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#### Rational Design, Synthesis and Evaluation of New Azido-Ester DOI: 10.1039/DODT02250K Structures as Green Energetic Plasticizers

Nasser Sheibani<sup>a</sup>, Narges Zohari \*<sup>a</sup>, Reza Fareghi – Alamdari \*<sup>a</sup>

Abstract: Computer-aided molecular design (CAMD) is a well-known tool for theoretical assessment of the chemical structures before their experimental synthesis. In this study using this method as well as considering the important criteria for a chemical structure as an energetic plasticizer for energetic azido binder, initially, the number of new azido-ester structures were designed and their physicochemical as well as energetic properties determined via theoretical calculation by using molecular dynamics simulations and machine learning-based methods. Then, considering the balances between several criteria, two of these theoretical chemical structures, including GTAA (glyceryl tris(azidoacetate)) and TEGBAA (triethyleneglycol bis(azidoacetate)), selected and synthesized as well as characterized. Comparison between the results of experimental and theoretical evaluation of the physicochemical properties of these new azido-ester plasticizers shows an acceptable agreement with each other. Finally, the compatibility and efficiency of these two new azido-ester plasticizers on the rheological and thermal properties of glycidyl azide polymer (GAP) are investigated using rheometry and DSC analyses and compared with some common energetic plasticizers. The results confirm that these two new azido-esters are appropriate plasticizers for GAP since they had higher safety over the comparative plasticizers in addition to the proper performance.

## Introduction

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Plasticizers are low molecular weight additives used to adjust the final polymer properties. Usually, plasticizers function via diffusion between the polymer chains and weakening the Van der Waals interactions that hold the polymer chains close together. In energetic material formulations, plasticizers and binders can be categorized into non-energetic (inert) and energetic. Energetic plasticizers contribute to the overall energy of formulation by an increase in the overall enthalpy of the system. Thus, the new approaches to the formulation of propellants and explosives initiative developed using energetic ingredients. Insertion of energetic azido (-N<sub>3</sub>), nitro (-NO<sub>2</sub>), or nitrate (-O-NO<sub>2</sub>) substituents in the small organic molecules is a valuable strategy to develop new energetic plasticizers.<sup>1-5</sup> Plasticizer migration is one of the composite energetic materials main challenges. From safety and hazard-risk reduction viewpoints of composite energetic materials, the compatibility between binder and plasticizer is an important criterion. The critical issue of the incompatibility includes the migration of plasticizer molecules from the binder. This phenomenon degrades the mechanical properties of the binder, which finally increase the hazardous properties such as impact and friction sensitivity. Energetic azido-ester plasticizers have a good compatibility with new energetic binders like GAP, BAMO, AMMO, and Poly NIMMO.<sup>6-8</sup> Moreover, these types of plasticizers have significant features such as high enthalpy of formation, exothermic decomposition, good thermal stability, low glass transition temperature, high density, low impact sensitivity, and environmentally friendly decomposition products.8-11

The development of new high-performance energetic materials along with safety requirements and environmental

considerations is an interesting research field of energetic materials.

Rational design is the innovative strategy to create new molecules with desired characteristics, based on the capability to predict how the molecular structure will affect its properties. The new structures can be designed from scratch or by manipulating a known molecular structure to obtain optimum properties. Comprehensive knowledge of the structureproperty relationships basic principles is an important criterion in the rational design process. This kind of knowledge finally led to more accurate desired properties in molecules.

Link between theoretical and experimental chemistry in energetic materials industry is not as common as pharmaceutical/biotechnology industry. The energetic materials industry is hazardous material industry. Any optimization of materials in this industry is very important from the environmental aspects and saving employees' lives. Plasticizer plays an important role in the mechanical properties and safety of modern composite energetic materials. It has two different hazards aspects (operation and environmental). From the operation viewpoint, the compatibility between binder and plasticizer is an important factor. The incompatibility leads to the plasticizer migration of which significantly increases hazardrisk and sensitivity to external mechanical stimuli. From an environmental aspect, the development of green plasticizers which have nitrogen-rich combustion products causes less environmental pollution. Comparison with hazardous nitrateester plasticizers, the azido-ester plasticizers possess better compatibility with new azide energetic binders as well as having green (nontoxic) combustion products.

Till now, several azido-ester based energetic plasticizers have been synthesized and reported in the literature. One of the earliest synthesis reports of azido-ester plasticizers was published by Frankel et al.<sup>12</sup>, where they introduced tetraazido polyesters as replacement of inert plasticizers in gun propellant formulations.<sup>12</sup> Witucki et al.<sup>13</sup> also introduced 6-azidohexyl-6azido hexanoate (AHAH) plasticizer, which in addition to the

<sup>&</sup>lt;sup>a.</sup> Faculty of Chemistry and Chemical Engineering, Malek-Ashtar University of Technology, Tehran, Iran. Tel: +982122945141 Corresponding authors. E-mail addresses: nargeszohari@gmail.com (N. Zohari), reza\_fareghi@yahoo.com (R. Fareghi – Alamdari).

energetic properties reduces the amount of flame in the exhaust gases.<sup>13</sup> Agrawal et al.<sup>14</sup> introduced bis(2azidoethyl)adipate (BAEA) energetic azido-ester plasticizer as a replacement of inert plasticizers such as a triacetin (TA) or diethyl phthalate (DEP) in the formulation of double base or composite modified double base (CMDB) propellants.<sup>14</sup> Drees et al.<sup>15</sup> developed a series of azido-ester plasticizers from ethylene glycol, diethylene glycol, trimethylol nitromethane, and pentaerythritol. They showed that the ethylene glycol derived azido-ester (EGBAA) has better efficiency than common nitrate-ester plasticizers like BTTN and TMETN in a 50% mixture with poly(3-nitratomethyl-3-methyloxetane) (polyNIMMO).<sup>15</sup> Kumari et al.<sup>7</sup> considering the good lubricating effects of inert plasticizers such as phthalate derivatives; introduced and synthesized a number of the di, tetra and hexa azido-esters as energetic plasticizers. Although some of their synthesized structures were solid and could not has the plasticizing ability. Their work<sup>7</sup> is one of the examples that further exemplifies the necessity of the theoretical evaluation before experimental synthesis. In fact, there would be no further requirement to synthesis many of their proposed chemical structures. Also, there are reports by Pant et al.<sup>16, 17</sup> on the topic of synthesis of dendrimer azido-esters as potential energetic plasticizers. In

