EILs – suitable substances for future energetic applications?

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ABSTRACT

Salts being liquid below 100 °C are defined as ionic liquids. They are receiving an increasing interest due to their unique properties and they are also under investigation in the field of energetic materials. Combining nitrogen-rich cations and oxygen-rich anions, it is possible to obtain energetic ionic liquids (EILs). Potential applications are plasticizers, high explosives, gun and rocket propellants. Because of the very low vapor pressure of EILs better storage and handling properties are expected.

However, only few work has been done in the field of EILs which show a glass transition temperature less than or equal to -40 °C, the so called low-temperature EILs (LT-EILs). Potential applications and limitations of LT-EILs based on 4-Amino-1-methyl-1,2,4-triazolium nitrate are presented. Some compounds of this class are studied as plasticizers in energetic binder systems (nitrocellulose and glycidyl azide polymer) and are compared to traditional energetic plasticizers like BDNPA/F and TMETN/BTTN.

INTRODUCTION

Ionic liquids (ILs) are commonly defined as organic salts being liquid at room temperature with unusually low melting points[1]. They are in the focus of recent research and finding application in more and more fields of life. The application range include novel reaction media[2], as electrolytes in batteries[3], solar cells[4], gas storing media[5], lubricants[6] and heat transfer fluids[7], to mention only a small excerpt of the investigated and in use applications. The research on ILs began already in 1888 with ethanolammonium nitrate (mp 52-54 °C), an energetic protic IL synthesized and characterized by Gabriel[8] and ethylammonium nitrate (mp 13-14 °C; Paul Walden 1914[9]). However, the new class of ionic liquids only became subject of interest in the late 1990s, where the publications on ILs started growing exponential. The fundamental principle of EILs is shown in Figure 1. The cation normally acts as a fuel and the anion as an oxidizer.

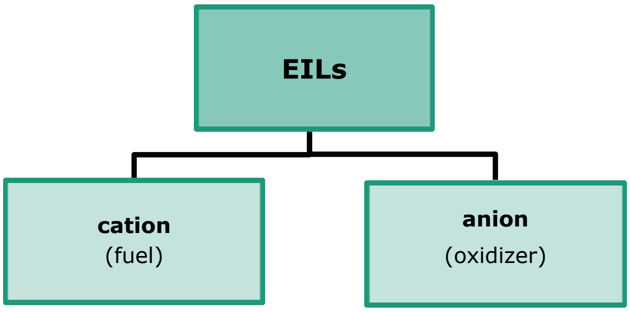

Figure 1: The fundamental principle of EILs.

In the field of energetic materials and processing, ionic liquids receive serious interest. The EILs can be divided into three different categories as shown in Figure 2.

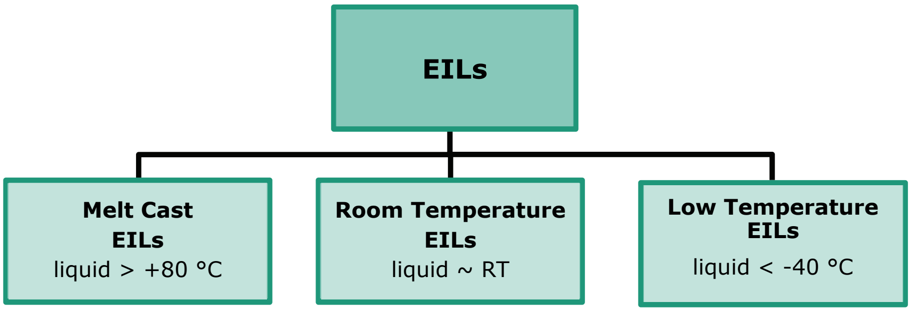

Figure 2: Subdivision scheme of EILs by temperature range.

