

# Surface Free-Energy Analysis of Energetic Poly(glycidyl azide) Networks Prepared by Different Reactive Systems

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**ABSTRACT:** Change in the surface free energy of poly(glycidyl azide) (PGA) networks prepared with different reactive systems was investigated using the van Oss-Good contact-angle evaluation methodology in order to estimate their wettability properties. The apolar Lifshitz–van der Waals (LW) component of the surface free energy of these energetic PGA networks was found to differ only in a minor amount and an average  $\gamma_S^{LW} = 32.2 \text{ mJ m}^{-2}$  was calculated. The network surface was found to be monopolar and basic (electron donor) in varying degrees in accordance with change of the network bulk structure, mainly due to the presence of oxygen atoms in the PGA chain. The set of the network containing only PGA and Desmodur N-100 components showed the highest  $\gamma_S^-$  values compared to the other two sets. The main  $\gamma_S^-$  contribution was found to come from the PGA polymer. A slight decrease of the  $\gamma_S^-$  component was seen when the Desmodur N-100 component was substituted with hexamethylene diisocyanate (HMDI); however a large decrease was seen when Desmodur N-100 was substituted with the isophorone diisocyanate (IPDI) component. This large reduction in the surface basicity of the network was due to increase of the apolar IPDI groups at the surface having low surface tension and also due to decrease of the oxygen atoms belonging to the main chain of PGA at the surface, which resulted in the minimization of the network's basic surface free-energy component. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2848–2855, 1999

**Key words:** poly(glycidyl azide) (PGA); glycidyl azide polymer (GAP); surface free energy; network

## INTRODUCTION

In rocket-propellant technology, functionally terminated liquid prepolymers having allylic hydroxyl or carboxyl functional groups have been widely used as binders. A typical composite propellant may be prepared by an end-linking reac-

tion of these aforementioned prepolymers with a suitable functionally active and low molecular weight polyfunctional reactant in the presence of particulate solids such as an oxidizer, fuel material, or crystalline explosives. In this manner, hydroxyl-terminated prepolymers can be end-linked with di- or polyfunctional isocyanates and carboxyl-terminated prepolymers can be end-linked with an aziridinyl or epoxy-type reactants. The most commonly used polymeric binders for solid rocket propellants are commercially available liq-

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uid prepolymers such as hydroxyl-terminated polybutadiene, carboxyl-terminated polybutadiene, and the polybutadiene–acrylonitrile–acrylic acid terpolymer.

In the last two decades, different azido polymers possessing energetic azide ( $-\text{N}_3$ ) groups were developed for use in the preparation of a highly energetic propellant binder, plasticizer, and gas generator. Poly(glycidyl azide) (PGA) is a typical example of these azido polymers. This prepolymer is a low molecular weight ( $\bar{M}_n \cong 2000$  g/mol) liquid prepolymer, having relatively low viscosity and high density as compared to other propellant binders, and terminal  $-\text{OH}$  groups on the main polyether chain. Therefore, PGA can be easily end-linked with NCO groups of conventional di- or polyfunctional isocyanates in the presence of trifunctional hydroxyl compounds, for example, trimethylol propane (TMP) and triethanol amine.<sup>1,2</sup> The resultant elastomeric network has a polyurethane structure. This prepolymer has a positive heat of formation (+957 kJ/kg at 293 K) and, therefore, decomposes exothermically.<sup>3</sup> This can be attributed to the decomposition of its pendant azide groups. This property has been exploited to prepare highly energetic, high specific impulse, high burning rate, and smokeless propellants and considerable effort has been devoted to the synthesis and characterization of the functionally terminated PGA.<sup>4–10</sup> The thermal decomposition behavior of PGA<sup>4,11</sup> and its solubility properties<sup>12</sup> were reported previously. The major component of a composite propellant is the inorganic oxidizer and the high-energy property of PGA is able to compensate the poor performance of a propellant when loaded with ammonium nitrate instead of ammonium perchlorate as an oxidizer. Recently, a smokeless propellant based on PGA and phase-stabilized ammonium nitrate (PSAN) were prepared and its mechanical characterization was performed.<sup>2,13</sup>