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addition to the above, several other azido-esters have been synthesized and reported as potential energietic plasticizers? 218026 Glycidyl azide polymer has some drawbacks such as poor mechanical properties and low-temperature characteristics resulted from the bulky polar -CH<sub>2</sub>N<sub>3</sub> side chains. Due to the excellent energetic properties of this binder, many efforts have been made to improve its weak mechanical properties. These efforts have generally included the introduction of new energetic plasticizers (azido-esters, azido-ethers or energetic ionic liquids) for this polymer.<sup>6, 7, 22, 24 27-30</sup> However, due to the polar nature of energetic azido functional group the most of these plasticizers show high viscosities. On the other hand, non viscous samples (e.g. EGBAA and DEGBAA<sup>16</sup>) due to their low molecular weights are volatile and migrate from the polymer. In the present work, our perspective is to solve this issue by design and introducing new energetic azido-ester plasticizers for energetic azido binders via the computer-aided molecular design approach. This approach utilizes several ideal energetic plasticizer performances and safety parameters as criteria to select the optimal molecular structures. This method reduces costs, hazards and time by transferring trial and error from laboratory to virtual screening (computer-based methods).

Table 1. Calculated physicochemical properties for theoretical azido-ester structures.

No.	Name	Formulation	δ (MPa <sup>0.5</sup> )	$\Delta H^{\circ}_{f(kJ.mol^{-1})}^{36}$	T <sub>G (°C)</sub> ³⁰	T <sub>d (°C)</sub> ⁴⁰	<b>ρ</b> (g.cm <sup>-3</sup> ) <sup>41</sup>	OB%	<b>M.W.</b> (g.mol <sup>-1</sup> )
1	N <sub>1</sub>	$C_{14}H_{15}N_9O_4$	18.616	430.49	-66.31	243.32	1.22	-134.98	373.38
2	N <sub>2</sub>	$C_{12}H_{13}N_9O_2$	19.611	841.49	-77.37	251.05	1.21	-144.61	315.34
3	N <sub>3</sub>	$C_{13}H_{15}N_9O_2$	19.949	749.10	-79.17	253.24	1.20	-153.02	329.37
4	N <sub>4</sub>	$C_{15}H_{19}N_9O_2$	16.613	868.26	-82.78	257.62	1.17	-167.87	357.43
5	N₅	$C_{10}H_{17}N_9O_2$	17.651	762.16	-94.16	246.67	1.24	-143.55	295.36
6	N <sub>6</sub>	$C_{11}H_{19}N_9O_2$	18.859	712.91	-95.96	234.05	1.23	-152.56	309.39
7	N <sub>7</sub>	$C_{10}H_{14}N_{18}O_2$	17.179	1199.18	-64.67	231.86	1.39	-95.60	418.42
8	N <sub>8</sub>	$C_{16}H_{20}N_{18}O_4$	17.492	576.05	-60.51	232.89	1.37	-115.03	528.54
9	N <sub>9</sub>	$C_9H_{14}N_{12}O_2$	16.456	739.86	-31.12	234.76	1.31	-114.16	322.35
10	N <sub>10</sub>	$C_{13}H_{18}N_{18}O_4$	17.270	587.77	-60.36	226.32	1.40	-101.12	490.49
11	N <sub>11</sub>	$C_9H_{14}N_{12}O_2$	18.943	517.02	-84.44	229.67	1.31	-114.16	322.35
12	G1	$C_9H_{11}N_9O_6$	22.966	89.75	-55.67	247.71	1.37	-82.04	341.29
13	G2	$C_{15}H_{23}N_9O_9$	21.232	-107.74	-66.50	233.40	1.29	-109.83	473.47
14	G₃	$C_{18}H_{26}N_{18}O_9$	20.901	453.88	-55.61	239.97	1.42	-100.22	638.62
15	P <sub>1</sub>	$C_{18}H_{20}N_{18}O_4$	18.635	1053.74	-57.22	252.08	1.35	-121.62	552.56
16	P <sub>2</sub>	$C_{18}H_{18}N_{12}O_8$	21.633	237.61	-36.36	227.86	1.30	-111.60	530.48
17	P <sub>3</sub>	$C_{12}H_{12}N_6O_4$	21.458	-112.68	-50.91	238.94	1.16	-136.71	304.26
18	P <sub>4</sub>	$C_{14}H_{14}N_{12}O_4$	20.163	123.72	-55.18	243.32	1.23	-119.69	414.34
19	$L_1$	$C_{13}H_{20}N_{12}O_4$	21.921	237.65	-72.95	241.13	1.25	-125.35	408.45
20	L <sub>2</sub>	$C_{10}H_{16}N_6O_6$	23.683	-434.88	-70.99	262.01	1.26	-111.30	316.27



Figure. 1. Molecular structure of newly designed aliphatic and aromatic azido-esters.

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No.	Name	N (mol.g <sup>-1</sup> ) <sup>a</sup>	<mark>™</mark> <sub>(g.mol<sup>-1</sup>)</sub> b	$\mathbf{Q}_{(cal.g^{-1})}^{c}$	D (km.s <sup>-1</sup> )	
1	N <sub>1</sub>	0.0429	15.83	559.27	5.24	
2	N <sub>2</sub>	0.0412	15.02	805.44	5.53	
3	N <sub>3</sub>	0.0425	14.09	705.06	5.32	
4	N <sub>4</sub>	0.0448	12.58	728.96	5.27	
5	N₅	0.0508	13.29	795.88	6.03	
6	N <sub>6</sub>	0.0517	12.58	721.79	5.82	
7	N <sub>7</sub>	0.0430	17.91	810.22	6.45	
8	N <sub>8</sub>	0.0435	16.71	461.28	5.48	
9	N <sub>9</sub>	0.0465	15.89	712.23	6.07	
10	N <sub>10</sub>	0.0449	17.38	501.91	5.83	
11	N <sub>11</sub>	0.0465	15.89	547.32	5.68	
12	G1	0.0469	19.08	528.20	6.09	
13	G2	0.0528	16.06	446.94	5.71	
14	G₃	0.0485	17.11	542.54	6.21	
15	<b>P</b> <sub>1</sub>	0.0416	16.71	647.70	5.78	
16	P <sub>2</sub>	0.0434	17.84	504.30	5.51	
17	P <sub>3</sub>	0.0427	16.02	258.13	4.20	
18	<b>P</b> <sub>4</sub>	0.0410	17.31	327.44	4.61	
19	L <sub>1</sub>	0.0490	15.02	396.74	5.15	
20	L <sub>2</sub>	0.0537	15.78	172.08	4.46	

