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Characterization of Segmented Block Copolyurethane Network Based on Glycidyl Azide Polymer and Polycaprolactone

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Abstract: To improve the poor mechanical and low-temperature properties of glycidyl azide polymer (GAP)-based propellants, the addition of binders was investigated using GAP and flexible polymer backbone-structural polycaprolactone (PCP) at various weight(wt) ratios, and varying the ratio of Desmodur N-100 pluriisocyanate (N-100) to isophorone diisocyanate (IPDI). Using Gee's theory, the solubility parameter of the PCP network was determined, in order to elucidate the physical and chemical interaction between GAP and PCP. The structure of the binder networks was characterized by measuring the cross-link densities and molecular weights between cross-links (M_c) obtained by a swelling experiment using Flory-Rhener theory. The thermal and mechanical properties of the segmented block copolyurethane (GAP-*b*-PCP) binders prepared by the incorporation of PCP into the binder recipes were investigated, along with the effect of the different curatives ratios.

Keywords: glycidyl azide polymer (GAP), polycaprolactone(PCP), network structure, thermal properties, mechanical properties.

Introduction

The composition of state-of-the-art solid rocket propellants includes low-vulnerability binders, including prepolymers/plasticizers and oxidizers, which contain energetic groups such as -N_3 (azide), nitro (C-nitro, O-nitro (nitrate ester) and N-nitro (nitramine)) and difluroamine groups. As a result, the internal energy of the formulation is improved, in addition to the overall oxygen balance.[1]

The polymeric binders used in propellants are typically cross-linked polyurethane elastomeric networks providing a matrix to bind the solids such as oxidizers and metal fuels with a plasticizer and other minor additives. Among energetic polymers, azide-polymers have been of great interest for the preparation of solid propellants. Glycidyl azide polymer (GAP) is a unique polymer of high density with positive heat of formation of +117.2 kcal/mol. Therefore, it stands unchallenged among azide polymers prepared during the last decades, due to its positive effect on the specific impulse and burning rate of solid composite propellants through the exothermic C-N_3 group scission reaction.[2,3] Generally, GAP is obtained by cationic ring-opening polymerization of epichlorohydrin followed by azidation of chlorine in side chains. The another application of GAP is as a solid fuel for air-breathing propulsion systems because its monopropellants possesses superior combustion properties.[4]

Recently, as well as the performance and vulnerability of propellants in manufacturing propellants, whether or not to use ammonium perchlorate (AP) oxidizer should be considered due to increasing concern over environmental factors. Though it has been used widely in production of solid propellants, AP releases chlorine products during combustion. Thanks to its unique thermal properties, GAP is capable of offsetting the reduced performance caused by the use of ammonium nitrate instead of AP in the preparation of eco-friendly chlorine-free and smokeless propellants.[5,6]

However, it has been recognized that GAP-based propellants do not exhibit excellent mechanical properties. Especially, they suffer from poor low-temperature properties such as the critical temperature (T_c), below where the binder starts to rapidly lose its elastomeric properties. This results from the poor polymer backbone flexibility of GAP having the rigid and conjugated azide side groups. It is noted that GAP-based propellants also don't exhibit the higher plasticization of GAP with nitrate ester (NE) plasticizers such as butanetriol trinitrate (BTTN) and trimethylolethane trinitrate (TMETN). It can seldom be plasticized above a plasticizer : polymer ratio of 1 : 1.[7] It has been reported that the poor mechanical properties of GAP-based propellant can be enhanced through the incorporation of oligomer-type GAP - especially chain-end azide-terminated GAP - as an ener-

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*Corresponding Author. E-mail: cmskmj@add.re.kr getic plasticizer.[1,8] Moreover, the use of a prepolymer with a higher molecular weight in the solid propellant is capable of improving the mechanical properties.[1,6] Unfortunately, the optimal molecular weight represents a trade-off between the rheological and mechanical properties. Also, the improvement in the mechanical properties of GAP possible with a particular plasticizer is limited by the stress and strain characteristics of a polymer being primarily determined by the chain flexibility.

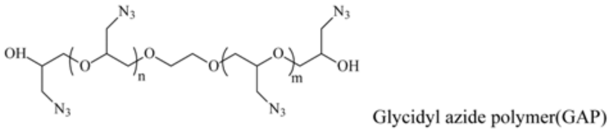
Generally, the polymeric binder characteristics can greatly influence the structural integrity of the propellant. So, the binder should be altered adequately to tailor the mechanical properties of the grains to the specific application, such as space transfers, launch vehicle/ballistic missiles, and tactical air-to-air missiles. The binder characteristics have previously been altered by modifying the polymer backbone using copolymers such as PBAA (poly(butadiene-*co*-acrylic acid)), PBAN (butadiene, acrylic acid, and acrylonitrile terpolymer), and HTPE (hydroxyl terminated polyether, poly(ethylene oxide (EO)-*co*-tetrahydrofurane (THF))), and copolymers of two different polymers.[9-11] GAP prepolymer has also been modified through the cationic copolymerization using HTPB (hydroxyl terminated polybutadiene) as a initiator or a monomer giving flexibility to the polymer backbone, like THF, EO, or other vinyl monomers in order to improve mechanical properties.[12-16]