For Melt Cast EILs, melting points (T_m) above 80 °C are crucial to replace the toxic Trinitrotoluene (TNT), which shows poor Insensitive Munitions (IM) properties [10].
The developments in this area began already at the beginning of the 20th century in search of castable explosive mixtures of energetic salts with low melting points (e. g. dimethylammonium nitrate or hydrazinium nitrate) [11].
Besides the hydroxylammonium based EILs, which are solid at RT (e. g. hydroxylammonium nitrate or hydroxylammonium azide [12] ammonium dinitramide (ADN) with its melting point of 92 °C [13] is part of the Melt Cast EILs and by far the most studied representatives of the entire EIL class.

RESULTS AND DISCUSSION

As an example of an energetic ionic liquid we investigated 4-Amino-1-methyl-1,2,4-triazole nitrate (AMTN), which was first mentioned in literature 2002 by Greg W. Drake et al.[14]. AMTN offers a wide operation temperature range from a glass transition temperature of -54 °C and a decomposition temperature above 200 °C. The mechanical sensitivity of AMTN towards friction and impact is low (20 Nm and >360 N) as shown in Figure 3.

properties		AMTN
impact sensitivity	[Nm]	20
fricition sensitivity	[N]	>360
glass transition temperature	[°C]	-54
decomposition temperature	[°C]	+249

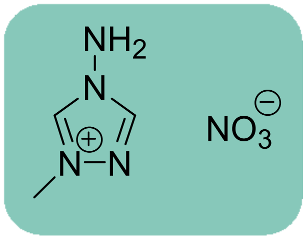

Figure 3: Mechanical sensitivity data, thermal properties and chemical structure of AMTN.

The density of this EIL is quite high with 1,4 g/cm^3 due to its ionic nature. The viscosity of C1 N (454 mPa s at 20 °C) is higher compared to traditional plasticizers. The density and viscosity of AMTN in relation to the temperature is shown in Figure 4.

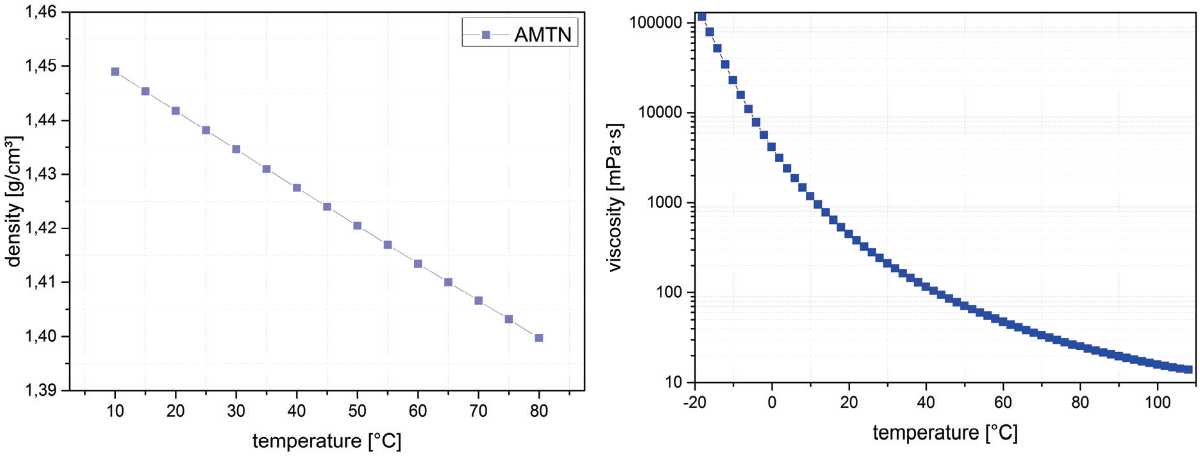

Figure 4: Temperature dependent density and viscosity of C1 N.