On the other hand, it is well known that the surface dynamics of polymers are considerably different from those of more rigid materials such as metals and ceramics, due to the high mobility of macromolecules at the surface.<sup>14</sup> Also, the composition of the copolymer surface is not necessarily the same as the composition in the bulk. The indirect determination of the surface free energy of the polymers by the one-liquid contact-angle method (the air–liquid–polymer) system was proposed by Fowkes<sup>15</sup> and by Girifalco and Good.<sup>16</sup> The change of the surface free-energy properties of the copolymer films with the copolymer compo-

sition were determined by applying these semiempirical approaches,<sup>17</sup> and, later, the use of nonlinear programming methods were adopted.<sup>18,19</sup> van Oss et al. introduced a theory and a practical methodology to estimate the interfacial tension between apolar and electron-acceptor and electron-donor molecules.<sup>20–22</sup> They assumed that surface and interfacial free energies consisted of two components; an apolar or a Lifshitz–van der Waals component (indicated by superscript LW) of electrodynamic origin and a polar component (indicated by superscript AB) caused by acid–base interactions. This methodology was successfully applied to polymers and protein interactions with liquids, surface free-energy determinations of polymers, polymer solubility predictions of solvents, and critical micelle concentrations of surfactants.<sup>20,22</sup> This approach was also tested with liquid–liquid interactions<sup>23</sup> and the calculated results agreed well with independent interfacial tension data from mercury interactions with the liquids.<sup>24,25</sup> This methodology was successfully used to determine the surface free-energy analysis of some copolymers.<sup>26–29</sup>

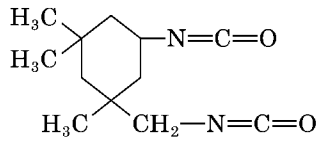
It is anticipated that the mechanical and the adhesive properties of a propellant are directly related to the wettability of the oxidizer particles with the polymeric binder. It was the purpose of this study to determine the change in surface free energy of PGA networks prepared with different reactive systems and at different junction-point densities.

## EXPERIMENTAL

### Materials and Characterization

PGA was purchased from ICT (Germany). The number-average molecular weight,  $\bar{M}_n$ , of PGA was determined as 1920 g/mol using vapor-pressure osmometry (VPO) with benzyl (MW = 210.2 g/mol) as a calibration standard. The hydroxyl equivalent of PGA was determined as 1.06 meq/g according to the method cited by Dee et al.<sup>30</sup> using *N*-methylimidazole as an acetylation catalyst. It was in the form of a viscous liquid with a density of 1.28 g/cm<sup>3</sup> and a viscosity of  $5.1 \times 10^3$  cP as determined by a volume-calibrated pycnometer and a Brookfield viscometer, respectively, at room temperature. Desmodur N-100 polyisocyanate was used as a polyfunctional reactant for end-linking of the PGA prepolymer, which is a reaction product of hexamethylene diisocyanate

**Table I Chemical Formulas of the Reactants**

Poly(glycidyl azide) (PGA)	$\text{HO} \left[ \begin{array}{c} \text{CH}_2 - \text{CH} - \text{O} \\   \\ \text{CH}_2 \\   \\ \text{N}_3 \end{array} \right]_n \text{H} \quad n = 20$
Hexamethylene diisocyanate (HMDI)	$\text{O}=\text{C}=\text{N}-(\text{CH}_2)_6-\text{N}=\text{C}=\text{O}$
Isophorone diisocyanate (IPDI)	
Desmodur N-100	$\begin{array}{c} \text{H} \\   \\ \text{O}=\text{C}-\text{N}-(\text{CH}_2)_6-\text{N}=\text{C}=\text{O} \\   \\ \text{O}=\text{C}=\text{N}-(\text{CH}_2)_6-\text{N} \\   \\ \text{O}=\text{C}=\text{N}-(\text{CH}_2)_6-\text{N}=\text{C}=\text{O} \\   \\ \text{H} \end{array}$
Trimethylol propane (TMP)	$\begin{array}{c} \text{CH}_2-\text{OH} \\   \\ \text{CH}_3-\text{CH}_2-\text{C}-\text{CH}_2-\text{OH} \\   \\ \text{CH}_2-\text{OH} \end{array}$