Our works have focused on enhancing the mechanical properties by preparing unfilled segmented block copolyurethanes based on GAP and a polyether or polyester having a flexible backbone, such as poly(ethylene glycol) (PEG) and polycaprolactone (PCP). The effects of blending GAP and PEG at various ratios of N-100 and IPDI were investigated in our latest work.[17] PCP has been used widely in solid propellants as well as pharmaceutical applications because it is hydrolysable and/or degradable and exhibits higher strain capability.[18-20]

In this study, PCP was incorporated into GAP-based binders to form segmented block copolyurethane networks. Since the composition of the polymer backbone can be modified by varying the weight ratio of the two polymers, the specific mechanical properties required in a particular application should be achievable simply by altering the ratio. The thermodynamic solution properties of segmented block copolyurethane networks were determined by swelling experiments. The effects of GAP/PCP blend ratios and N-100/IPDI ratios on thermal properties and mechanical properties of the copolyurethane networks were also described.

Experimental

Materials. The polymers used in this study were hydroxyl-bi- and trifunctionalized GAPs with molecular weights and hydroxyl indexes of 2,400 g/mol, 0.74 eq/kg, and 5,500 g/mol, 0.49 eq/kg, respectively, which were purchased from 3M under the trade names GAP diol (L9961) and GAP polyol (5527).

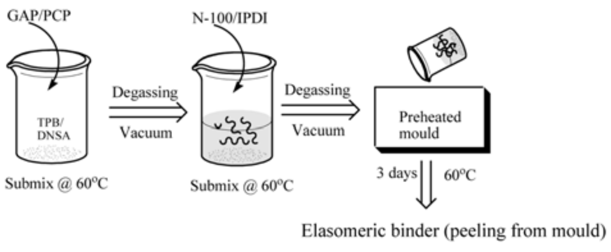


Glycidyl azide polymer(GAP)

Hydroxyl-bifunctionalized and trifunctionalized PCP with a molecular weight/hydroxyl index of 3,000 g·mol^{-1}/0.64 eq·kg^{-1} and 900 g·mol^{-1}/3.40 eq·kg^{-1}, respectively, were purchased from Union Carbide Co. under the trade name TONE 0260 diol and Tone 0310 Polyol(triol). IPDI and Desmodur N-100 with a molecular weight/isocyanate index of 222 g·mol^{-1}/8.86 eq·kg^{-1} and 478 g·mol^{-1}/5.06 eq·kg^{-1}, respectively, were purchased from Mobay and Thorson Chemical and used individually or together as a curative for preparing polyurethane binders. Triphenyl bismuth (TPB, 0.07 wt%) obtained from Samchun Pure Chemical was used as a curing catalyst. Dinitro salicyclic acid (DNSA, 0.03 wt%) purchased from Aldrich Co. was used to activate TPB catalyst. All of the solvents used for determining the solubility parameters of PCP were used as received.

Preparation of Copolyurethane Networks. All of the reagents were dried overnight in a vacuum oven at 60 °C before use. The polyurethanes were prepared at 60 °C so as to prevent the PCP from solidifying as shown in Scheme I. The copolyurethane networks based on GAP and PCP were prepared by mixing the two polymers in four GAP : PCP wt. ratios: 1 : 0, 9 : 1, 7 : 3, and 5 : 5, and with TPB/DNSA under an NCO/OH equivalent ratio of 1.1, followed by degassing in a vacuum oven at 60 °C. Then, the required amount of IPDI and N-100 was added and the mixture was finally degassed in a vacuum oven before being poured into a Teflon-coated mold, which was followed by curing at 60 °C for 3 days. The swelling, thermal and mechanical properties of these copolyurethane networks were then characterized.

Measurement of Swelling Characteristics. In order to determine the solubility parameter of PCP network itself, the swelling tests were carried out in many organic solvents with solubility parameters in the range 14.0-30.0 MPa$^{1/2}$. The swelling characteristics of all copolyurethanes, such as the cross-link densities and molecular weights (M_c) of the



Scheme I. The process of preparation of copolyurethane binder.

polymer chains between cross-links, were determined in dimethyl acetamide (DMAc, δ_{DMAc} = 22.1 MPa$^{1/2}$) at room temperature. Specimens (0.5-1.5 g) were immersed in solvents until swelling equilibrium was reached, and specimens in the swollen state were blotted and weighed to obtain the swelling ratio (Q):

$$Q = 1 + (w_2/w_1 - 1)\,\rho_2/\rho_1 \tag{1}$$

where w_1 and w_2 are the weights of the deswollen and swollen specimens, and ρ_1 and ρ_2 are the densities of the solvent and the individual polymer.

Measurement of Mechanical and Thermal Characteristics. Thermal analyses were performed using differential scanning calorimetry (DSC; Model 4200, TA instrument, USA) at a scanning rate of 10 °C/min to obtain the glass transition temperature (T_g) and monitor the presence of PCP crystalline domain within network. The mechanical properties of die-cut dumbbell-shaped specimens (measuring 33 × 4.0 × 3.5 mm) were determined using a universal testing machine (Model 5567, Instron, USA) at a crosshead rate of 50 mm/min at room temperature.