**Table 2**. Calculated detonation properties of theoretical azido-ester structures.

<sup>a</sup>. The number of moles of gas produced per gram of explosives. <sup>b</sup>. The average molar weight of detonation products. <sup>c</sup> The chemical energy of detonation.

## **Computational details**

In this work diverse ideal energetic plasticizers performance and safety parameters including solubility parameter ( $\delta$ ), the heat of formation  $(\Delta H_{f})$ , glass transition temperature  $(T_{G})$ , density ( $\rho$ ), decomposition temperature (T<sub>d</sub>), detonation velocity (D) and impact sensitivity (h<sub>50%</sub>) used as criteria for assessing the physicochemical, detonation and sensitivity properties of the designed azido-ester structures. In addition, some other parameters such as low-cost available starting materials, straightforward synthetic route, oxygen balance (OB%) as well as the tendency to migration (refers to M.W. and  $\delta$ ) also considered. The designed azido-esters are categorized into four series as shown in Figure 1. The calculated performance parameters are given in Tables 1 and 2. In the later sections, we introduce the methods used to evaluate the physicochemical properties of the designed potential energetic azido-ester plasticizers.

#### Solubility parameter

The solubility parameter was firstly introduced by Hildebrand and Scott,<sup>31, 32</sup> which is defined as the square root of the cohesive energy density (CED). The cohesive energy density is a needed energy level for the elimination of the unit volume of molecules from their nearby to infinite dissociation. In terms of a mathematical equation, the cohesive energy density defined as a cohesive energy per unit of volume:<sup>33</sup>

$$CED (J.m^{-3}) = \frac{E_{coh}}{V} = \frac{\Delta H_V - RT}{V}$$
(1)

Also, the solubility parameter defined as:

$$\delta \left(J.m^{-3}\right)^{0.5} = \sqrt{CED} \tag{2}$$

Therefore, the solubility parameter is a numerical representation of the degree of interaction between materials, and according to "like dissolves like" principle, it will give a good estimation of the miscibility which is a very important criterion for selection of plasticizer for the specific polymer. It was commonly accepted that if the difference between the solubility parameter of polymer and plasticizer lies amongst 1.2 up to 2.1, they would expect to be miscible.<sup>34</sup> Here, the solubility parameters ( $\delta$ ) of the designed energetic azido-ester structures are theoretically determined by molecular dynamics (MD) simulations using the Materials Studio software package.<sup>35</sup> The CED was calculated by the Forcite and Amorphous Cell modules of Materials Studio using the COMPASS (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) force field. More details are given in the supporting information section.

#### **Heat of formation**

The standard enthalpy of formation of new azido-ester structures are assessed using the proposed 3D QSPR method in reference<sup>36</sup> by the following equation:

$$\Delta H_f^{\circ} = 697.60 - 1091.71 \frac{n_o}{n_N} - 197.24 \frac{n_c}{n_N} + \Gamma$$
(3)

The unit of  $\Delta H_f^{*}$  in this equation is kJ.mol<sup>-1</sup>.  $n_O$ ,  $n_N$  and  $n_C$  is the number of oxygen, nitrogen and carbon atoms in the molecular formula respectively.  $\Gamma$  is the plural of Dragon software<sup>37</sup> molecular descriptors:

 $\Gamma = 272.82 (B06[N - 0]) + 330.88 (MATS6p) + 74.90 (Mor07e) - 261.63 (RDF135p) - 101.66 (H - 052) - 2672.77 (R3e +)$ (4)

It's also necessary to optimize the 3D molecular structures of new azido-ester structures using the AM1 semi-empirical method implemented in HyperChem software.<sup>38</sup>

#### **Glass transition temperature**

The glass transition temperature of these azido-esters assessed using the following method:<sup>39</sup>

$$T_G = -124.29 + Y + 9.57 n_{-C00} - 53.32 n_{N_3} + 14.68 \theta^+ - 14.68 \theta^-$$
(5)  
$$Y = 29.65 \frac{n_c}{n_v} - 2.55 n_H + 22.03 n_N$$
(6)

The unit of  $T_G$  is degree centigrade;  $n_{-COO}$  and  $nN_3$  are the numbers of ester and azido functional groups in the molecular formula, respectively. The  $\vartheta^+$  and  $\vartheta^-$  shown the positive and negative contribution of non-additive structural parameters in the glass transition temperature, respectively.<sup>39</sup> Also in Equation (6), the  $n_H$ ,  $n_C$ , and  $n_N$  are the number of hydrogen, carbon and nitrogen atoms, respectively.<sup>39</sup>

#### **Decomposition temperature**

The decomposition temperature of these potential energetic plasticizers assessed using the following method:<sup>40</sup>

$$T_d = 225.74 - 12.14 \, n_{-COO} + 2.16 \, n_C + 4.03 \, \frac{n_N}{n_{N_3}} + 21.00 \, \tau^+ - 29.59$$
  
$$\tau^- \qquad (7)$$

Here also the unit of T<sub>d</sub> is degree centigrade. The definition of the  $n_c$ ,  $n_N$ ,  $n_{-COO}$  and  $nN_3$  are the same as the previous section.  $\tau^+$  and  $\tau$  shown increasing and decreasing contribution of non-additive structural parameters in the decomposition temperature, respectively.<sup>40</sup>

#### Density

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The density of these new azido-ester structures is assessed with the introduced method in reference<sup>41</sup> using the following equations:  $\rho = 1.21 + \omega + 0.04 \rho^+ - 0.52 \rho^-$  (8)

$$\omega = 0.01 \, n_N + 0.26 \, \frac{n_0}{n_c} - 0.1 \, \frac{n_c}{n_N} \tag{9}$$

