Central European Journal of Energetic Materials
ISSN 1733-7178; e-ISSN 2353-1843

Cent. Eur. J. Energ. Mater. 2017, *14*(3): 708-725; DOI: 10.22211/cejem/69575

Research on the Mechanical Properties and Curing Networks of Energetic GAP/TDI Binders

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Abstract: This research focused on correlations between the macroscopic mechanical performance and microstructures of energetic binders. Initially a series of glycidyl azide polymer (GAP)/toluene diisocyanate (TDI) binders, catalyzed by a mixture of dibutyltin dilaurate (DBTDL) and triphenyl bismuth (TPB), was prepared. Uniaxial tensile testing, and low-field nuclear magnetic resonance and infrared spectroscopy were then used to investigate the mechanical properties, curing networks, and hydrogen bonding (H-bonds) of these binders. Additionally, a novel method based on the molecular theory of elasticity and the statistical theory of rubber elasticity was used to analyze the integrity of the networks. The results showed that the curing parameter R strongly influences the mechanical properties and toughness of the binders, and that a tensile stress (σ_m) of 1.6 MPa and an elongation (ε_m) of 1041% was observed with an R value of 1.6. The cross-linking density increased sharply with the curing parameter, but only modestly with an R value $\geq$ 1.8. The proportion of H-bonds formed by the imino groups increased with the R value and reached 72.61% at an R value of 1.6, indicating a positive correlation between the H-bonds and σ_m. Molecular entanglement was demonstrated to increase with R and to contribute dramatically to the mechanical performance. The integrity of these networks, evaluated by a correction factor (A), varies with R, and a network of the GAP/TDI binder with an R value of 1.6 is desirable.

Keywords: glycidyl azide polymer (GAP), curing networks, hydrogen bonding, entanglement, integrity

1 Introduction

The energetic binder glycidyl azide polymer (GAP) has attracted the attention of researchers for its reportedly superior performance, high density (1.3 g·cm^{-3}), high positive enthalpy of formation (1172 kJ·kg^{-1}), low sensitivity, and clean exhaust [1-6]. Consequently, GAP is widely used in insensitive, high-energy, minimum-exhaust signature propellants. Despite its unique energy characteristics, GAP binders exhibit weak mechanical properties because of their shorter molecular chains and rigid conjugated azide side groups ($-N_3$), which greatly limit the mobility of the polymer chains and reduce entanglement, thus affecting the intermolecular forces between adjacent chains. Moreover, secondary hydroxyl groups on the chains weaken the reaction activity of GAP, resulting in an incomplete polyurethane reaction (low conversion) with isocyanate [7]. Comparisons of GAP with other binders, such as hydroxyl-terminated polybutadiene (HTPB), copolymers of ethylene oxide and tetrahydrofuran (PET), and polyethylene glycol (PEG) used in solid propellants [8-11], have shown that GAP binders and GAP-based propellants exhibit poor mechanical properties and create problems [12-14]. Except in the cases of molecular structures or conformations, a key factor that has a significant influence on the poor mechanical performance of GAP prepolymers is the use of curing agents. Because the generally used GAP prepolymer has a lower degree of branching, diisocyanates lead to fewer cross-linking sites and therefore cause difficult molding processes and lower fracture strength after curing. Elastomers cured by the polyfunctional isocyanate (N100) exhibit brittleness because of excessive cross-linking [12]. Binders cured by the complex agent N100/di-isocyanate still proved to have weak tensile strength. Although the complex curing agent trimethylolpropane (TMP)/toluene diisocyanate (TDI) can dramatically improve the strength and elongation of GAP binders [15], its application to propellants is rarely reported. Therefore, improving the mechanical performance of GAP, as well as GAP-based propellants, without energy loss (modified by non-energetic chemical groups or binders) would be a significant improvement. Before addressing this intractable matter for GAP binders, fundamental research should explore the curing networks of GAP binders and the correlation between the micro-structure and the macro-performance.