In contrary to conventional plasticizers like NGL, Bu-NENA and DNDA57, AMTN does not evaporate upon heating in nitrogen stream up to 120 °C due to its ionic nature (see Figure 5). Because of this very low vapor pressure a significantly reduced environmental risk and better storage and handling properties are expected.

plasticizer	mass loss [wt%]
NGL	30
Bu-NENA	23
DNDA57	12
AMTN	0

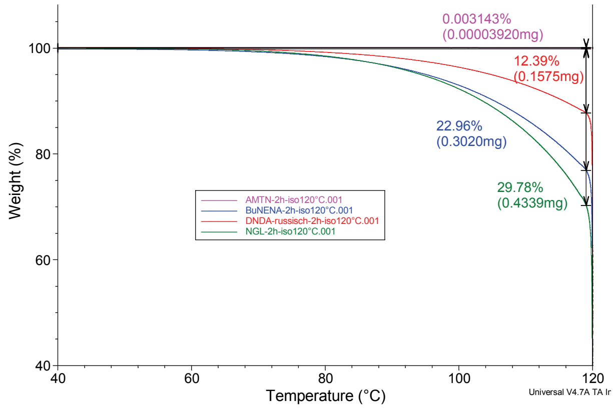

Figure 5: Mass loss of different energetic plasticizers during heating in a nitrogen stream.

Properties of conventional energetic plasticizers and AMTN are shown in Figure 6 and Figure 7. AMTN offers a wide operating temperature range with good mechanical insensitivity and a high gas volume yield at decomposition conditions.

	Glass transition temperature (DSC midpoint) [°C]	Decomposition temperature (TGA midpoint) [°C]	Impact sensitivity [Nm]	Heat of explosion [c] [J/g]	Oxygen balance [%]	Gas volume [d] [cm^3/g]
NGL	+13[a]	149	0,2	6675	+3.5	512
EGDN	-23[a]	78 (155)[b]	0,2	7289	0	483
BTTN	-65	176	1	6022	-16.6	634
TMETN	-62	155	1	5053	-34.5	794
Bu-NENA	-48	152	6	3573	-104.3	1045
DNDA57	-52	159	3	3848	-72.3	1078
BDNPAF	-67	182	3	3469	-57.6	957
AMTN	-54	249	20	3468	-64.6	1049

Figure 6: Comparison of conventional energetic plasticizers to AMTN.
[a] melting point [b] vaporisation of EGDN / in brackets with semi-closed vessel [c] calculated by ICT-Thermodynamic code (water liquid) [d] without H_2O at 25 °C.

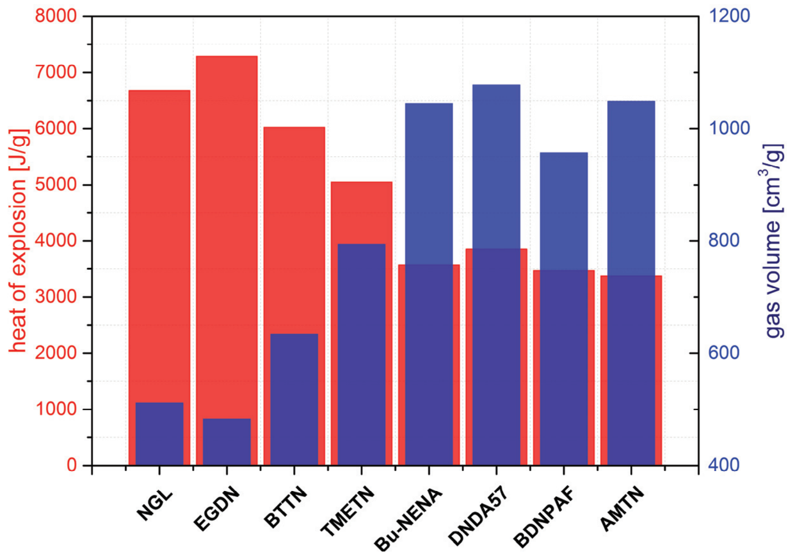

Figure 7: Heat of explosion and gas volume of energetic plasticizers.

The long term stability was investigated and found to be very good. A TAM measurement of AMTN at 80 °C and 15 days revealed no significant generation of heat as shown in Figure 8.