The unit of  $\rho$  is g.cm<sup>-3</sup> and  $n_o$ ,  $n_c$  and  $n_N$  are the number of oxygen, carbon and nitrogen atoms, respectively.  $\rho^+$  indicates the positive contribution of the non-additive structural parameters and  $\rho^-$  shown the negative contribution of these parameters.<sup>41</sup>

#### **Detonation velocity**

Based on the calculated density and standard enthalpy of formation, the detonation velocity predicted using the empirical Kamlet–Jacobs equation:<sup>42, 43</sup>

$$D = 1.01 \left( N\overline{M}^{0.5}Q^{0.5} \right)^{0.5} (1 + 1.30\rho)$$
(10)

*D* is the detonation velocity in km.s<sup>-1</sup>, *N* is the number of moles of line gaseous produced per gram of explosive,  $\overline{M}$  is the mean moles of line weight of detonation products, *Q* is the heats of detonation in cal.g<sup>-1</sup> and  $\rho$  is the density in g.cm<sup>-3</sup>. Since all the designed azido-ester structures composed of *C*, *H*, *N*, and *O* atoms, the detonation products for calculating *N*,  $\overline{M}$ , and *Q* assumed as  $N_2$  (g),  $H_2O$  (g),  $CO_2$ (g), and *C* (s).<sup>43</sup>

#### Impact sensitivity

To provide an evaluation of the hazardous risk of the designed azidoesters to accidental external stimuli, the impact sensitivity ( $h_{50\%}$ ) of them estimated using this method:<sup>44</sup>

 $h_{50\%} = a_1 + a_2 \exp\left[-(a_3[Q - a_4])\right]$  (11)

h<sub>50%</sub> is impact sensitivity according to the BAM drop hammer test in cm, *Q* is the heat of detonation in kcal.g<sup>-1</sup> and  $a_1-a_4$  are equals:  $a_1=$  27.8331 cm,  $a_2=$  0.1135 cm,  $a_3=$  11.0793 g.kcal<sup>-1</sup>,  $a_4=$  1.6606 kcal.g<sup>-1</sup>.

### **Results and discussion**

As shown in Figure 1, the proposed structures divided into four main series (*N*, *G*, *P*, *L*).

The *N* series consists of 11 azido-esters that have dendrimer like structures and based on tribromo-neopentyl alcohol as well as tribromopivalic-acid as main starting materials. The most interesting features of this series are appropriate glass transition and onset decomposition temperatures, which are two of the most important performance factors affecting the plasticizing efficiency. However, in terms of the solubility parameter, the calculated  $\delta$  values of these structures are significantly different from experimental reported  $\delta$  value for GAP ( $\delta$ =22.51 MPa<sup>0.5</sup>).<sup>45</sup> The estimated theoretical  $\delta$  value for hydroxyl-terminated 10 monomeric units GAP chain using MD simulations in the present study is 22.07 MPa<sup>0.5</sup>.

The *G* series consists of three azido-esters based on glycerol as the main starting material. The structure of these series is close to 1,2,3 triacetoxypropane (triacetin), which is used as an inert plasticizer, and nitroglycerin (NG) as the first known nitrateester energetic plasticizer. From Table 1, it's apparent that this series is superior in oxygen balance and density. Molecular dynamics simulations show that the solubility parameter of all three proposed azido-esters has the least discrepancy with the experimental GAP solubility parameter and the  $G_1$  azido-ester, which is the azidated counterpart of nitroglycerin has the closest  $\delta$  value to GAP.

Since phthalic acid ester derivatives widely used as plasticizers, the *P* series is based on phthalate ester inert plasticizers, like dioctyl phthalate (DOP) and di(2-ethylhexyl)phthalate (DEHP). From the solubility parameter point of view in this series,  $P_1$  and  $P_2$  azido-esters have the closest  $\delta$  values to GAP.

The *L* series consists of two linear azido esters. The  $L_1$  is a tetra azido-ester and proposed by considering the bis(1,3-diazido prop-2-yl)malonate and bis(1,3-diazido prop-2-yl)glutarate azido esters.<sup>22</sup> Theoretical calculations show the superiority of  $L_1$  over these two azido ester plasticizers in terms of thermal

decomposition and glass-transition temperature. The  $L_2$  azidoester is a continuation of the work of Drees et al.<sup>15</sup> who reported azido ester derivatives of ethylene glycol (EGBAA) and diethylene glycol (DEGBAA). This structure is an azido ester derivative of triethylene glycol (TEGBAA) as well as from another perspective is an azidated counterpart of triethylene glycol dinitrate (TEGDN) which used as an energetic plasticizer in explosive and propellant formulations. Also, the solubility parameters of these two azido esters indicate their compatibility for application as an energetic plasticizer for GAP.

# Theoretical evaluation of the physicochemical and detonation properties of the new azido-esters

The calculated theoretical physicochemical properties of these azido-esters are given in Table 1. According to this table, it is clear that with the exception of  $L_2$ ,  $P_3$ , and  $G_2$  azido-esters, all of the azido-ester structures have high positive heat of formation values and the  $N_7$  has the highest value among all. From the glass transition temperature point of view, the best result is related to the  $N_6$  azido-ester. Although the glass transition temperature of all azido-ester structures at an acceptable level. In terms of thermal stability, Table 1 indicates that the decomposition temperature of these azido-ester derivatives varies from 220 up to 260 °C. Also, the highest decomposition temperature is related to the  $L_2$  azido-ester. The density results of these structures show that  $G_3$  has the highest density. A comparison of the oxygen balance values of these azido-esters indicates the superiority of  $G_1$ .

The molecular weight range of the plasticizers used in energetic material formulations varies between 200 up to 2000 g.mol<sup>-1.1</sup> Provatas<sup>46</sup> investigation shows that there is an inverse relationship between the diffusion rate of energetic plasticizer migration from a polymeric binder and the molecular weight of the energetic plasticizer. So, the energetic plasticizer with lower molecular weight tends to be volatile, while plasticizer with higher molecular weight tends to be more viscous. From the aforementioned perspective, the  $N_5$ ,  $N_8$ ,  $P_1$ ,  $P_2$ , and  $G_3$  azidoesters seem to be not suitable for energetic plasticizer applications.