Once the relevant GAP problems were recognized, much of the work discussed in the next section was based on fundamental research. Initially, GAP prepolymers, with an average functionality of 2.04, were cured using TDI with catalysis by dibutyltin dilaurate (DBTDL)/triphenyl bismuth (TPB), to form GAP/TDI polyurethane binders. Then, uniaxial tensile experiments were used to investigate the macroscopic mechanical behaviour of these binders. Additionally, low-field nuclear magnetic resonance (NMR) spectroscopy and Fourier transfer infrared spectroscopy were used to explore the cured networks and hydrogen bonding, respectively. Finally, a novel approach based on the molecular theory of elasticity and the statistical theory of rubber elasticity was proposed to evaluate the integrity of the networks of these energetic binders. Our research, as well as the relevant methodology, provides guidance for improving or applying GAP binders. Moreover, this work developed the methodology required for correlating macroscopic properties and microstructures.

2 Experimental

2.1 Materials

GAP prepolymer with an average molecular weight of 3600 g·mol^{-1}, hydroxyl group content of 0.55 mmol·g^{-1} and an average functionality of 2.04, was purchased from Liming Research Institute of Chemical Industry, Henan, China. Toluene diisocyanate with a molecular weight of 174 g·mol^{-1} and functionality of 2, curing catalyst dibutyltin dilaurate (0.5%) and triphenyl bismuth (0.5%) were dissolved separately in dioctyl sebacate (DOS). These agents were purchased from Beijing Chemical Works. GAP was dried in vacuum for 2 days at 80 °C before use.

2.2 Preparation of GAP/TDI binders

Preprocessed GAP and TDI were weighed accurately and thoroughly mixed. After continuous stirring for 10 min, a 3% solution of the mixed curing catalyst DBTDL/TPB (optimal mixing ratio 1:2) was added to the mixture and stirred for a further 10 min. The mixture was cast into a polypropylene mold to form a film of approximately 2-mm thickness. Subsequently, evacuation for 2 h at 40 °C was required to remove entrapped air or moisture, which if present could lead to poor mechanical properties. The GAP binders were then cured at a constant temperature of 60 °C for 7.5 d (cured completely). After the polyurethane reaction was complete, the films were used directly for infrared spectroscopic testing, and parts of these films were sliced into dumbbell-shaped samples for mechanical or curing network tests.

2.3 Measurements

Mechanical test samples were prepared according to ASTM standard D-412-87. All of the tensile mechanical properties were measured using an Instron 26022

Universal testing machine in accordance with GB/T528-1998. Cuboid samples, < 20-mm long, were prepared for the curing network tests using a VTMR20-010V-T low-field NMR spectrometer (provided by the Shanghai Niumai Corporation). Infrared spectroscopic testing was conducted using a Nicolet 8700 Fourier transform infrared spectrometer in the reflection mode.

3 Results and Discussion

3.1 Mechanical properties

The curing parameter R value denotes the equivalent ratio of isocyanate (−NCO) to hydroxyl (−OH) groups, and has a significant influence on the mechanical behaviour of polyurethane films. Theoretically, the hydroxyl and isocyanate groups react completely when the R value is set to 1.0; as a result, superior mechanical performance of the polyurethane films can be obtained. However, the secondary hydroxyl group, which has a low activity on the GAP molecular chains, leads to an incomplete curing reaction and further influences the mechanical properties. Thus, the R value should be adjusted appropriately according to the actual situation.