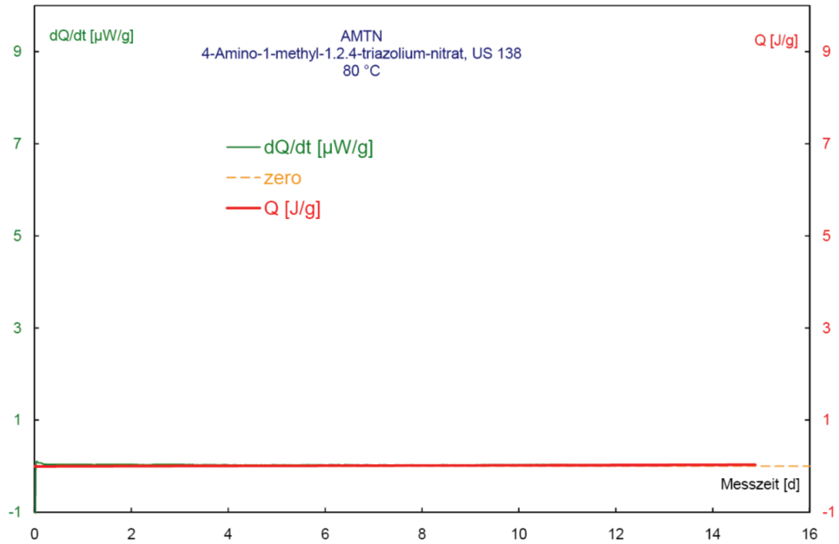

Figure 8: Heat Flow Calorimetry measurement of AMTN in a Thermal Activity Monitor calorimeter at 80 °C and 15 days.

Additionally AMTN has interesting plasticizing abilities. The gelatination of NC (N = 12.6%) with AMTN (50:50 wt%) is fast and produces transparent flexible foils which is shown in Figure 9. Thermal analysis of the material revealed a glass transition temperature of -33 °C and an onset decomposition temperature of 170 °C (DSC, HR5, Figure 10). However, the onset decomposition temperature is 4 °C lower compared to NGL/NC measured under the same conditions.

Figure 9: Microscopic picture of AMTN / NC (left) and flexible, transparent foil of C1 N / NC.

	DSC onset [°C]
NC	194
NC / NGL	174
NC / AMTN	170

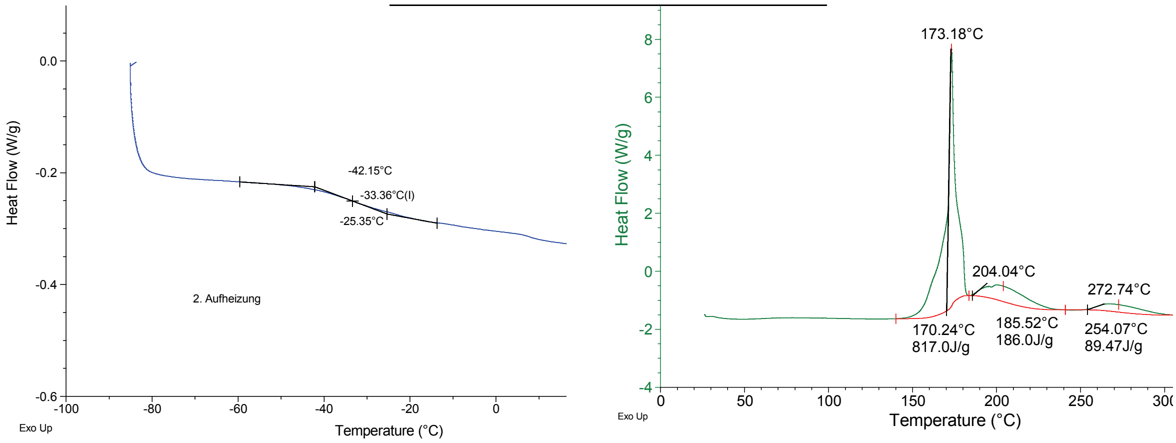

Figure 10: Glass transition temperature and decomposition temperature of NC/AMNT and comparison to NGL and pure NC.