Although the new azido-esters are not explosives, an evaluation of the detonation properties plays a major role in determining the energy content of these new energetic materials. A comparison of the detonation properties of these azido-esters in Table 2 indicates the superiority of  $N_{7}$ ,  $G_3$ , and  $G_1$ .

The sensitivity of the azido-esters to impact is estimated by the Equation  $(11)^{44}$  which is based on experimental results from the "Fall Hammer Method" using 2 kg drop weight and its results indicate the height of 50% probability of explosion of the sample  $(h_{50\%})$ .<sup>47</sup> The estimated results which are based on computed heats of detonation show that all of these new azido-esters were insensitive toward mechanical stimuli up to 170 cm (33.35 J). Since it is possible that due to the relatively low heat of detonation (Q) values of these compounds, the accuracy of predictions using Equation  $(11)^{44}$  are not reliable (see reference 44), we decided to evaluate the impact sensitivity of these compounds in another way. Therefore, we used Energetic Materials Designing Bench (EMDB), Version 1.0 software

package<sup>48</sup> that estimates impact sensitivity of energetic materials based on the molecular structure. The evaluation results using this software also confirm the low h<sub>50%</sub> impact sensitivities of the designed azido-ester structures. Therefore, based on these results, it can be inferred that the designed azido-esters shows low impact sensitivities.

#### Selection of synthesis candidates

Some of the common necessities for an ideal energetic plasticizer comprised of:

compatibility with the binder, high oxygen balance, positive heat of formation value, low glass transition temperature, low tendency to migration, high decomposition temperature, high density, low impact sensitivity, low-cost available starting materials, straightforward synthetic route, and low toxicity.

Since these requirements are sometimes incompatible with each other, it is challenging to find out an energetic plasticizer with optimum physicochemical properties. Therefore, depending on the expectations of the formulation, each of these azido-ester structures can be selected as a superior energetic plasticizer.

The compatibility between polymer and plasticizer is a very important factor and there is no plasticizing effect in case of incompatibility between them. Therefore, in terms of compatibility with GAP, the  $G_1$  azido-ester (glyceryl tris(azidoacetate) abbreviated as GTAA) have the best result according to MD simulations. This azido-ester also has the highest oxygen balance among all and possesses a positive heat of formation value. Compared with its nitrate-ester counterpart (NG), the theoretical evaluation indicates a low sensitivity of this azido-ester to external mechanical stimuli. In addition, it does not reveal a complex synthesis reaction and has accessible starting materials. Accordingly, this structure has the proper characteristics as an energetic plasticizer for GAP as well as an alternative for NG.

From another perspective, the L2 azido-ester (triethyleneglycol bis(azidoacetate) abbreviated as TEGBAA) also one of the proposed structures which present good compatibility with GAP ( $\delta$ =23.68 MPa<sup>0.5</sup>). Simple synthesis reaction along with the appropriate theoretical properties as well as the idea of comparing its plasticizing effect with TEGDN are some attractive factors of this azido-ester. The theoretical evaluation also indicates the high safety of this azido-ester since it has the highest decomposition temperature among all.

Consequently, future sections will focus on the synthesis, evaluation, performance as well as comparison of these two azido-esters with other plasticizers.

#### Materials

All used chemicals with the exception of mixed acid (1:1 mixture of concentrated  $HNO_3$  and  $H_2SO_4$ ) were purchased from Sigma-Aldrich and used without further purification. These chemicals include chloroacetic acid, glycerin, ethylene glycol, diethylene glycol, triethylene glycol, epichlorohydrin and sodium azide as reactants; dimethyl sulfoxide, dimethylacetamide, dichloromethane, 1,2-dichloroethane and toluene as solvents; stannic tetrachloride, lithium chloride, trifluoroacetic acid, and The reaction progress has monitored using silica gel TLC plates. The IR spectrums took using a Perkin-Elmer FT-IR spectrometer. The NMR spectrums were taken by Varian Unity Inova-500 MHz spectrometer in CDCl3 at 298 K. The DSC analysis was taken by a METTLER TOLEDO DSC 1 at the heating rate of 5 K.min<sup>-1</sup> for GAP and a mixture of GAP-plasticizer and 10 K.min<sup>-1</sup> for the plasticizers under N<sub>2</sub> flow. The impact sensitivity determined by the BAM fall hammer method using 2 kg drop weight. GPC conducted on Agilent PL-GPC 50 system equipped with PLgel  $3\mu$ m 100A 300 x 7.5 mm column using THF. The viscosity has measured by an Anton Paar EC-twist 502 rheometer.

#### Synthesis

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As explained in the previous sections, the GTAA and TEGBAA azido-esters were selected for synthesis and experimental evaluation as well as comparing between theoretical and experimental results. In addition, ethylene glycol bis(azidoacetate) (EGBAA) and diethylene glvcol bis(azidoacetate) (DEGBAA) azido-ester plasticizers<sup>15</sup> and one nitrate-ester plasticizer (TEGDN) also synthesized for comparative study.

## Table 3. The detail of the synthesized plasticizers and polymers.

The synthesis of TEGDN plasticizer performed by mixed acid nitration reaction method. This method involves the gradual addition of triethylene glycol (TEG) to the mixed acid with temperature control.<sup>49</sup>

GAP synthesized using azidation of polyepichlorohydrin (PECH) with sodium azide in dimethylacetamide (DMAc) as a solvent and LiCl as a catalyst.<sup>50</sup> PECH synthesized by cationic ringopening polymerization of epichlorohydrin (ECH) monomers using SnCl<sub>4</sub> and trifluoroacetic acid (TFA) as a catalyst and 1,4butanediol (BDO) as an initiator. The ratio of BDO/ECH was 1:37.<sup>50</sup>

The details of the conditions and steps of the synthesized plasticizers and GAP are given in Table 3 and supporting information.

