})$
5570	25	9.1*
5570	40	5.3*
5570	55	3.7
2210	25	( $\approx 22$ ) 9.1*
2210	40	( $\approx 15$ ) 6.2*
2210	55	( $\approx 11$ ) 3.7*
177	25	12.7
177	40	9.3
177	55	6.5
		$(E_a \approx 17 \text{ kJ mol}^{-1})$

<sup>a</sup> The values with asterisks were determined from the long time end and those in the brackets from the initial slope of the compliance curves shown in Figure 10.

time process. When  $\sigma$  is decreased to 5570 to 2110, the  $J$  curve becomes sigmoidal, implying that the mechanochemical creep process is now a multi-mode retardation process. When the  $\sigma$  is further decreased to 177 Pa, however, the mechanochemical creep process is again a single retardation-time process.

The equilibrium compliance  $J_\infty$  was estimated by extrapolating  $\log J_\infty$  vs. reciprocal time  $t^{-1}$  plot to  $t^{-1} \rightarrow 0$ . Figure 11 shows plots of  $\ln\{[J_\infty - J(t)]/\text{Pa}^{-1}\}$  against  $t$ . The plots are roughly linear for those under the largest and smallest  $\sigma$  used here. On the other hand, the two plots for the film under the intermediate loads are slightly downward concave, implying that a slow creep process appears earlier, but the rapid creep process, later. The tendency is completely opposite to the mechanical creep behavior of ordinary crosslinked polymer networks. From the slope of these plots, we can estimate the corresponding mechanochemical retardation times  $\tau$ . The results are summarized in Table I. We see that  $\tau$  for the creep under the largest  $\sigma$  is approximately the same as that of the later process under intermediate  $\sigma$  rather than that under the smallest  $\sigma$ , when compared at the same temperature.

The activation energy  $E_a$  for the mechanochemical creep process was estimated from the plots of  $\ln \tau$  vs. reciprocal temperature  $T^{-1}$ , although only three data points are available on each curve. The results are also listed in Table I. The  $E_a$  for the mechanochemical creep under the largest load is about  $36 \text{ kJ mol}^{-1}$ , while that under the smallest load is about  $17 \text{ kJ mol}^{-1}$ . For those of the two intermediate loads, the  $E_a$  cannot be determined, because the three-point Arrhenius plots are not linear. These results imply that the mechanochemical creep process is likely to involve at least two processes: One of the processes prevails in the creep under the small load, but the other, under the large load. The former slow process is likely to be caused by certain chemical reactions such as complex dissociation and/or hydration of PAA segments. The hydrogen



bond energy was reported to be of the order of 8 to 21 kJ mol<sup>-1</sup>,<sup>32</sup> and this value corresponds to the  $E_a$  for the creep under the smallest load. On the other hand, the later fast process is presumably due to the viscoelastic retardation of the soft swollen network after the complex has been dissociated.

An interesting feature of the mechanochemical creep of the present POE:PAA full-IPN is that under small  $\sigma$ , the chemical process that has a longer retardation time proceeds before the mechanical process having shorter retardation time. This behavior is entirely opposite to mechanical creep behavior of ordinary polymer networks. Presumably, the dissociation of POE:PAA complex proceeds at pH jump from the low to high value rather rapidly assisted through the mechanical creep of the IPN under large stress, but rather slowly under small load without the influence of the mechanical creep. The additional physical crosslinks due to the complex formation are effective during the creep after the pH jump only under a load small enough that hydrogen bonds in the POE:PAA complex are not disrupted.

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## REFERENCES AND NOTES

- To distinguish topologically different multicomponent polymer systems (polymer alloys) composed of the same poly(A) and poly(B) pair, we employ the following convention: Block and graft copolymers as poly(A)-poly(B) or A-B; polymer blends as poly(A)/poly(B) or A/B in which chemical bonds are not intentionally introduced between the two components; and polymer complex as poly(A):poly(B) in which secondary interaction such as hydrogen bonds prevail.
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