(HMDI) with water. It was a gift from Bayer (Germany) and used as received. Its number-average molecular weight was determined as 610 g/mol using VPO. The functionality value of the polyisocyanate was evaluated at 3.2 from the following expression: functionality ( $f$ ) =  $\bar{M}_n/\text{equivalent weight}$ , where the equivalent weight was determined from the isocyanate (NCO) group content to be 5.24 meq/g using the standard di-*n*-butyl-amine back-titration method.<sup>31</sup> Mixtures of trimethylol propane (TMP) with isophorone diisocyanate (IPDI) and HMDI were used as polyfunctional reactants in the preparation of PGA networks. IPDI and HMDI were purchased from

Fluka AG (Buchs, Switzerland) (98% purity), and TMP was purchased from Aldrich (Milwaukee, WI) with a purity of 98%. They were used as received. The chemical structures of all the compounds are given in Table I.

### Preparation of PGA Networks

PGA is a difunctional hydroxyl-terminated prepolymer. Therefore, the networks were obtained by the end-linking process of linear PGA chains using polyfunctional reagents (i.e., Desmodur N-100 polyisocyanate, a mixture of TMP with IPDI or HMDI). To observe the type of reactive

**Table II Composition of the PGA Networks<sup>1</sup>**

NCO/OH Reactive Group Ratio	Set I (wt %)		Set II (wt %)			Set III (wt %)		
	PGA	DesmodurN-100	PGA	TMP	IPDI	PGA	TMP	HMDI
1.0	83.17	16.83	81.43	2.57	16.00	84.74	2.68	12.58
0.9	84.59	15.41	82.08	2.59	15.33	85.82	2.71	11.47
0.8	86.07	13.93	84.13	2.67	13.20	—	—	—
0.7	87.59	12.41	—	—	—	—	—	—

system and the reactive group ratios of networks on their surface free energy, PGA networks were prepared as three sets of formulations having different NCO/OH ratios (Table II).

In Set I, Desmodur N-100 polyisocyanate was used as a polyfunctional reagent alone. In Sets II and III, mixtures of TMP with IPDI and HMDI were used as polyfunctional reagents, respectively. In these sets, the reactive group ratio of  $\text{OH}_{(\text{TMP})}/[\text{OH}_{(\text{PGA})} + \text{OH}_{(\text{TMP})}]$  was kept constant at 0.4.<sup>1</sup>

To prepare the networks of Sets II and III, TMP was dissolved in previously degassed PGA at 65°C under a vacuum by continuously mixing for 15 min and a calculated amount of diisocyanate (IPDI or HMDI) was added. After additional mixing for 3 min, the mixture was cast into the glass mold and the end-linking reaction was then continued for a total of 7 days at 65°C under a nitrogen atmosphere to obtain a film having a thickness of 1–1.5 mm. For the preparation of the PGA networks of Set I, a calculated amount of Desmodur N-100 was mixed with previously degassed PGA for 3 min and the end-linking reaction was allowed to complete under the same conditions described above.