Compound Solvent		Solvent	T (°C)	Time (h)	Yield (%)	State	Analysis
	GTAA	Toluene	90	7	81.00	Colorless liquid	IR (KBr): v(cm <sup>-1</sup> ) = 790.71 (C-Cl), 1170.41 (C-O), 1760.35 (C=O), 2960.64 (C-H).
Chloro-e	TEGBAA	Toluene	90	7	76.96	Pale yellow liquid	<b>IR (KBr):</b> v(cm <sup>-1</sup> ) = 781.22 (C-Cl), 1188.23 (C-O), 1755.33 (C=O), 2881.83 (C-H).
)-ester	EGBAA	Toluene	90	7	70.00	Colorless crystal	<b>IR (KBr):</b> v(cm <sup>-1</sup> ) = 781.22 (C-Cl), 1172.79 (C-O), 1759.19 (C=O), 2966.71 (C-H).
	DEGBAA	Toluene	90	7	70.00	Pale yellow liquid	<b>IR (KBr):</b> v(cm <sup>-1</sup> ) = 781.22 (C-Cl), 1186.30 (C-O), 1753.40 (C=O), 2883.76 (C-H).
	GTAA	DMSO	40	30	85.00	Yellow liquid	IR (KBr): v(cm <sup>-1</sup> ) = 1188.82 (C-O), 1751.26 (C=O), 2111.89 (N <sub>3</sub> ), 2926.51 (C-H). <sup>1</sup> H NMR (500 MHz, CDCl <sub>3</sub> ): δ(PPM) = 3.85 (S, 2CH <sub>2</sub> N <sub>3</sub> ), 3.90 (S, CH <sub>2</sub> N <sub>3</sub> ), 4.45 (dd, CH <sub>2</sub> OC=O), 4.25 (dd, CH <sub>2</sub> OC=O), 5.35 (tt, CHOC=O). <sup>13</sup> C NMR (125 MHz, CDCl3): δ(PPM) = 50.19 (2CH <sub>2</sub> N <sub>3</sub> ), 50.14 (CH <sub>2</sub> N <sub>3</sub> ), 63.05 (2OCH <sub>2</sub> ), 70.23 (OCH <sub>2</sub> ), 168.29 (2C=O), 168.65 (C=O).
Azido-ester	TEGBAA	DMSO	40	24	77.00	Yellow liquid	IR (KBr):           ν(cm <sup>-1</sup> ) = 1199.80 (C-O), 1747.62 (C=O), 2110.26 (N <sub>3</sub> ), 2922.34 (C-H). <sup>1</sup> H NMR (500 MHz, CDCl <sub>3</sub> ): $\delta$ (PPM) = 3.65 (s, 2OCH <sub>2</sub> ), 3.75 (t, 2OCH <sub>2</sub> ), 3.92 (s, 2CH <sub>2</sub> N <sub>3</sub> ), 4.35 (t, 2CH <sub>2</sub> OC=O). <sup>13</sup> C NMR (125 MHz, CDCl3): $\delta$ (PPM) = 50.22 (2CH <sub>2</sub> N <sub>3</sub> ), 64.65 (2CH2OC=O), 68.82 (2OCH <sub>2</sub> ), 70.53 (2OCH <sub>2</sub> ), 168.30 (2C=O).
	EGBAA	DMSO	40	24	70.00	Pale yellow liquid	IR (KBr): v(cm <sup>-1</sup> ) = 1186.30 (C-O), 1751.48 (C=O), 2112.19 (N <sub>3</sub> ), 2928.13 (C-H). <sup>1</sup> H NMR (500 MHz, CDCl <sub>3</sub> ): $\delta$ (PPM) = 3.77 (s, 2CH <sub>2</sub> N <sub>3</sub> ), 4.25 (s, 2OCH <sub>2</sub> ).
	DEGBAA	DMSO	40	24	75.00	Amber yellow liquid	IR (KBr): v(cm <sup>-1</sup> ) = 1197.87 (C-O), 1747.62 (C=O), 2110.26 (N <sub>3</sub> ), 2914.62 (C-H). <sup>1</sup> H NMR (500 MHz, CDCl <sub>3</sub> ):

							δ(PPM) = 3.57 (t, 20CH <sub>2</sub> ), 3.77 (s, 2CH <sub>2</sub> N <sub>3</sub> ), 4.17 (t, 2CH <sub>2</sub> OC=O <sub>2</sub> ). Online
							DOI: 10.1039/D0DT02250K
Nitrate-ester	TEGDN	-	5	0.75	83.92	Light yellow liquid	IR (KBr): v(cm <sup>-1</sup> ) = 908.42 (C-O), 1632.18 (O-NO <sub>2</sub> ), 2897.83 (C-H). <sup>1</sup> H NMR (500 MHz, CDCl <sub>3</sub> ): $\delta$ (PPM) = 3.62 (s, 2OCH <sub>2</sub> ), 3.77 (t, 2OCH <sub>2</sub> ), 4.6 (t, 2CH <sub>2</sub> ONO <sub>2</sub> ). <sup>13</sup> C NMR (125 MHz, CDCl3): $\delta$ (PPM) = 67 (2CH <sub>2</sub> ONO <sub>2</sub> ), 70 (2OCH <sub>2</sub> ), 73 (2OCH <sub>2</sub> ).
	PECH	1,2-DCE	70	0.5	85.00	Viscous colorless liquid	IR (KBr): v(cm <sup>-1</sup> ) = 3472.59 (O-H), 2919.06 (C-H), 1119.95 (C-O), 747.34 (C-Cl). Mn = 1920
 Polymer	GAP	DMAc	90	6	90.00	Viscous yellow liquid	IR (KBr): v(cm <sup>-1</sup> ) = 3446.70 (O-H), 2927.13 (C-H), 2099.36 (N <sub>3</sub> ), 1282.39 (C-O), 1126.97 (C-O). <sup>1</sup> H NMR (500 MHz, CDCl <sub>3</sub> ): δ(PPM) = 3.3 (CH <sub>2</sub> N <sub>3</sub> ), 3.7 (OCH <sub>2</sub> and OCH). <sup>13</sup> C NMR (125 MHz, CDCl3): δ(PPM) = 51.61 (CH <sub>2</sub> N <sub>3</sub> ), 71.14 (OCH <sub>2</sub> ), 78.61 (OCH). Mn = 2190