Results and Discussion

Swelling Characterization. The solubility parameter is the fundamental thermodynamic property of polymers and is often referred to discuss the miscibility of two materials, one or both of which may be polymers. In case of this work, the solubility parameters of copolymer networks prepared with different GAP : PCP wt. ratios should be determined in order to determine the cross-link density and molecular weight between cross-link points.[21] Thus, the physical and chemical interactions between copolymers and NEs in preparation of propellants can be demonstrated. In our last work, the solubility parameter of GAP network was determined as δ_{GAP} = 22.506 MPa$^{1/2}$, via swelling experiments using Gee's theory, represented by following eq. (2).[22]

$$Q/Q_{max} = \exp[-\,aQ(\delta_{solvent} - \delta_{polymer})^2] \tag{2}$$

where Q_{max} is the maximum swelling ratio and a is a constant. This equation can be rewritten as

$$[Q^{-1}\ln(Q_{max}/Q)]^{1/2} = |a^{1/2}(\delta_{solvent} - \delta_{polymer})| \tag{3}$$

By plotting $[Q^{-1}\ln(Q_{max}/Q)]^{1/2}$ against $\delta_{solvent}$ for a series of solvents, $a^{1/2}$ and $\delta_{polymer}$ can be determined from the slope and the intersection with the horizontal axis, respectively, where for various solvents the swelling data can be correlated with a linear relation supporting eq. (2), but there is no such correlation for solvents having strong and moderate H-bonding groups such as methanol, ethanol, dioxane and acetone.[23]

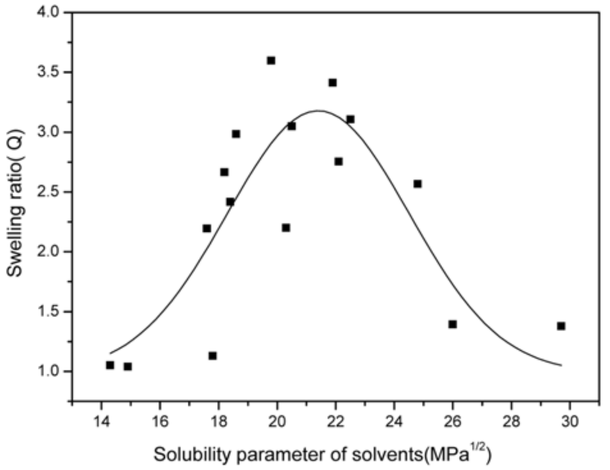


Figure 1. The relationship between the swelling ratio of the PCP-based binder network and the solubility parameter of the various solvents.

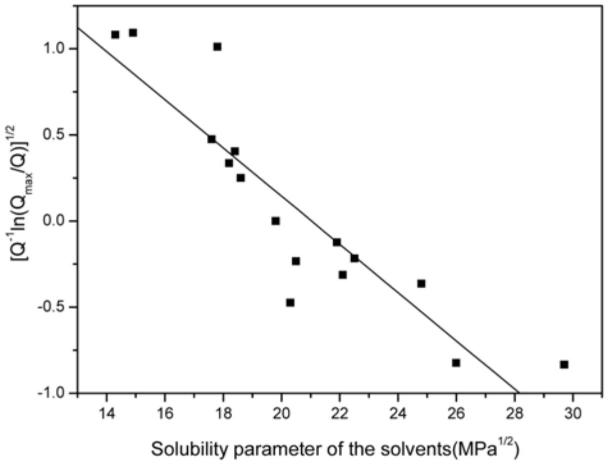


Figure 2. The plot of $[Q^{-1}\ln(Q_{max}/Q)]^{1/2}$ versus the solubility parameter of the various solvents.

Figure 1 shows the relationship between swelling ratios of PCP-based networks and the solubility parameters of various solvents. The PCP networks exhibited the maximum swelling ratio (Q_{max} = 3.60) in methylene chloride (δ = 19.8 MPa$^{1/2}$) among the solvents used. From the linear plot given in Figure 2, the solubility parameter of PCP network has been determined as δ_{PCP} = 21.03 MPa$^{1/2}$, which is almost similar to the theoretical value $\delta_{\rm PCP}$ = 21.85 MPa$^{1/2}$ calculated by group contribution method using the values of Fedors. It can therefore be confirmed that the compatibility of GAP with PCP is a little superior to with PEG (δ_{PEG} = 19.99 MPa$^{1/2}$).

Using the solubility parameters of GAP network and PCP network, the solubility parameters of copolymers prepared with different GAP:PCP wt. ratios could be obtained using the following equation.

$$\delta_{mix} = \frac{V_1\delta_1 + V_2\delta_2}{V_1 + V_2} \tag{4}$$

Where V, δ are volume fraction and solubility parameter of GAP and PCP networks, respectively and V values are determined from the density values (GAP, 1.29 g/cm^3, PCP, 1.02 g/cm^3) of polymers.