### Instrumentation

The number-average molecular weights of the PGA prepolymer and Desmodur N-100 were determined by a Knauer-type vapor-pressure osmometer. The contact angle measurements were carried out using a Model G-III contact angle meter (KERNCO Instrument Co., El Paso, TX) at the specified temperatures and ambient humidity. Only advancing angles were determined immediately. Experiments were performed using liquid drops deposited from a microliter syringe onto the freshly prepared smooth polymer substrates. All polymer surfaces were cleaned by washing with ethyl alcohol, then water containing soap, and later with distilled water and dried at 50°C for 4 h under a 1–2 mmHg vacuum. The contact angles of triple-distilled water, glycerol, ethylene glycol, formamide, methylene iodide, and paraffine oil drops were measured. All the reported contact angles were an average of three measurements and deviated within  $\pm 2^\circ$ .

## THEORY

### Surface Free-energy Components

The Young equation<sup>32</sup> describes the thermodynamic equilibrium of the three surface tensions:

$\gamma_{\text{SV}}$ ,  $\gamma_{\text{SL}}$ , and  $\gamma_{\text{LV}}$ , existing at the phase boundaries of a drop of liquid at rest on a solid surface:

$$\gamma_{\text{LV}} \cos \theta = \gamma_{\text{SV}} - \gamma_{\text{SL}} \quad (1)$$

where  $\gamma_{\text{LV}}$ ,  $\gamma_{\text{SV}}$ , and  $\gamma_{\text{SL}}$  are, respectively, the free energies of a liquid and a solid against their saturated vapor and of the interface between the solid and liquid. Subscripts L, S, and V refer to liquid, solid, and vapor, respectively. In this equation, the phases are supposed to be mutually in equilibrium and the spreading film pressure of the observed vapor of the liquid on the solid is neglected. The work required to pull the liquid away from the surface leaving the equilibrium absorbed film (i.e., the total work of adhesion) is given by the Dupre equation<sup>33</sup>:

$$-\Delta G_{\text{SL}}^{\text{TOT}} = W_{\text{A}} = \gamma_{\text{SV}} + \gamma_{\text{LV}} - \gamma_{\text{SL}} \quad (2)$$

By eliminating  $\gamma_{\text{SL}}$  from eqs. (1) and (3), the well-known Young–Dupre equation is obtained:

$$-\Delta G_{\text{SL}}^{\text{TOT}} = W_{\text{A}} = \gamma_{\text{LV}}(1 + \cos \theta) \quad (3)$$

According to the Van Oss–Good theory,<sup>20–22</sup> the surface and interfacial free energies (or tensions) consist of two components: an apolar or a Lifshitz–van der Waals component (indicated by superscript LW) of electrodynamic origin and a polar component caused by Lewis acid–base interactions (indicated by superscript AB). The two components are additive. The total interfacial tension between a solid and a liquid,  $\gamma_{\text{SL}}^{\text{TOT}}$ , is now given as

$$\gamma_{\text{SL}}^{\text{TOT}} = \gamma_{\text{SL}}^{\text{LW}} + \gamma_{\text{SL}}^{\text{AB}} \quad (4)$$

and the total surface tension for a solid,  $\gamma_{\text{SV}}^{\text{TOT}}$ , and for a liquid,  $\gamma_{\text{LV}}^{\text{TOT}}$ , is accordingly given as

$$\gamma_{\text{SV}}^{\text{TOT}} = \gamma_{\text{SV}}^{\text{LW}} + \gamma_{\text{SV}}^{\text{AB}} \quad (5a)$$

$$\gamma_{\text{LV}}^{\text{TOT}} = \gamma_{\text{LV}}^{\text{LW}} + \gamma_{\text{LV}}^{\text{AB}} \quad (5b)$$

They suggested that LW forces include not only the London dispersion forces ( $d$ ) but also the Keesom orientation ( $p$ ) and Debye induction ( $i$ ) forces:

$$\gamma_{12}^{\text{LW}} = \gamma_{12}^d + \gamma_{12}^p + \gamma_{12}^i \quad (6)$$