# Characterization

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The physicochemical properties of the synthesized compounds are given in Table 4. The results of the thermal analysis are also given in Figure 2. The individual DSC curve of each compound is provided in supporting information. The sensitivity of new azido-esters to impact was determined using 2 kg drop weight by Fall Hammer Method. This method based on the calculation of the critical height of which led to 50% ignitions ( $h_{50\%}$ ). The results showed that these two azido-esters are insensitive to mechanical stimuli up to 33.35 J (170 cm). Thus, new azido-esters are much safer than their nitrate-ester counterparts (NG=0.2 J and TEGDN=12.70 J).<sup>51</sup> Also, the TEGBAA is insensitive compared with linear azido-ester plasticizers EGBAA and DEGBAA (5.5 J and >10 J respectively).<sup>15</sup>

#### Comparison between theoretical and experimental characterization

A comparison of the results of the experimental evaluation in Table 4 with the theoretical results (see Table 1) shows appropriate and acceptable concordance for GTAA and TEGBAA azido-esters. The deviation from the experimental glass transition temperature is 0.04 and 9.01 °C for GTAA and TEGBAA azido-esters, respectively. For decomposition temperature, the deviations become 2.06 and 5.31 °C, respectively. The experimental density of these azido-esters has about 0.04 g.cm<sup>3</sup> deviation from theoretical. Also, as predicted theoretically, both synthesized azido-esters are insensitive to external mechanical stimuli. Therefore, the use of molecular dynamics simulations and machine learning methods provides useful tools for the theoretical evaluation of these azido-esters before experimental synthesis and characterization.

Table 4. Physicochemical properties of the synthesized plasticizers and GAP.

Name	Т <sub>G (°С)</sub>	<b>Τ<sub>d (℃)</sub></b>	ρ <sub>(g.cm<sup>-3</sup>)</sub>	Viscosity at 25°C (cP)
GTAA (G <sub>1</sub> )	-55.63	245.65	1.42	71.21
TEGBAA (L <sub>2</sub> )	-61.98	256.70	1.30	40.80
DEGBAA	-65.73	254.99	1.00	36.12
EGBAA	-70.07	251.18	1.34	19.80
TEGDN	<-80	214.57	1.31	10.68
GAP	-53.16	241.41	1.26	1455.92



# **Compatibility with GAP**

The compatibility between binder and plasticizer is an important criterion for choosing optimum plasticizer. The ability to form a homogenized system is one important indication of compatibility between specific polymer and plasticizer. Therefore, to study the compatibility, all synthesized energetic plasticizers were mixed with GAP at a ratio of 50:50 (w/w) at room temperature, and resultant compositions were kept for a month to investigate any phase separation. After this period, no separation and multilayer formation observed. This homogeneity is one indication of the physical compatibility of plasticizers with GAP.

For further investigation, the thermal properties of these compositions examined using DSC analysis. The results of this analysis are given in Figure 3 as well as Table 5. From Table 5, it's clear that all five compositions show a reduction in glass transition temperatures. This lowering is due to diffusion of plasticizer molecules between the polymer chains resulting increase of free volume, which led to weakening the Van der Waals interactions that hold the polymer chains close together. From the thermal stability viewpoint, the azido-esters GTAA ( $G_1$ ), TEGBAA ( $L_2$ ), and DEGBAA<sup>15</sup> have improved the thermal stability of the GAP while EGBAA<sup>15</sup> degrades the thermal stability of its composition with this binder. In the case of TEGDN, there is a different situation. It seems that this nitrateester plasticizer is not fully compatible with GAP since it does not form a homogenized composition. As seen in Figure 3, the two T<sub>d</sub>-values for GAP-TEGDN composition has seen. The glass transition temperature of a GAP-TEGDN composition below -80 °C, due to DSC instrument limitations, it is not possible to accurately detect its transition peak and give an opinion about whether or not it was a single-point. In a homogeneous composition, a single transition peak expected.

The rheological analysis also performed to evaluate the compatibility of these plasticizers with GAP. The viscosity/shear rate curve at 25 °C for GAP and various GAP/plasticizer compositions (50:50) are given in Figure 4. As shown in this plot, the viscosity of the compositions remains almost constant as the shear rate increases. Thus, these compositions exhibit a Newtonian fluid manner. As shown in Table 5, all compositions reduced the viscosity of GAP. The TEGBAA and DEGBAA<sup>15</sup> azidoesters do not appear to make a significant difference in reducing the viscosity of GAP. But the TEGBAA azido-ester is superior to DEGBAA<sup>15</sup> in terms of safety, thermal stability, and molecular weight. The best reduction in viscosity related to GAP/TEGDN composition. GTAA and EGBAA<sup>15</sup> azido-esters almost possess similar viscosity results of their GAP compositions.

Thus, considering the high sensitivity of organic nitrate ester plasticizers, GTAA ( $G_1$ ) and TEGBAA ( $L_2$ ) azido-esters appear to be suitable plasticizers for GAP, since they improve the glass transition temperature, thermal stability, and viscosity of this binder simultaneously. Especially considering factors like the heat of formation, oxygen balance, density, safety, and molecular weight, the GTAA azido-ester seems an ideal energetic plasticizer for GAP.

# Comparison of GTAA and TEGBAA with some energetic azido plasticizers

In the Table 6 the physicochemical and energetic properties of some reported energetic azido-ester and azido-ether plasticizers are compared with GTAA and TEGBAA. The impact sensitivity data in this table show that GTAA and TEGBAA are much safer than comparative plasticizers. The heat of formation of ABAMPA<sup>24</sup> and TADONA<sup>27</sup> are higher than GTAA. But GTAA has a higher density, as we know it, the density has a stronger impact on the energetic properties than heat of formation. Because the density is directly related to the amount

of loadable mass in the constant volume, which ultimately lead to higher energy release per unit volume. In fact, the density has a strong effect on detonation velocity of energetic molecules. So we see that although ABAMPA<sup>24</sup> and TADONA<sup>27</sup> have a higher heat of formation than GTAA, they are actually at the same detonation velocity level. As a result, considering the higher safety of GTAA over ABAMPA<sup>24</sup> and TADONA<sup>27</sup>, this plasticizer can be considered as superior energetic plasticizer in terms of energy and safety properties. In addition, the GTAA as its nitrate-ester counterpart (NG) has a higher oxygen balance among all applicable azido plasticizers. Higher oxygen balance of GTAA is an indication of lower oxygen-deficiency in this plasticizer that finally reduce the amount of needed oxidizer in any formulation. Therefore, due to the specific properties such as high oxygen balance and density, low viscosity, positive heat of formation along with high safety and ultimately good compatibility and high molecular weight (which causes lower migration of this plasticizer from GAP comparing  $\Delta^{22}$  and TADONA<sup>27</sup>), the GTAA seems to be a promising engetic plasticizer for GAP.