Using these solubility parameters of copolymer networks, the cross-link density (ν_e), defined as the number of moles in the effective network chain per cubic centimeter, and the average molecular weight of the polymer chains between cross-linked points (M_c) - which are the most important parameters for characterizing three-dimensional networks - were determined using the following Flory-Rehner equation, which is valid as long as the swelling is isotropic, there are tetrafunctional cross-links at zero volume, and polymer chains are cross-linked in the solid state:[24]

$$\frac{\upsilon}{M_c} = -\frac{[\ln(1-\upsilon_{2,s}) + \upsilon_{2,s} + \chi\upsilon_{2,s}^2]}{V_1\left(\upsilon_{2,s}^{1/3} - \frac{\upsilon_{2,s}}{2}\right)} = \nu_e \qquad (5)$$

where υ is the density of polymer, V_1 is the molar volume of solvent, $\upsilon_{2,s}$ is the polymer fraction in the swollen gel at equilibrium (the reciprocal of volume-swelling ratio, Q), ν_e is the cross-link density, and χ is the polymer-solvent interaction parameter that may be obtained from the solubility parameter using the following equation:

$$\chi = \chi_S + \chi_H \approx 0.34 + \frac{V_1}{RT}(\delta_{polymer} - \delta_{solvent})^2 \qquad (6)$$

where χ_S and χ_H are the entropic and enthalpic contributions, respectively, R is the gas constant, and T is the absolute temperature.

Figures 3 and 4 show the effects of the ratios of different curatives and polymer blends on M_c values of copolyurethane networks. An increase of IPDI content in N-100/IPDI curative systems increased the M_c values linearly, resulting in looser networks. And M_c values increased with increasing GAP content in the GAP/PEG blend. This tendency was also observed in our earlier research on GAP-*b*-PEG binders, but the incorporation of PEG in binder recipes didn't have a marked influence on M_c values of networks as much as PCP did. In GAP/PEG networks, the M_c values between networks with GAP : PEG weight ratios of 7 : 3 and 5 : 5 were almost the same.

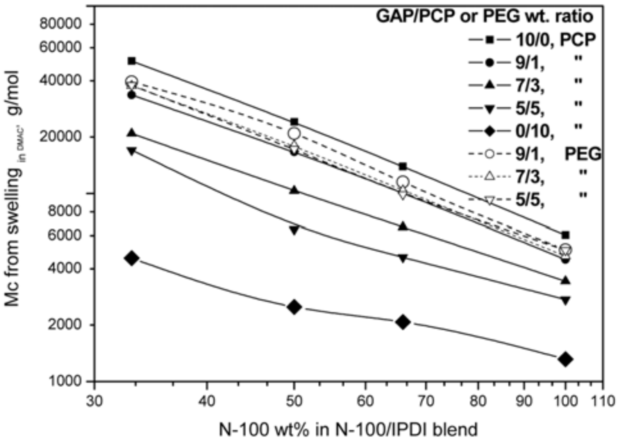


Figure 3. The effect of the concentration of N-100 in a mixture of N-100 and IPDI on M_c in copolyurethane (GAP-*b*-PCP or -PEG) networks.

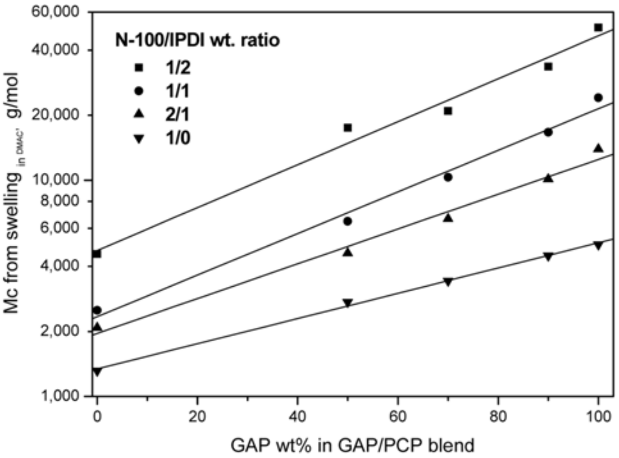


Figure 4. The effect of the concentration of PCP in GAP/PCP blend on M_c in copolyurethane (GAP-*b*-PCP) networks.

Generally, the polymer triol along with polymer diol has often been used to improve the mechanical properties of NEPE (Nitrate ester polyether) propellants. The oligomer-type PCP with 900 g/mol (PCP 0310) as a typical triol is widely used together with a PCP diol with 3,000 g/mol. A GAP triol (Mw. 4,500 g/mol, GAP polyol) is also being applied to GAP diol-based binders. The effects on network structure (M_c) of PCP triol and GAP triol incorporated into GAP diol- and PCP diol-based binders, respectively, are illustrated in Figure 5. In a GAP diol-*b*-PCP triol binder, M_c decreased non-linearly with increasing PCP triol content. In