When only LW interactions are considered, that is, for the interactions between two completely apolar compounds, the Good–Girifalco–Fowkes<sup>15,16</sup> combining rule is applicable and the geometric-mean combining rule is used:

$$\gamma_{SL}^{LW} = \gamma_S^{LW} + \gamma_L^{LW} - 2\sqrt{\gamma_S^{LW}\gamma_L^{LW}} \quad (7)$$

or

$$\gamma_{SL}^{LW} = (\sqrt{\gamma_S^{LW}} - \sqrt{\gamma_L^{LW}})^2 \quad (8)$$

Between many liquid–solid interfaces, in addition to LW interactions, polar interactions of the hydrogen bonding type often occur. All electron-acceptor and electron-donor interactions or Lewis acid–base (AB) interactions are of this type. Unlike LW interactions, AB interactions are essentially asymmetrical and can only be satisfactorily treated by taking that asymmetry into account.<sup>20–22</sup> Van Oss and coworkers adopted Small's<sup>34</sup> combining rule for acid–base interactions which is not a geometric mean and the  $\gamma^{AB}$  component comprises two nonadditive parameters. These are the electron-acceptor surface free-energy component (designated as  $\gamma^+$ ) and the electron-donor component (designated  $\gamma^-$ ). These two parameters can be combined so that, in the AB interaction between materials S and L, the electron acceptor of S interacts with the electron donor of L and the electron donor of S interacts with the electron acceptor of L. Thus, the free energy of AB interactions between S and L is expressed as

$$-\Delta G_{SL}^{AB} = \mathbf{W}_{SL}^{AB} = 2(\sqrt{\gamma_S^- \gamma_L^-} + \sqrt{\gamma_S^+ \gamma_L^+}) \quad (9)$$

where  $\gamma_i^+$  is the Lewis acid and  $\gamma_i^-$  is the Lewis base parameter of surface tension.  $\gamma_{SL}^{AB}$  is now given as

$$\gamma_{SL}^{AB} = 2(\sqrt{\gamma_S^+ \gamma_S^-} + \sqrt{\gamma_L^+ \gamma_L^-} - \sqrt{\gamma_S^+ \gamma_L^-} - \sqrt{\gamma_S^- \gamma_L^+}) \quad (10)$$

or

$$\gamma_{SL}^{AB} = 2(\sqrt{\gamma_S^+} - \sqrt{\gamma_L^+})(\sqrt{\gamma_S^-} - \sqrt{\gamma_L^-}) \quad (11)$$

Then, the free energy of cohesion for LW interactions in each solid and liquid phase is defined as

$$\Delta G_i^{LW} = 2\gamma_i^{LW} \quad (12)$$

By combining eqs. (2) and (7) in the LW form, one obtains

$$-\Delta G_{SL}^{LW} = 2\sqrt{\gamma_S^{LW}\gamma_L^{LW}} \quad (13)$$

Now, since by definition,

$$-\mathbf{W}_A = \Delta G_{SL}^{TOT} = \Delta G_{SL}^{LW} + \Delta G_{SL}^{AB} \quad (14)$$

and by combining eqs. (9), (13), and (14), one obtains

$$-\Delta G_{SL}^{TOT} = 2(\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + \sqrt{\gamma_S^+ \gamma_L^-} + \sqrt{\gamma_S^- \gamma_L^+}) \quad (15)$$

By combining eqs. (3) and (15) and taking  $\gamma_{LV} = \gamma_L$  as usual, the complete Young–Dupre equation, the general contact-angle equation, comprising both the apolar and polar interactions, becomes

$$\gamma_L(1 + \cos \theta) = 2(\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + \sqrt{\gamma_S^+ \gamma_L^-} + \sqrt{\gamma_S^- \gamma_L^+}) \quad (16)$$

and the total interfacial tension is given from the sum of eqs. (8) and (11):

$$\gamma_{SL}^{TOT} = (\sqrt{\gamma_S^{LW}} - \sqrt{\gamma_L^{LW}})^2 + 2(\sqrt{\gamma_S^+} - \sqrt{\gamma_L^+})(\sqrt{\gamma_S^-} - \sqrt{\gamma_L^-}) \quad (17)$$