Rheological measurement of energetic plasticizers with 5 wt% NC shows that AMTN has the lowest absolute viscosity of the investigated mixtures demonstrating its promising gelatination abilities which even exceeds NGL. EGDN with the addition of 5 wt% NC shows too high viscosity to be measured under chosen conditions.

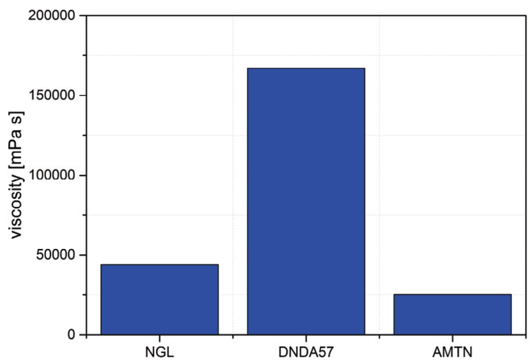

Figure 11: Viscosity of NGL, DNDA57 and AMTN with 5 wt% of NC at a shear rate of 10,8 s^{-1}.

Upon performing long term stability tests at 80 °C and 105 °C for 20 and 75 hours AMTN revealed to be not long term stable with NC. Even with the addition of traditional stabilizers like Centralite I and Akardite II the maximum allowed mass loss was exceeded reproducible. The investigated samples turned yellow to brown. The long term incompatibility of AMTN with nitrate ester groups derives most likely from the slightly acid nature of the proton in the position number 5 in the ring shown in Figure 12.

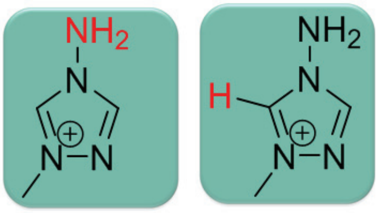

Figure 12: N-Amino functionality (left), slightly acid proton in position 5 of AMTN (right).

An example of an extreme incompatibility of NC with ILs is the commercial 1-Ethyl-3-methylimidazolium acetate shown in Figure 13.

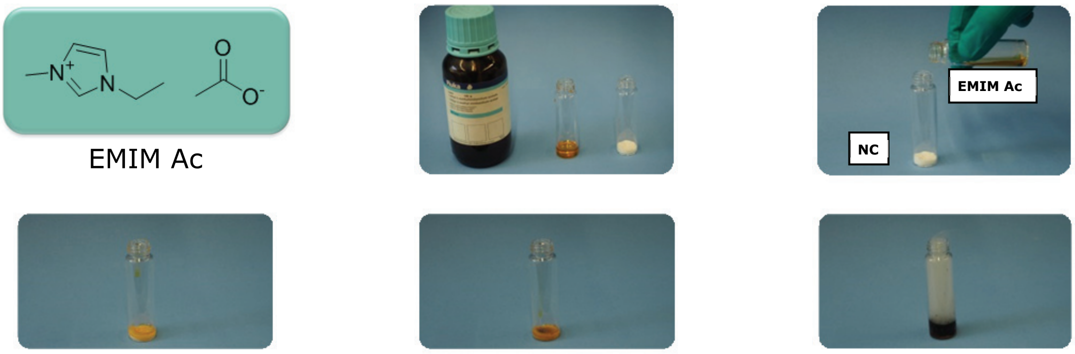

Figure 13: Decomposition of NC by the commercial IL 1-Ethyl-3-methylimidazolium acetate.

Upon pouring EMIM Ac on NC the NC turns black and will subsequently decompose violently.

The use of AMTN as an energetic plasticizer in GAP formulations was investigated by mixing GAP-Diol with AMTN (90/10 wt%) and by using DESMODUR N 100 as the isocyanate compound (NCO/OH = 1:1) to produce tensile test specimens (dog bone shape). Besides AMTN traditional energetic plasticizers like BDNPA/F and TMETN/BTTN were used shown in Figure 14.