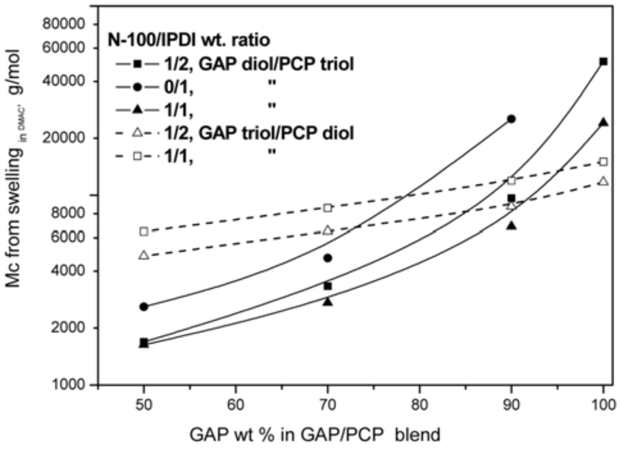


Figure 5. The effect of the concentration of polymer triols on M_c in copolyurethane (GAP-*b*-PCP) networks.

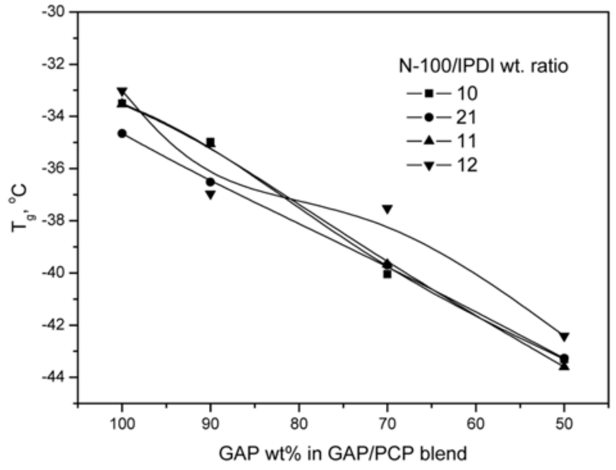


Figure 6. The effect of the concentration of PCP diol on T_g in copolyurethane networks.

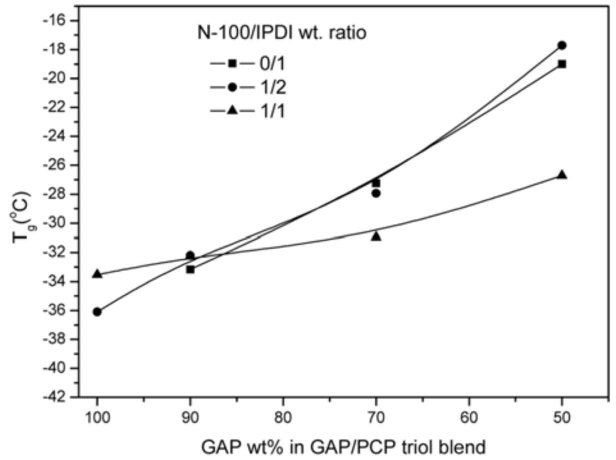


Figure 7. The effect of the concentration of PCP triol on T_g in copolyurethane networks.

the case of GAP triol-*b*-PCP diol binder, it was interesting to note that M_c increased linearly with increasing content of GAP triol. It would seem that the GAP triol functioned only as a chain extender rather than a cross-linker, unlike PCP triol, due to its higher molecular weight and its high free volume. This resulted from the presence of its bulky side groups (-CH_2N_3) in polymer backbone.

Thermal Characterization. As shown in Figure 6, the T_g of copolyurethanes decreased with increasing content of PCP diol whose T_g (-65 °C) is much lower than that of GAP (-45 °C). The block copolyurethane networks prepared under three curative systems (N-100 alone, and 2/1 and 1/1 ratios of N-100 and IPDI) caused a linear-like change in the T_g with PCP content. However, for the networks prepared

Table I. The Values of Cross-link Density and Molecular Weight between Cross-link Points in the Segmented Block Copolyurethane (GAP-*b*-PCP) Network Binders Prepared by Varying the Wt. Ratio of N-100 and IPDI Curatives

No.	GAP/PCP, N-100/IPDI (wt. ratio)	ν_e (mol/cm^3 × 10^4)	M_c^1 (g/mol)	M_c^2 (g/mol)
1	1/0, 1/0	2.56	5,047	4,642
2	9/1, 1/0	3.03	4,479	4,657
3	7/3, 1/0	3.86	3,428	3,346
4	5/5, 1/0	4.66	2,738	2,789
5	1/0, 2/1	0.91	13,955	12,958
6	9/1, 2/1	1.31	10,132	9,749
7	7/3, 2/1	1.96	6,642	6,905
8	5/5, 2/1	2.73	4,605	3,167
9	1/0, 1/1	0.54	24,074	25,421
10	9/1, 1/1	0.79	16,698	17,568
11	7/3, 1/1	1.25	10,341	9,240
12	5/5, 1/1	1.93	6,466	2,507
13	1/0, 1/2	0.25	50,934	57,887
14	9/1, 1/2	0.38	33,539	40,051
15	7/3, 1/2	0.58	20,923	6,017
16	5/5, 1/2	0.69	17,051	2,416
17	1(GAP triol)/0, 1/1	1.02	11,744	13,518
18	9(GAP triol)/1, 1/1	1.45	8,720	8,952
19	7(GAP triol)/3, 1/1	1.94	6,491	6,838
20	5(GAP triol)/5, 1/1	2.59	4,809	4,796
21	9/1(PCP 0310), 1/1	1.96	6,846	6,291
22	7/3(PCP 0310), 1/1	4.9	2,722	2,765
23	5/5(PCP 0310), 1/1	7.97	1,630	1,810
24	9/1(PCP 0310), 1/2	1.38	9,659	9,286
25	7/3(PCP 0310), 1/2	3.98	3,330	3,306
26	5/5(PCP 0310), 1/2	7.67	1,693	2,246
27	9/1(PCP 0310), 0/1	0.52	25,264	28,102
28	7/3(PCP 0310), 0/1	2.8	4,687	4,700
29	5/5(PCP 0310), 0/1	4.94	2,590	2,777