To find the AB interactions of cohesion in a solid or liquid phase, eq. (9) is rewritten for a single phase:

$$-\Delta G_i^{AB} = 4\sqrt{\gamma_i^+ \gamma_i^-} \quad (18)$$

Since  $-\Delta G_i^{AB} = 2\gamma_i^{AB}$  by definition; then, eq. (18) becomes

$$\gamma_i^{AB} = 2\sqrt{\gamma_i^+ \gamma_i^-} \quad (19)$$

If both  $\gamma_i^+$  and  $\gamma_i^-$  are present, the substance is termed as “bipolar.” If one of them is not present (equals to zero), the substance is termed as “monopolar.” If both  $\gamma_i^+$  and  $\gamma_i^-$  are absent, the substance is termed as “apolar.” Therefore,  $\gamma_i^{AB} = 0$  for apolar and monopolar substances and  $\gamma_i^{AB}$  is present for only bipolar substances.

The most important consequence of eq. (17) is that the contribution of an acid–base interaction results in negative total interfacial tension (or free energy) in some circumstances. This occurs if

**Table III Contact-angle Results of PGA Networks**

Liquid	Temperature (°C)	Set I NCO/OH				Set II NCO/OH			Set III NCO/OH	
		0.7	0.8	0.9	1.0	0.8	0.9	1.0	0.9	1.0
Distilled water	23	68	67	70	67	97	93	91	74	76
Methylene iodide	23	42	42	40	47	52	43	43	44	46
Ethylene glycol	23	54	55	52	54	81	73	56	54	53
Glycerine	15	75	72	69	69	90	89	75	89	89
Formamide	15	56	56	58	61	83	74	71	64	62
Paraffin	23	16	19	25	25	24	16	19	17	19

$\gamma_L^+ > \gamma_S^+$  and  $\gamma_L^- < \gamma_S^-$  or if  $\gamma_L^+ < \gamma_S^+$  and  $\gamma_L^- > \gamma_S^-$  and if  $|\gamma_{SL}^{AB}| > |\gamma_{SL}^{LW}|$ . A solid–liquid system may be stable although it has negative  $\gamma_{SL}$ .<sup>20–22</sup>

### Computation of the Surface Free-energy Components

$\gamma_S^{LW}$  can be determined first by using apolar liquids. For an apolar liquid,  $\gamma_L^+ = \gamma_L^- = 0$  and, therefore,  $\gamma_L = \gamma_L^{LW}$ . Then, eq. (16) can be written in the form

$$\gamma_L(1 + \cos \theta) = 2(\sqrt{\gamma_S^{LW} \gamma_L}) \quad (20)$$

Consequently, the  $\gamma_S^{LW}$  value can be determined directly and the results of apolar liquid (methylene iodide and paraffine) contact angles are averaged for a single value. When two polar liquids are used, two equations of the form of eq. (16) constitute a set of two simultaneous equations which can be solved for the two unknown properties of the solid  $\gamma_S^+$  and  $\gamma_S^-$ . Then, the  $\gamma_S^+$  and  $\gamma_S^-$  results are averaged for a single value. Water-drop contact-angle values are always used in these sets in order to avoid large discrepancies between simultaneous equation solutions.<sup>22</sup>

## RESULTS AND DISCUSSION

The compositions of PGA networks prepared by three different reactive systems are tabulated in Table II. All the contact-angle measurement results are given in Table III. The surface free-energy component values of the liquids used are taken from ref. 22 and are given in Table IV. The LW component of the surface free energy of the networks were calculated by using eq. (20) and the methylene iodide and paraffin oil drop contact-angle values and their averages are given in Table V. As seen in this table, the  $\gamma_S^{LW}$  values did not differ much as expected, giving an average value of  $32.2 \pm 1.7 \text{ mJ m}^{-2}$  with a deviation of 5.3% from the mean, which is in the range of experimental error.