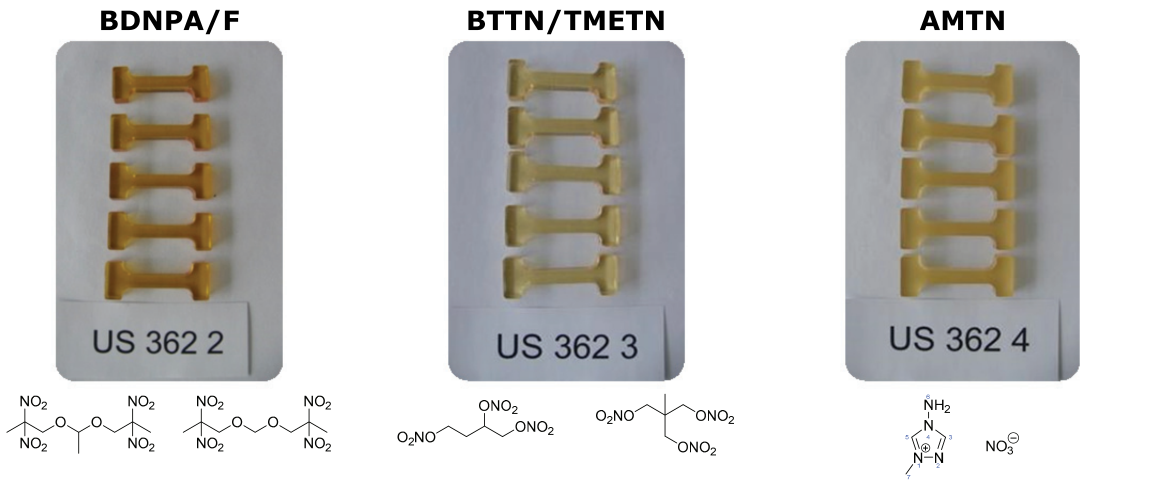

Figure 14: Cured GAP-Diol Isocyanate (N100) tensile specimens with BDNPA/F (left), BTTN/TMETN (middle) and AMTN (right) as energetic plasticizers (10wt%).

The mechanical test results of the different cured GAP/N100 binder systems with energetic plasticizers are shown in Figure 15.