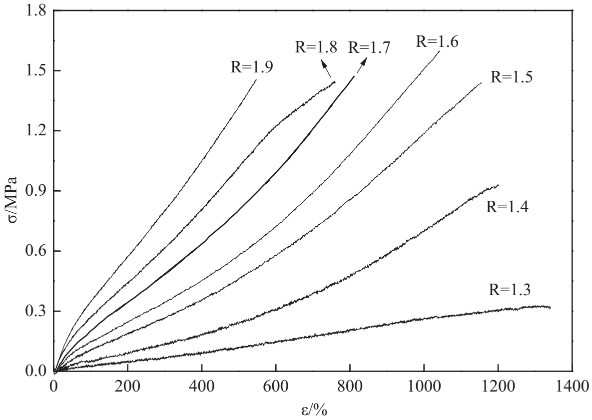


Figure 1. Tensile curves of the GAP/TDI binders

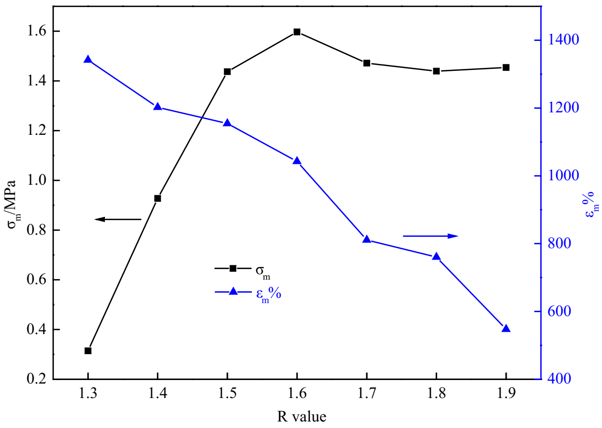


Figure 2. Variations of σ_m and ε_m versus R values

The uniaxial tensile curves of the GAP/TDI binders are shown in Figure 1, and the corresponding relationship of fracture strength (σ_m) and elongation (ε_m), which were captured on the tensile curves, are shown in Figure 2. Several observations may be made from these figures. Firstly, the fracture strength increased and reached its maximum value (1.6 MPa) as R was increased from 1.3 to 1.6 and then decreased with further increase in R. As was reported in [16], the polyurethane reaction cannot proceed completely because of moisture, which can react with the TDI to produce polyurea and carbon dioxide (CO_2). Considering the inevitable influence of moisture, a feasible method for obtaining a higher reaction extent would be to increase the TDI content to compensate. For the GAP binders cured with TDI, the extent of the reaction and the fracture strength increased with R in the range 1.3-1.6. However, the R value should be adjusted within an appropriate range. Otherwise, the excess of TDI molecules cannot enter the curing network, which might lead to an incomplete binder matrix and undesirable mechanical strength. For variations of elongation (Figure 2), ε_m decreased continuously within the whole range of the R values, and this effect stems from the increase in cross-linking level and the synchronously reduced conformational entropy of the chains, which might inhibit the rotation and stretching motions of the chain segments.

The toughness of the GAP/TDI binders was analyzed by integrating the stress σ over the strain ε. The value of $\int \sigma d\varepsilon$ can be used to evaluate the tearing resistance or to reflect the toughness of the binders [17]; the larger the integration value, the tougher the polyurethane binder is, and this value is the combined result of σ and ε. For a specific material in the tensile process:

$$\sigma = \frac{F}{S}\ ,\ \varepsilon = \frac{L}{L_0} \tag{1}$$

$$\int \sigma d\varepsilon = \frac{1}{L_0} \times \int \left(\frac{F}{S}\right) dL \tag{2}$$

$$W = \int F dL \tag{3}$$

where *F* is the tensile force, *S* is the cross-sectional area, *L* is the extension length, L_0 is the original length of the sample, and *W* is the work until fracture. Thus integration of the stress-strain curves can provide a close approximation to the work done by the force *F* until fracture (see Figure 3).

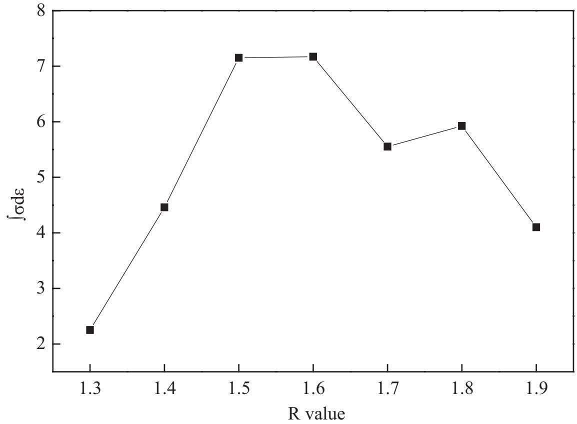


Figure 3. Variations of fracture work versus R values

As shown in Figure 3, the fracture work *W* is at its maximum with an R value of 1.6 and is smaller at the other R values. As mentioned previously, this parameter is affected significantly by either stress or elongation. It is noteworthy that the lack of cross-linking points results in lower strength when the R value is small; similarly, defects in the curing networks with excess TDI lead to lower elongation, and both of these cases result in lower fracture work. Evidently, the conclusion can be drawn that for the GAP/TDI binders, better comprehensive mechanical properties and toughness can be obtained with an R value of 1.6.