M_c^1 : from swelling in DMAC. M_c^2 : from mechanical measurement.

with 1/2 the ratio of N-100/IPDI in the mixed curative systems, a nonlinear change was observed. The nonlinear change appears to be acceptable because the networks prepared under 1/2 the weight ratio of N-100/IPDI were not formed uniformly. This is attributable to the greater difference in reactivities both between polymers and especially between curatives as explained henceforth.

Actually, the T_g of polymers is dependent on molecular motion. Like these cross-linked polymers, the greater the value of M_c, that is, the longer the effective chain length, the better the capability of molecular motion in networks, in the long run, to lower the T_g of the cross-linked polymer. But the incorporation of PCP diol decreased the T_g of networks even though the M_c decreased. The introduction of the PCP triol in copolyurethane networks also increased the cross-link density and decreased M_c, but unlike the PCP diol, the T_g values of the networks increased linearly with increasing PCP triol, as shown in Figure 7. As mentioned above, the PCP triol was applied as a cross-linker rapidly increasing the cross-link densities of GAP diol/PCP triol-based networks with its content as shown in Table I. On the other hand, the PCP diol was only incorporated as a polymer, gradually increasing the cross-link densities of GAP diol/PCP diol-based networks with its content.

As observed in GAP-PEG copolyurethane networks, the reactivity of PCP is higher than that of GAP (primary vs. secondary OH).[17] Therefore, it could be assumed that, when both GAP and PCP is used together, first PCP will form polyurethane (PU) and then GAP will form PU together some PCP which didn't participate in forming PCP-PU. The resulting network polymers will consist of the PCP-PU domain and GAP-*b*-PCP PU domain, that is, the network binders will be composed of the two phases. It would expect that the network binders possess two T_g. However, as shown in Figure 8, the segmented block copolyurethane binders (GAP-*b*-PCP) exhibited only one T_g, though the melting peaks of PCP-PU were found to be at around 50 °C. In view of the T_g of PCP homopolyurethane exhibited at around -50 °C as shown in Figure 8, it is inferred that the T_g curves of copolyurethane (GAP-*b*-PCP) and PCP-PU coexist.

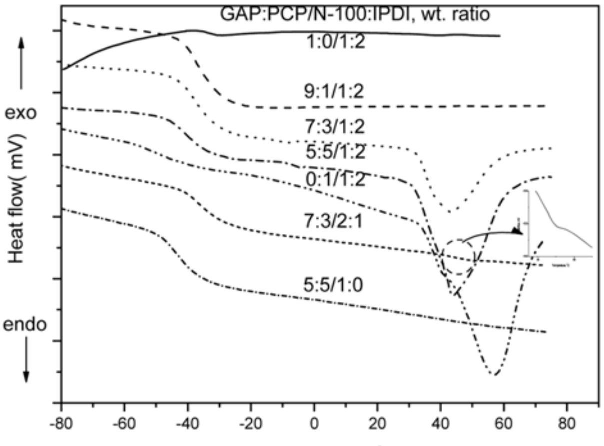


Figure 8. The DSC thermograms of the segmented block copolyurethane networks.

The copolyurethane (GAP/PCP wt. ratio, 9/1) didn't exhibit the melting peak and only one T_g was observed. This indicates that GAP and PCP segments are well-dispersed and blended within the network and thus, the copolyurethane consists of one-phase. Based on chemical kinetics directly proportional to the concentration of reactants, the absence of a PCP-PU domain resulted from higher concentrations of GAP in the polymer blend. In 30 wt% of PCP-containing copolyurethane prepared under a N-100 : IPDI weight ratio of 2 : 1, the endothermic peak of the PCP-PU domain was exhibited. But it was a very small compared to that of a copolyurethane prepared under a N-100 : IPDI weight ratio of 1 : 2. Though PCP-PU was formed within the network, its formation was suppressed very significantly by the higher concentration of PCP and N-100 in the polymers and curatives, respectively. Besides, it was noticeable that the melting peak of PCP-PU was not observed in even 50 wt% of PCP-containing copolyurethane prepared under the curative system that used only N-100, unlike GAP/PEG networks. The absence of PCP-PU could be also confirmed from the appearance of the network binder (yellow transparent). Generally, the crystallinity of PCP is lower than that of PEG, and the reactivity of PCP is also lower than that of PEG due to the presence of a carbonyl group in the PCP backbone. Moreover, the reactivity of the curative system that used only N-100 is much higher than that of curative systems using a mixture of N-100 and IPDI. And, because TPB/DNSA curative catalysts accelerate the reaction rate of polymers and curatives substantially, GAP and PCP segments would take part in polyurethane network formation competitively. As a result, the segmented block copolyurethane based on GAP and PCP was formed uniformly without PCP-PU.