$\gamma_S^+$  and  $\gamma_S^-$  values were calculated using the general contact-angle equation, where previously found  $\gamma_S^{LW}$  values were inserted. Water–glycerol, water–ethylene glycol, and water–formamide sets were simultaneously solved and the results are given in Table V. As seen in this table, the network surface was basic (electron donor) in varying degrees, due to the presence of oxygen atoms in the main chain of PGA and carbonyl groups in Desmodur N-100. Although the solu-

**Table IV Surface Free-energy Component Values of the Liquids Used<sup>22</sup> (mJ m<sup>-2</sup>)**

Liquid	$\gamma_L$	$\gamma_L^{LW}$	$\gamma_L^{AB}$	$\gamma_L^+$	$\gamma_L^-$
Water	72.8	21.8	51.0	25.5	25.5
Glycerol	64.0	34.0	30.0	3.92	57.4
Ethylene glycol	48.0	29.0	19.0	1.92	47.0
Formamide	58.0	39.0	19.0	2.28	39.6
Methylene iodide	50.8	50.8	0	0	0
Paraffine oil	28.9	28.9	0	0	0

**Table V** Surface Free-energy Components of Polymers ( $\text{mJ m}^{-2}$ )

Isocyanate Type	NCO/OH Ratio	$\gamma_{\text{S,average}}^{\text{LW}}$	$\gamma_{\text{S}}^-$	$\gamma_{\text{S}}^+$	$\gamma_{\text{S}}^{\text{AB}}$	$\gamma_{\text{S}}^{\text{TOT}}$
Desmodur N-100	0.7	33.2	20.5	0.15	3.5	36.7
Desmodur N-100	0.8	33.0	21.1	0.08	2.6	35.6
Desmodur N-100	0.9	32.9	16.4	0.11	2.7	35.6
Desmodur N-100	1.0	31.1	21.5	0.06	2.3	33.4
HMDI	0.9	32.6	19.2	0.43	5.8	38.4
HMDI	1.0	31.9	16.0	0.77	7.0	38.9
IPDI	0.8	29.8	3.5	0.37	2.3	32.1
IPDI	0.9	32.9	3.9	0.22	1.9	34.8
IPDI	1.0	32.7	1.9	0.47	1.9	34.6

tions of the simultaneous equations resulted in minor quantities of surface acidity,  $\gamma_{\text{S}}^+$ , it is conventional to accept these surfaces as monopolar and to neglect the  $\gamma_{\text{S}}^+$  values.<sup>22</sup> Consequently, there may be two approaches: If we assume that  $\gamma_{\text{S}}^+ = 0$ , then we obtain  $\gamma_{\text{S}}^{\text{AB}} = 0$  from eq. (19) and, therefore,  $\gamma_{\text{S}}^{\text{TOT}} = \gamma_{\text{S}}^{\text{LW}}$  from eq. (5a). The other alternative is to assume that  $\gamma_{\text{S}}^+ \neq 0$  and to use the  $\gamma_{\text{S}}^+$  values in Table V, from eq. (19), to obtain  $\gamma_{\text{S}}^{\text{AB}}$  and in eq. (5a) for the corresponding  $\gamma_{\text{S}}^{\text{TOT}}$  values which are also given in Table V. In each case, we recognized minor deviations from the mean values for  $\gamma_{\text{S}}^{\text{TOT}}$ .