3.2 Curing network structures

A low-field NMR system was used to investigate the network structures of the GAP/TDI binders, and the core principle of this technology can be easily understood. Hydrogen atoms on the polymer chains have different transverse relaxation times because of their various chemical environments. Therefore, the transverse relaxation time () is generally used to characterize the chain-segment movement on the basis of the sensitivity of the relaxation mechanism to the chain movement [18, 19]. After repeated attempts for the testing parameters and the fitting method, the XLD model (Equation 4) [20, 21] was used to analyze the cross-linking density of the GAP/TDI binders.

$$M(t) = Aexp\left(-\frac{t}{T_{21}} - \frac{qM_{rl}t^2}{2}\right) + Bexp\left(-\frac{t}{T_{22}}\right) + A_0 \tag{4}$$

where $M(t)$ is the attenuated signal, A and B denote the signal proportions of the cross-linking and suspension chains, respectively, A_0 is the direct-current component and has no physical meaning, T_{21} and T_{22} are the relaxation times of the cross-linking and the suspension chain-related signals, respectively, q represents the anisotropy of the cross-linking chains, and M_{rl} is the dipole moment below the glass-transition temperature. Equation 4 was used to estimate these parameters, and the cross-linking density of the GAP/TDI binders can be calculated by Equation 5.

$$V_e = \frac{5\rho N\sqrt{qM_{rl}}}{3CM} \tag{5}$$

where ρ is the density of the binder, N is the bond number of the repeat units on the backbone chains, C is the bond number in the Kuhn chain unit, and M is the molar mass of the repeat unit. The signal strength of T_{21}, monitored with the increase in relaxation time, can be seen in Figure 4; the cross-linking densities of the binders with various R values are given in Table 1.

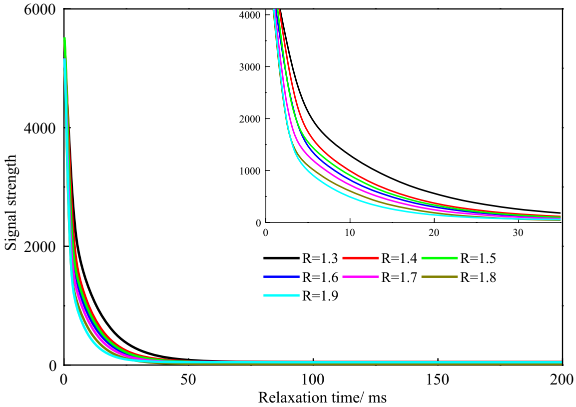


Figure 4. Signal strength monitored with changes in relaxation time

Table 1. Curing network parameters of the GAP/TDI binders

Sample	T_{21} [ms]	ρ [g·cm^{-3}]	$V_e \times 10^{-4}$ [mol·cm^{-3}]	$M_c \times 10^3$
R = 1.3	11.86	1.27	0.68	18.68
R = 1.4	9.57	1.27	0.73	17.40
R = 1.5	8.96	1.27	0.82	15.49
R = 1.6	8.32	1.26	0.93	13.55
R = 1.7	8.35	1.27	1.04	12.26
R = 1.8	8.30	1.26	1.20	10.50
R = 1.9	7.19	1.26	1.24	10.19

Figure 4 clearly shows that rate of decrease of the transverse relaxation times of various samples increased with the R value. The fitted data of T_{21} (presented in Table 1) decreased continuously as the R value increased in the range 1.3-1.9, indicating that more H-bonding accompanied the increases in cross-linking density (V_e), and finally stabilized at approximately 1.2×10^{-4} mol/cm^3. The V_e of the GAP/TDI binder system appeared to be smaller than that of the N100 cured system, which was reported previously. The reason for this is that the doubly functional isocyanate TDI cannot serve as a cross-linking agent and can only link the GAP polyether chains with the generated carbamate (−NHCOO−) segments. Real cross-linking sites are the branch points on the GAP polymer chains. Generally, the continuously increasing V_e is to some extent caused by the increased curing degree, although the R value is greater than 1.0. This behaviour occurs because the conversion ratio of the hydroxyl groups on the chains cannot reach 100%. Excess isocyanate is advantageous for the polyurethane reaction, however V_e increased slowly when R was greater than or equal to 1.8. The molecular weight between the cross-linking points (M_c) tended to correlate negatively with that of V_e; the order of magnitude of M_c was approximately 10^4, which is why these binders exhibited excellent elongation.