Mechanical Characterization. The improvement of the mechanical properties of GAP-based binders was already observed by blending GAP with linear, flexible polymers like PEG under a mixture of N-100 and IPDI.[17] As shown in Figure 9, the incorporation of PCP into GAP-based binders improved elongation as well. Especially in network binders prepared under a mixture of N-100 and IPDI curatives, the effect of PCP on elongation was greater with the increase of IPDI content in N-100/IPDI curatives. But, the effect of PCP on elongation was not observed in GAP-*b*-PCP binders prepared under curative systems using only N-100 as revealed in GAP-*b*-PEG binders. Therefore, it was proved that the introduction of PCP into binder recipes had a positive effect on elongation under N-100/IPDI curative systems.

In GAP-based-only networks, the increase of N-100 content in N-100/IPDI curative systems strengthened the stress

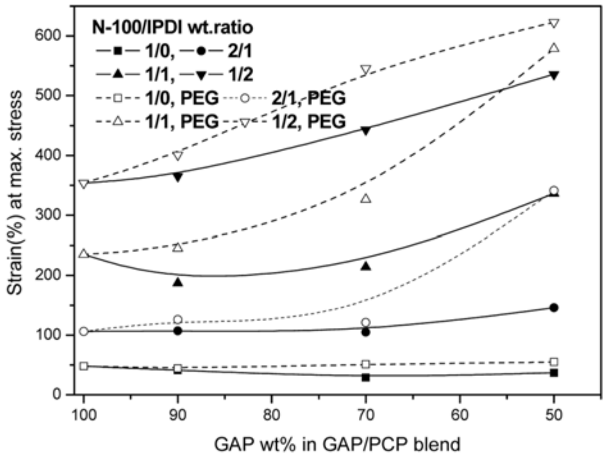


Figure 9. The effects of the concentration of PCP and PEG on elongation in copolyurethane (GAP-*b*-PCP or-PEG) networks.

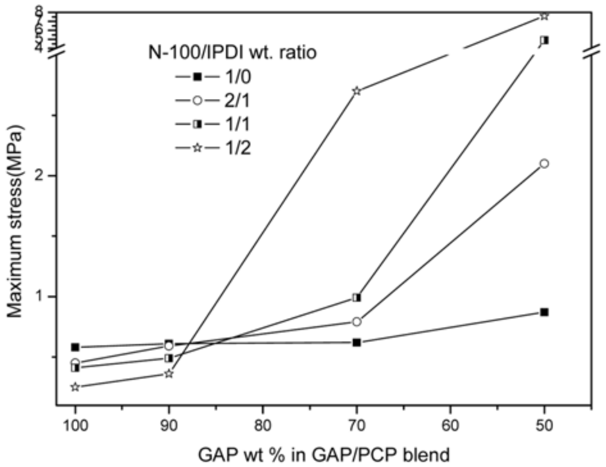


Figure 10. The effect of the concentration of PCP on the mechanical strength in copolyurethane (GAP-*b*-PCP) networks.

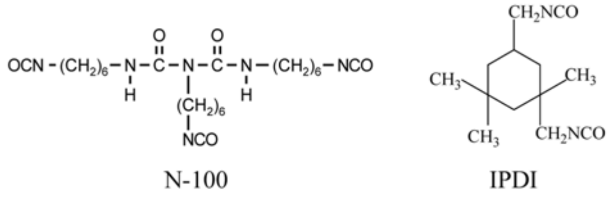


Figure 11. The structures of N-100 and IPDI curatives.

(maximum stress at maximum load) of network binders as shown in Figure 10. This is attributable to higher functionality and reactivity of aliphatic N-100 compared to cyclic IPDI as shown in Figure 11. As stated in the section on swelling, the incorporation of PCP into binder recipes increased the cross-link densities of the resulting block copolyurethane networks. As a result, the molecular interactions within binder networks were reinforced more with the increase of the PCP content. Therefore, the stress of binder networks increased with increasing PCP content. However, sudden increases of stress resulting in high initial modulus occurred at over 30 wt% of PCP-containing copolyurethanes prepared under N-100/IPDI curative systems. Therefore, the order of strength of binders was reversed. This is attributable to the crystallization of PCP within binders containing above 30 wt% of PCP. The sudden increase of maximum stress caused by the crystallization of PCP segments happened distinctly with the increase of IPDI in N-100/IPDI curative systems. This results from the difference in reactivities both between polymers and between curatives. With the increase of lower reactive IPDI in curative systems, some of PCP (1 °-OH) segments react with the higher reactive N-100 curative, that is, the crystallization of PCP segments is occurred before GAP-*b*-PCP phase is formed.