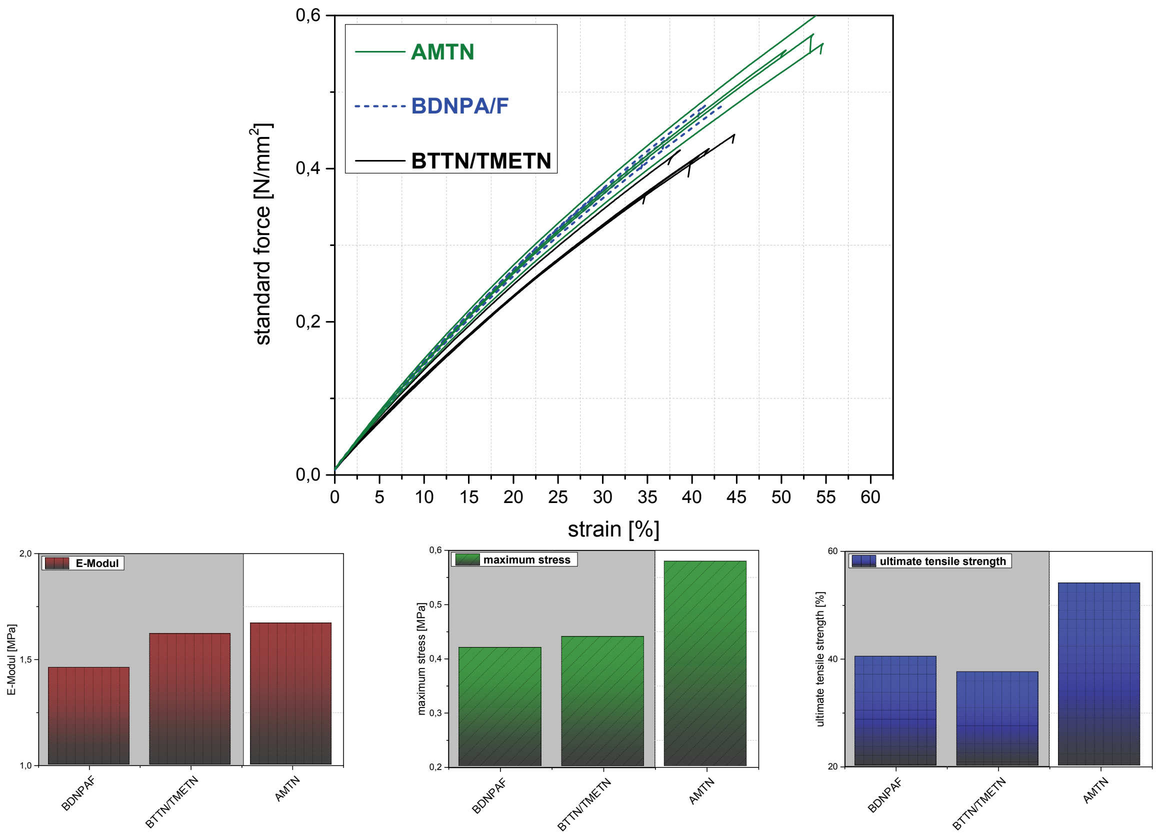

Figure 15: Mechanical properties of produced test specimens with GAP/N100 and energetic plasticizers.

The binder system GAP containing AMTN as an energetic plasticizer shows a higher E-module, higher maximum stress and a higher ultimate tensile strength (strain at maximum stress) compared with identical compositions in which AMTN has been replaced by traditional energetic plasticizers like BDNPA/F and BTTN/TMETN.

The thermal properties were investigated with accelerating rate calorimeter (ARC) shown in Figure 16. Compared to BDNPA/F and BTTN/TMETN the binder system with AMTN as an energetic plasticizer shows enhanced thermal stability.

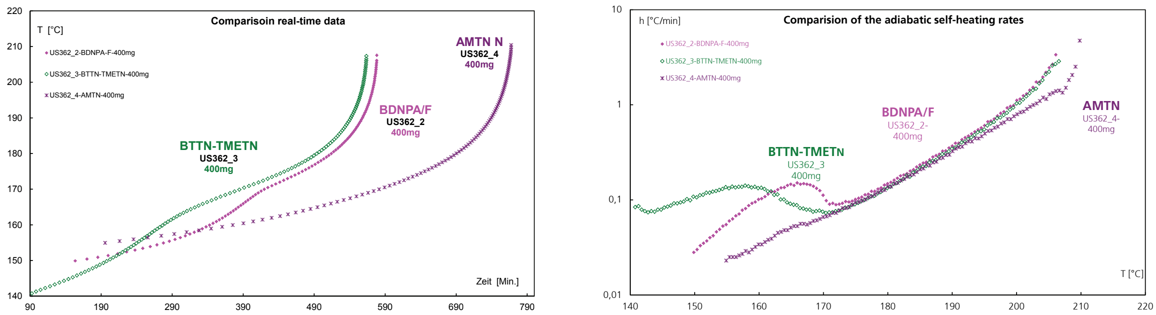

Figure 16: Accelerating rate calorimeter of cured binder system (GAP/N100) and energetic plasticizers (BDNPA/F, BTTN/TMETN and AMTN).

CONCLUSION

The nitrate based EIL AMTN offers promising properties like very low vapor pressure combined with good energetic performance and insensitivity compared to traditional energetic plasticizers. However, AMTN is not compatible with nitrocellulose in terms of long term stability. In the binder system GAP/N100 with energetic plasticizers the AMTN containing binder system is superior in terms of mechanical properties and thermal stability.

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