Furthermore, the curing network evidently influences the mechanical behaviour. The trend of ε_m agreed with that of the M_c. σ_m showed a similar correspondence with V_e when R was less than 1.7, because the curing network tends to be unity. However, when R lay between 1.7 and 1.9, σ_m decreased slightly because the excess of the small TDI molecules do not enter the network but exist as an isolated state in these binders. Hence, the network tends to be incomplete.

3.3 Hydrogen bonding

Except for the chemical cross-linking, thermosetting polyurethane binders have many physical functions, such as hydrogen bonding and physical entanglement. Of these, the hydrogen-bonding (H-bonds) interaction is of concern mainly because of its stronger contribution to the mechanical properties of the polymers [20]. For the GAP/TDI binders, H-bonds are formed either by the carbonyl (C=O) and imino (−NH−) groups on the carbamate or by the ether (−O−) and imino (−NH−) groups. These strengthen the chain segments dramatically [21], leading to excellent macro-mechanical properties. Generally, the infrared absorption spectra of the carbonyl groups might be shifted towards a lower frequency on formation of an H-bond [22]; the stronger the H-bond, the greater the absorption spectral shift. The percentage of the carbonyl groups which participate in forming H-bonds can be calculated by analyzing its relative content before and after the curing reaction.

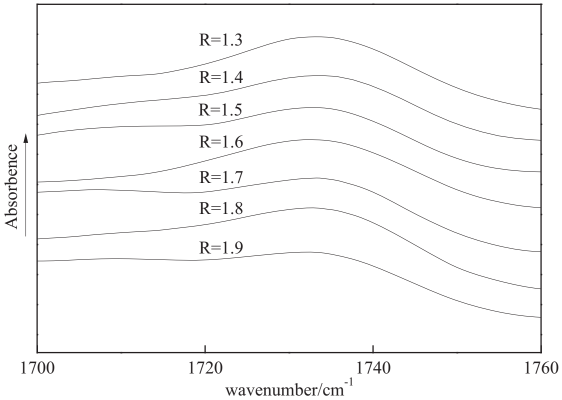


Figure 5. Carbonyl region of the FTIR spectra for the GAP/TDI binders

Figure 5 shows the FTIR spectra of the carbonyl groups in the GAP/TDI binders. The central wave number of the spectral absorption peak of the carbonyl groups is generally located in the region 1695-1735 cm^{-1}. However, the extent to which the different absorption peaks of H-bonded and free carbonyl groups overlap makes it difficult to analyse the distinctions. These overlapped bands were resolved through multi-peak Gaussian fitting to obtain the area and area percentage of each peak. The detailed solution process and final results are shown in Figure 6 and Table 2, respectively.

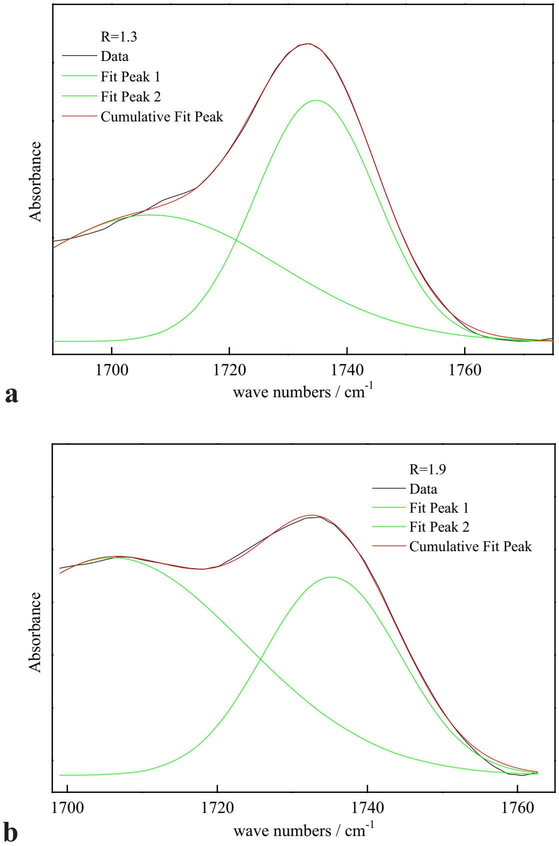


Figure 6. Gaussian multi-peak fitting for the FTIR spectra of the carbonyl region

Table 2. Peak area and percentage of H-bonded carbonyl groups in the GAP/TDI binders