On the other hand, a comparison of the azido-ester derivatives of ethylene, diethylene and triethylene glycol indicates high safety and thermal stability of TEGBAA comparing DEGBAA<sup>15</sup> and EGBAA<sup>15</sup>. In terms of the glass transition temperature, the EGBAA<sup>15</sup> seems to be in a better position, but this plasticizer is volatile due to its low molecular weight. So it's not a suitable plasticizer for GAP. Among this series, considering the similar viscosity and efficiency of DEGBAA<sup>15</sup> and TEGBAA on GAP, TEGBAA certainly superior plasticizer for GAP due to its higher molecular weight and safety.

Table 5. Effect of plasticizers on the thermal properties of GAP.

1       GAP + 50% GTAA (G1)       242.32       -63.79       192.30         2       GAP + 50% TEGBAA (L2)       246.80       -68.56       261.69	<b>Τ</b> <sub>G</sub> (℃)	b. Compositions $T_{d}(\tilde{c})$	Viscosity at 25°C <sub>(cP)</sub>
2         GAP + 50% TEGBAA (L <sub>2</sub> )         246.80         -68.56         261.69	-63.79	GAP + 50% GTAA (G <sub>1</sub> ) 242.32	192.30
	-68.56	<b>GAP + 50% TEGBAA (L<sub>2</sub>)</b> 246.80	261.69
<b>3 GAP + 50% DEGBAA</b> 242.97 -71.26 260.64	-71.26	<b>GAP + 50% DEGBAA</b> 242.97	260.64
4         GAP + 50% EGBAA         238.16         -73.12         171.16	-73.12	GAP + 50% EGBAA 238.16	171.16
5         GAP + 50% TEGDN         207.20, 243.47         <-80	47 <-80	<b>GAP + 50% TEGDN</b> 207.20, 243.47	100.39



Figure 3. Thermal stability of the different GAP/plasticizer compositions.



Figure 4. The viscosity of the different GAP/plasticizer compositions.

Table 6. Comparison of GT.	A and TEGBAA with	some azide plasticizers.
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Name	IS <sub>(J)</sub>	<b>ρ</b> (g.cm <sup>-3</sup> )	$\Delta H^{\circ}_{f(kJ.mol^{1})}$	D (km.s <sup>-1</sup> )	OB%	η <sub>(25°C) (cP)</sub>	Т <sub>d (°С)</sub>	Т <sub>G (°С)</sub>	M.W. (g.mol <sup>.1</sup> )
GTAA	>33.35	1.42	89.75	6.46	-82.04	71.21	245.65	-55.63	341.29
TADONA <sup>27</sup>	>25.20	1.28	857.30	6.80	-97.21	-	236.80	-88.90	296.25
ABAMPA <sup>24</sup>	16.00	1.32	1725.00	6.41	-92.52	-	235.90	-50.40	294.24
TEGBAA	>33.35	1.30	-434.88	4.46	-111.30	40.80	256.70	-61.98	316.27
DEGBAA <sup>15</sup>	>10	1.00	-328.86	4.74	-99.92	36.12	254.99	-65.73	272.22
EGBAA <sup>15</sup>	5.50	1.34	-167.36	5.74	-84.15	19.80	251.18	-70.07	228.20

# Conclusions

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Two new azido-ester plasticizers include glyceryl tris(azidoacetate) (GTAA) and triethyleneglycol bis(azidoacetate) (TEGBAA) selected, synthesized, and characterized among 20 theoretical chemical structures using computer-aided molecular design. These plasticizers selected considering the balance between several criteria including solubility parameter ( $\delta$ ), the heat of formation ( $\Delta H_{f}^{\circ}$ ), glass transition temperature ( $T_G$ ), density ( $\rho$ ), decomposition temperature ( $T_d$ ), detonation velocity (D), impact sensitivity (h<sub>50%</sub>), low-cost available starting materials, straightforward synthetic route, oxygen balance (OB%), and tendency to migration. Theoretical calculations performed using molecular dynamics simulations as well as machine learning-based methods. Comparisons of the results of theoretical calculations and experimental analyses were mutually acceptable. The compatibility of synthesized plasticizers with glycidyl azide polymer (GAP) also investigated using rheometry and thermal analyses. The results show that these two new azido-ester plasticizers improved the viscosity, glass transition temperature as well as the thermal stability of glycidyl azide polymer simultaneously. In addition, the compatibility results of these two new azido-ester plasticizers compared with ethylene glycol bis(azidoacetate) (EGBAA), diethylene glycol bis(azidoacetate) (DEGBAA) and triethylene glycol dinitrate (TEGDN) plasticizers. The results of this comparison show that the plasticizing effect of TEGBAA is similar to DEGBAA, also TEGBAA safer than DEGBAA and its nitrate-ester counterpart (TEGDN) in terms of impact sensitivity. In addition, the molecular weight of TEGBAA higher than DEGBAA which means that this new plasticizer has a lower migration tendency. The results also showed that the GTAA is an ideal energetic plasticizer for GAP because it simultaneously improves the thermal, rheometrical, and energetic properties of GAP. This study also showed that the azidoester plasticizers are more compatible with GAP than highly sensitive nitrate-ester plasticizers.

# Conflicts of interest

There are no conflicts to declare.

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Figure 2.

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Figure 3.



Figure 4.

# **Table of Content**

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Theoretical evaluation applied to select optimal green energetic plasticizers from theoretic structures. Two azido-esters synthesized and evaluated for GAP.



TOC graphic

112x45mm (299 x 299 DPI)