The most important difference was found to be in the surface basicity,  $\gamma_{\text{S}}^-$ , or the electron-donor coefficient of surface free energies of the networks. When the three sets are compared, Set I, containing only PGA and Desmodur N-100, showed higher  $\gamma_{\text{S}}^-$  values than those of the other two sets. This could be explained by the fact that this set contains the highest amount of oxygen atoms and carbonyl groups in its bulk structure and this property is reflected by its surface properties. There was not much difference in the  $\gamma_{\text{S}}^-$  values within this set with decrease of the Desmodur N-100 component giving an average value of  $19.9 \text{ mJ m}^{-2}$ , showing that the main  $\gamma_{\text{S}}^-$  contribution is coming from the PGA polymer. Since the weight compositions of the networks did not differ much in the bulk, only an average  $\gamma_{\text{S}}^-$  could be sensed by the contact-angle method. When Set III is considered, the replacement of Desmodur N-100 with TMP and HMDI resulted in an average value of  $17.6 \text{ mJ m}^{-2}$ , which is  $2.3 \text{ mJ m}^{-2}$  lower than Set I. We may speculate that the contribution from the presence of Desmodur N-100 was about in the  $2.3 \text{ mJ m}^{-2}$  range.

When we consider Set II, we observed a large decrease of the measured surface basicity. The

average  $\gamma_{\text{S}}^-$  value was found to be  $3.1 \text{ mJ m}^{-2}$ , which was about one-sixth of Set III. This large reduction in the surface basicity was due to the high increase of the apolar IPDI groups at the surface. IPDI has a large apolar pendant group nearly twice as large as of the hexamethylene group of HMDI. Although the bulk compositions of Sets II and III were similar, increase of the apolar IPDI having lower surface free energy at the surface resulted in the minimization of the network's basic surface free-energy component. In addition, the cyclic structure of IPDI prevents the mobility of IPDI-PGA copolymer chains when compared with the mobility of HMDI-PGA chains. The lower the mobility of the copolymer chain, the lower is the possibility of surface enrichment of oxygen atoms belonging to PGA at the copolymer surface, thus resulting in lower surface basicity.

The surface characterization of the PGA copolymers gives an idea of the thermodynamic work of adhesion between the polymeric propellant and the inorganic oxidizer particles such as ammonium perchlorate and ammonium nitrate. Also, it will help the selection of the most appropriate pairs. As known from acid-base adhesion theory, when the surface acidity of one component is high and the surface basicity of the other component is also high, then strong adhesion between the components, and better compatibility, occurs. However, in actual practice, thermodynamic work of adhesion calculations is not sufficient to decide on a suitable pair of polymer-inorganic oxide components. The experimental investigation of the adhesion and compatibility is also required due to the different chain diffusion and viscoelastic behavior of the polymer component. Therefore, the surface characterization of the polymeric component is only a guide for this pair-selection process.

## CONCLUSIONS

The LW component of the surface free energy of the energetic PGA networks prepared by different reactive systems was found to differ only in a minor amount and an average  $\gamma_S^{LW} = 32.2 \text{ mJ m}^{-2}$  was calculated. The network surface was found to be basic (electron donor) in varying degrees, due mainly to the presence of oxygen atoms in the PGA chain. Since very small figures of the  $\gamma_S^+$  values were found, then these network surfaces were assumed to be monopolar and the  $\gamma_S^+$  coefficients were neglected. The most important difference was found to be in the surface basicity,  $\gamma_S^-$ , or the electron-donor coefficient of surface free energies of the networks with the change of the network bulk structure. The network set containing only PGA and Desmodur N-100 components showed the highest  $\gamma_S^-$  values compared with the other two sets. The main  $\gamma_S^-$  contribution was found to come from the PGA polymer. A slight decrease of the  $\gamma_S^-$  component resulted when Desmodur N-100 was substituted with HMDI; however, a large decrease was seen when Desmodur N-100 was substituted with the IPDI isocyanate component. This large reduction in the surface basicity was due to the high increase of the low surface tension apolar IPDI groups at the surface. In addition, the oxygen atom concentration belonging to the PGA component decreased at the surface due to the inflexibility introduced by cyclic IPDI group in the IPDI-PGA copolymers. This fact resulted in the decrease of the network's basic surface free-energy component.

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