According to Plazek *et al.*, lower ν_e values (i.e., higher M_c) are favorable in solid propellants because they indicate the presence of more lightly cross-linked networks, which scatters input mechanical energy more readily and exhibit greater resistance to fracture and rupture.[25] Therefore, to meet the requirements of mechanical properties and hazard of solid propellants for specific applications, the amount of PCP should be modulated appropriately.

It has been known that the tensile stress-strain properties of networks are strongly dependent on the length of the elastically effective networks chains, that is, the molecular weight of chain between cross-links. Figure 12 shows the relationship between M_c and elongation in copolyurethane networks. The elongation of networks prepared at a constant ratio of GAP and PCP was improved with the increase of M_c which was tuned by varying the ratio of N-100 and IPDI. Especially, it was worth noting that while the GAP/PCP binders with blend ratios of 9 : 1 and 7 : 3 brought about a linear change in elongation with M_c values, for other

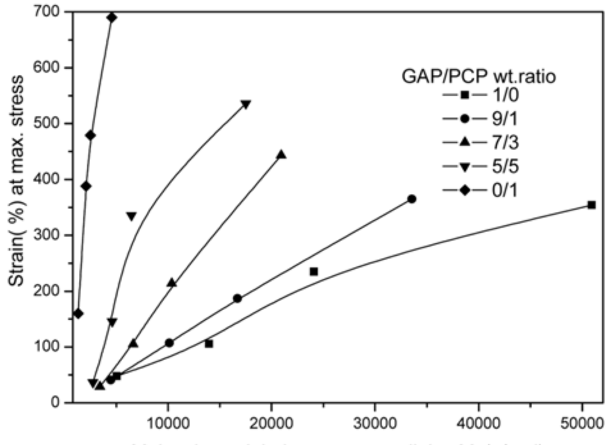


Figure 12. The relationship between elongation and M_c in copolyurethane networks.

binders, nonlinear changes were observed. Figure 12 also indicates that the improvement of elongation by PCP was much better than by increase of IPDI content in N-100/IPDI curatives, though the M_c values were diminished by the incorporation of PCP.

The M_c value can be obtained by the statistical mechanical theory of rubber elasticity: At equilibrium this theory describes the coiled/mixed (convoluted) networks chains between cross-link points as having a most probable end-to-end chain configuration. Deformation changes this distribution and the entropy of the chains, resulting in varying the free energy. This theory has been being used to obtain the correlation between the strength of networks and the cross-link density: The elasticity behavior of the dry test specimen is inferred by the following equation.[24,26]

$$\sigma = \nu_e RT(\lambda - \lambda^{-2}) = (\rho RT/M_c)(\lambda - \lambda^{-2}) \qquad (7)$$

where σ is the ultimate strength, $\lambda(1 + \varepsilon, \varepsilon$: strain) is the extension ratio (L/L_o, L and L_o are the length of stressed and unstressed specimen, respectively).

The M_c values of copolyurethane networks were calculated through the tensile stress-strain measurements using eq. (7). The results were listed in Table I, along with the M_c values and the cross-link densities derived from the swelling experiments. Interestingly, the M_c values obtained from the swelling and mechanical measurements were almost consistent, except for a few network binders which represented a sudden increase of stress on networks which resulted from the crystallization of PCP within the binders. This consistency seems to be desirable because even the network defects (loop, dangling chain ends, and trapped entanglements) as well as the elastically effective chains do a role in the stress-strain behavior of copolyurethane network binders.

Conclusions

The segmented block copolyurethane networks were prepared using GAP and PCP with various blend ratios of two polymers, varying the ratio of N-100 and IPDI curatives. To elucidate the physical and chemical interaction between polymers, the solubility parameter of PCP network was estimated as δ_{PCP} = 21.03 MPa$^{1/2}$ using Gee's theory, which is very close to that of GAP (22.67 MPa$^{1/2}$). Through the swelling characterization using Flory-Rhener equation, it has been proved that larger quantities of GAP and IPDI in polymer blend and N-100/IPDI curative systems, respectively, leaded to form the looser network binders.

The T_g values of segmented block copolyurethane binders decreased with increasing PCP content in spite of the decrease in the M_c of the binders by PCP. The segmented block copolyurethanes exhibited only one T_g, however, the PCP-PU domain existed within the network, which could be confirmed through the presence of a melting peak in DSC analysis. After all, the resulting networks consisted of two phases (PCP-PU and GAP-*b*-PCP PU). This was because the difference in the reactivities of GAP and PEG toward curatives was large as was those of N-100 and IPDI toward polymers. However, it was noted that a PCP-PU domain didn't form within 50 wt% of PCP-containing copolyurethane prepared under the curative system using only N-100, unlike those prepared under N-100/IPDI curative systems.

Though the incorporation of PCP into binder recipes showed an increase in the cross-link density of binders, the mechanical properties were improved. Also, the cross-link densities decreased with the increase of IPDI content in N-100/IPDI curative systems, resulting in improved elongation. Interestingly, it was observed that the M_c values estimated from mechanical measurements closely matched those from the swelling experiments.

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