Sample	Carbonyl peaks		Percent H-bonded carbonyl [%]
	Area (1705 cm^{-1})	Area (1735 cm^{-1})	
R = 1.3	0.84	0.59	58.66
R = 1.4	0.68	0.46	59.69
R = 1.3	0.71	0.43	62.41
R = 1.6	1.66	0.63	72.61
R = 1.7	1.33	0.46	74.35
R = 1.8	1.60	0.57	73.84
R = 1.9	1.23	0.53	69.79

The area of these peaks and their percentages are given in Table 2. Obviously hydrogen bonding exists within the GAP/TDI binders and the central wave number of the carbonyl peak shifts from 1735 cm^{-1} to approximately 1705 cm^{-1}, suggesting that the majority of the carbonyl groups contribute to the formation of H-bonds. Moreover, a rising trend in the percentage of H-bonded carbonyl groups occurs within the range R = 1.3-1.7, because of the increasing concentration of carbamate (−NHCOO−) groups, and the probability of bonding between the proton donating imino group (−NH−) and the carbonyl group (C=O) or the ether group (−O−, on the GAP backbone) also increases. However, when R is increased from 1.7 to 1.9, it is worth noting that this interaction is reduced to 69.79%. The main reason for this is that the supersaturated TDI reduces the concentration of the hydrogen-bonded carbonyl groups by affecting the structures of the H-bonded chains, whose formation is sensitive to the distance between the atoms or groups and the angle between the bonds. This results in the tendency of the imino and carbonyl groups to be disordered; thus, the probability of H-bond formation is decreased. Moreover, the excess of TDI also contributes to the side reaction (generating polyurea and carbon dioxide), which has a lower utilization of oxygen atoms.

3.4 Entanglements

In this section the contributions of chemical cross-linking, physical entanglement, and hydrogen bonding to Young's modulus are analyzed, based on the theory of elasticity for crosslinking-entanglement networks [23] and the statistical theories of rubber elasticity [24]. Furthermore, the integrity degree of the GAP/TDI curing networks was evaluated semi-quantitatively. Initially the physical entanglement in the GAP/TDI binders was studied, and the phenomenological theory of rubber in large elastic deformation. This gives the stored energy function expressed in terms of the strain invariables [25]:

$$W = \sum_{i,j,k}^{\infty} C_{ijk}\left(I_1^i - 3^i\right) ln\left(\frac{I_1}{3}\right)^j ln(I_3) \tag{6}$$

Because the stored energy function (W) in the phenomenological theory of rubber in large elastic deformation is equal to the elastic free energy of deformation (ΔF), on the basis of this equivalent relation W can be substituted by the second-order approximation of the elastic free energy of deformation (ΔF) in the general deformation range, thus:

$$W = C_{100}(\alpha_1^2 + \alpha_2^2 + \alpha_3^2 - 3) + C_{010} ln\left(\frac{\alpha_1^2+\alpha_2^2+\alpha_3^2}{3}\right) + C_{200}((\alpha_1^2 + \alpha_2^2 + \alpha_3^2)^2 - 3^2) \tag{7}$$

where W is the stored energy function, I_1, $ln(I_1/3)$ and $ln(I_3)$ denote the principal deformation variables, respectively, α is the elongation ratio corresponding to τ, and C_{100}, C_{020}, and C_{200} represent the contributions of chemical cross-linking, entanglement, and non-Gaussian chains to the elastic modulus, respectively. According to the relations between W and the deformation derived from the statistical theories of rubber elasticity [26], the expression of the stress-strain relationship during uniaxial tension can be expressed as:

$$\tau^1 = 2(\alpha - \alpha^{-2})\left[C_{100}^{(1)} + C_{020}^{(1)}/(\alpha^2 + \tfrac{2}{\alpha})\right] \tag{8}$$

$$\tau^2 = 2(\alpha - \alpha^{-2})\left[C_{100}^{(2)} + \frac{C_{020}^{(2)}}{\alpha^2+\frac{2}{\alpha}} + 2C_{200}^{(2)}(\alpha^2 + \tfrac{2}{\alpha})\right] \tag{9}$$

where τ denotes tensile stress. Equations 8 and 9 are the first- and second-order approximations of $\tau \sim \alpha$, respectively. In a comparison of Equation 8 and the first-order approximation of ΔF, the expansion of C_{cij} can be rewritten as:

$$C_{100} = \frac{1}{2}kT\left(\xi_C^0 B_C^0 + \xi_e^0 B_e^0\right) \tag{10}$$

Similarly, the C_{cij} in the second-order approximation of these equations can be derived as:

$$C_{020} = \frac{1}{2}kT\xi_e^0 D_e^0 \tag{11}$$

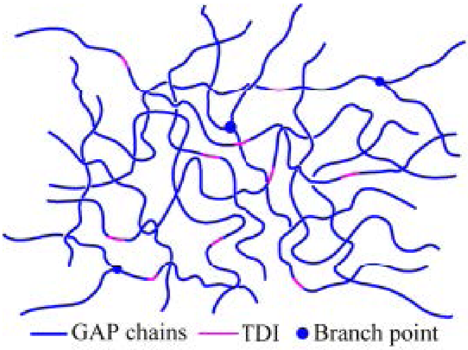
$$C_{200} = \frac{1}{2}kT\left(\xi_C^0 C_C^0 + \xi_e^0 C_e^0\right) \tag{12}$$

where k is the Boltzmann constant, T is the thermodynamic temperature, and $\xi_C^0 B_C^0$ and $\xi_e^0 B_e^0$ represent the parameters determined by the original states and the crosslinking-entanglement network structures. As can be deduced, C_{100}, C_{020}, and C_{200}, denote respectively the contributions of long chains (effective network chains), physical entanglement, and non-Gaussian chains to the elastic modulus. To compare the intensity of these interactions, the algorithm of successive approximations proposed in [27] was used here to estimate the parameters C_{cij} through regression analysis on the tensile curves. The results are given in Table 3.

Table 3. C_{ijk} parameters of the GAP/TDI binders

Parameter Sample	$C_{100}^{(2)}$	$C_{020}^{(2)}$	$C_{200}^{(2)}$	Deformation mode and range of uniaxial tension
	$C_{ijk} \times 10^{-2}$ [N·mm^{-2}]			
R = 1.3	0.285	1.634	0.015	0.040.30
R = 1.4	0.472	3.690	0.032	0.030.25
R = 1.5	0.564	8.451	0.082	0.030.25
R = 1.6	1.093	8.900	0.110	0.040.27
R = 1.7	0.958	12.65	0.258	0.040.28
R = 1.8	0.420	21.47	0.347	0.050.30
R = 1.9	1.080	23.20	0.474	0.050.27

By comparing the parameters for in Table 3, it is obvious that these kinds of parameters generally rank in the order $C_{020}^{(2)} > C_{100}^{(2)} > C_{200}^{(2)}$, indicating stronger molecular chain entanglement in the GAP/TDI binders. As in the GAP thermoplastic binders, in which the functionality of GAP is less than 2, the application of a chain extender with TDI leads to slight cross-linking in this system and long molecular chains between the cross-linking points (Sketch 1). These long GAP chains are limited by weaknesses at the cross-linking points and therefore have a large conformational entropy that favours various chain movements, such as extension, crimping, and shrinkage. Thus, the physical entanglement effect of long chains after curing contributes significantly to the macroscopic enhancement of the elastic modulus and fracture strength. Generally, the parameter $C_{100}^{(2)}$ has the same trend as that of the R value (except for R = 1.8, attributable perhaps to experimental error); the V_e values are given in Table 1. Additionally, the non-Gaussian effect of the polymer chains appears to be weak because of the smaller numerical value of $C_{200}^{(2)}$,.



Sketch 1. Diagrammatic entanglement in the GAP/TDI binders

3.5 Integrity of curing networks

Finally, the degree of integrity of the GAP/TDI binders will be discussed by comparing the difference between the real elastic modulus and the calculated one deduced from . The statistical theory of rubber elasticity [24] presents the interrelations between the shear modulus (G) and the curing network parameters:

$$G = NkT = \frac{N_A \rho kT}{M_c} = \frac{\rho RT}{M_c} \tag{13}$$

where N is the chain number in the curing network, N_A is the Avogadro constant, ρ is the density, and R is the molar gas constant. Equation 13 is applicable to an ideal network on the premise that no network defects exist and no molecular interactions are occurring in the curing system. However, real networks cannot be described by this equation because of hydrogen bonding and various defects such as entanglements, enclosed rings, pendant groups, and free chains. The H-bonds and the first kind of defect are favorable for the modulus and the strength of the polymer [28]; however the last two conditions adversely affect the mechanical performance. It is difficult to describe or count these interactions and defects quantitatively because of the limits in the experimental conditions. Therefore, a new approach is proposed to reflect the degree of integrity of the GAP/TDI networks by analyzing the comprehensive contributions of the H-bonds and the entanglement and defects to the modulus. The definite value of the contribution of each item (interaction or defect) is difficult to assess for this analysis, however the final result can be used. Equation 13 can be rewritten by introducing a correction factor A:

$$\lambda G = E = \lambda V_e RT + A \tag{14}$$

where G is the shear modulus, E is the elastic modulus, λ is the Poisson ratio, and the correction factor A represents the comprehensive contributions to the modulus of the interactions and defects. If A is demonstrated to be positive, indicating that the influence of the H-bonds and entanglement on the modulus is more significant than that of the other defects, or vice versa, then the correction factor A can be used to reflect the relative integrity of the curing network for the GAP/TDI elastomers. Factor A and the other parameters related to the integrity are given in Table 4 for a comprehensive analysis.

Table 4. Curing network integrity of the GAP/TDI binders

Sample	E [MPa]	$V_e \times 10^{-4}$ [mol·cm^{-3}]	H-bonded carbonyl [%]	$C_{020}^{(2)}$	A
R = 1.3	0.04	0.68	58.66	1.63	−0.15
R = 1.4	0.14	0.73	59.69	3.69	−0.13
R = 1.5	0.24	0.82	62.41	8.45	−0.12
R = 1.6	0.33	0.93	72.61	8.90	−0.12
R = 1.7	0.34	1.04	74.35	12.65	−0.14
R = 1.8	0.45	1.20	73.84	21.47	−0.15
R = 1.9	0.55	1.24	69.79	23.20	−0.13

Clearly, as presented in Table 4, the correction factors A of the GAP/TDI binders are all negative because the measured elastic moduli are higher than those of the computed ones. Although the correction factor remains negative, the relatively superior network which has the maximal , might be selected for application. Parameter A increased continuously from −0.15 to −0.12 within the R range 1.3-1.6, which is mainly because the curing degree characterized by V_e tended to be greater with an increase in R; thus, more polymer chains and curing agent enter the binder network along with the high conversion. Moreover, hydrogen bonding and physical entanglement exhibit the same trend with the R value. All of these chemical cross-linking and physical actions contribute to the modulus and to the integrity of the curing network within the R range 1.3-1.6. However, excess of TDI in the binder cannot completely enter the cross-linking network, and the remainder reacts with moisture (V_e increases because of the generated polyurea) and has negative effects on the network. Another result was a reduction in the relative content of carbamate and decreased hydrogen bonding. Therefore, the factor A has an opposite trend with the R value within the R range 1.6-1.9, although the entanglement parameter increased continuously, suggesting a deterioration of the network in this range. Finally, a conclusion derived from this analysis is that the most complete curing network exists in the binder with an R value of 1.6.

4 Conclusions

Promising, energetic GAP/TDI binders with various curing parameters were prepared in this research, and uniaxial tensile tests served to investigate their mechanical performance. The best result was achieved with R = 1.6; σ_m= 1.6 MPa and $\varepsilon_m\%$ = 1041%, by which fracture work also reaches its maximum. To study the factors that influence the mechanical properties, the curing networks, hydrogen bonding interactions, and physical entanglements in the binders were also investigated, by low-field NMR and infrared spectroscopy, and by applying the theory of elasticity for crosslink-entanglement networks, respectively. The results showed that the cross-linking density of GAP/TDI is approximately 1.04×10^{-4} mol/cm^3 and increases with R. The proportion of hydrogen bonding varies with the R value and reaches 72.61% with an R value of 1.6. Molecular entanglements are positively correlated with the R value and contribute significantly to the mechanical properties. On the basis of the statistical theory of elasticity, the integrity of the curing networks was finally analyzed and showed that lower or higher R values lead to smaller correction factors for the modulus and incomplete networks, and that a curing parameter of 1.6 is preferable.

Acknowledgements

This research was supported by NSAF funding (No. U1630142). We also thank Prof. Li Guoping for her assistance during the preparation of this manuscript.

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