



Energetic Nitrogen-Rich Polymers Based on Cellulose

Franziska M. BETZLER, Thomas M. KLAPÖTKE
and Stefan SPROLL

*Department of Chemistry,
Ludwig-Maximilians University of Munich,
Butenandtstr. 5-13 (Haus D), D-81377 Munich, Germany
E-mail: tmk@cup.uni-muenchen.de*

Abstract: New nitrogen-rich polymers, based on cellulose, were synthesized using common procedures. The point of interest was the introduction of tetrazole and nitramine moieties. The polymers were characterized by elemental analysis and vibrational spectroscopy (IR). The energetic properties were investigated using differential scanning calorimetry and bomb calorimetric measurements. Several detonation parameters, such as the detonation pressure, velocity, energy and temperature were computed using the EXPLO5 code. In addition, the sensitivities towards impact and friction were tested using the BAM drophammer as well as a friction tester.

Keywords: energetic polymer, nitrogen rich polymer, cellulose, tetrazole, nitramine

Introduction

Nitrogen-rich polymers are to date used as binder in energetic compositions [1] and as gas generating agents [2]. So far, commonly used polymers are nitrocellulose [3], azidocellulose nitrate [4], or glycidyl azide polymer (GAP) [5]. The disadvantages of these polymers are the energetic azide [6] and nitro group [7] moieties. These compounds are toxic and can be released into the environment by degradation of residues of unburned parts of the explosive composition [8]. In order to replace these toxic substances, new energetic polymers have to be developed.

The advantage of cellulose as a polymer is the easy and cheap availability,

as well as the high amount of contained oxygen [9]. This can be improved by nitration, or addition of nitrogen rich compounds, generating desired decomposition products. Due to this matter of fact, nitrocellulose [10] has been established as a binder and propellant.

The free hydroxyl groups of cellulose can be used to link the polymer to small, nitrogen rich molecules. But the applications of nitrocellulose are limited, because no further modifications are possible. Therefore, the search for molecules that can be linked to cellulose and that offer more possibilities than nitrocellulose, could lead to a new group of energetic polymers. Nevertheless, these molecules should contain a high amount of oxygen and nitrogen by themselves, because when used as explosive binder or propellant, they should not decrease the efficiency of the compound.

To date, only few efforts have been made to develop new energetic materials based on cellulose. Nevertheless, tetrazole and nitramine moieties can be applied to cellulose to form energetic polymers which can be more energetic as well as on the other hand be more thermal and physical stable, than nitrocellulose.

Experimental

The impact and friction sensitivity tests were carried out according to STANAG 4489 [11] and STANAG 4487 [12] modified instructions [13] using a BAM (Bundesanstalt für Materialforschung) drophammer and friction tester [14]. The classification of the tested compounds results from the "UN Recommendations on the Transport of Dangerous Goods". The Bomb calorimetric measurements were determined with a Parr 1356 isoperibol bomb calorimeter with a Parr 207A oxygen bomb. The calorimeter was calibrated by means of the combustion of benzoic acid in oxygen atmosphere at 60 bar in an 1104 oxygen combustion bomb. Differential scanning calorimetry (DSC) measurements to determine the melt- and decomposition temperatures were performed in covered Al-containers containing a hole in the lid and a nitrogen flow of 20 mL per minute on a Linseis PT 10 DSC [15] calibrated by standard pure indium and zinc at a heating rate of 5 °C min⁻¹. The carbon, hydrogen, nitrogen and sulfur content were determined by an Elementar vario EL by means of high temperature decomposition. The infrared spectra were determined by a Perkin Elmer Spectrum BX FT-IR-System.

A determining problem of doing experiments with cellulose is the insolubility of this material in any common solvent, because of the supra-molecular structure [9a]. The dissolution of cellulose destroys the highly organized hydrogen-

bonding system surrounding the single polyglucan chain. The system *N,N*-dimethylacetamide (DMA)/LiCl as solvent, shows an enormous potential for the analysis of cellulose and for the preparation of a wide variety of derivatives. Its usefulness in analysis derives from the fact that the solvent is colorless and dissolution succeeds without or at least with negligible degradation, even in case of high molecular weight polysaccharides.

Consequently, the first step in doing reactions with cellulose is its dissolution. This was performed by the procedure of K. Rahn *et al.* [16] gaining a solution containing 4.3 wt. % cellulose.

Therefore, dried cellulose (Avicel PH 101) was suspended in *N,N*-dimethylacetamide, kept at 160 °C for one hour and stirred. In order to replace water bound to cellulose, a small amount of *N,N*-dimethylacetamide was removed by heating the solution. After the slurry had been cooled down to 100 °C, anhydrous lithium chloride was added. By cooling to room temperature and stirring, the cellulose dissolved completely within some hours, resulting in a yellowish solution of 4.3 wt. % cellulose.

1-Cellulose-2-(1*H*-tetrazol-1-yl) acetate (CTA)

2-(1*H*-Tetrazol-1-yl) acetic acid (0.5 g, 3.9 mmol) and a cellulose solution (4.3 wt. %, 3.7 g, 1.02 mmol) were refluxed with 4-toluenesulfonyl chloride (0.75 g, 3.9 mmol) in 5 mL *N,N*-dimethylacetamide at 60 °C. After 24 hours the resulting suspension was emptied into water. The product was filtered off, washed with acetonitrile and the remaining solvent was removed under reduced pressure. The polymer was obtained as brown solid. (0.24 g, 96%).

IR $\tilde{\nu}$ / cm⁻¹ (intensity): 3260 (s), 2963 (m), 2918 (m), 2252 (w), 2128 (w), 1753 (s), 1629 (m), 1552 (m), 1420 (m), 1325 (m), 1261 (m), 1166 (m), 1166 (s), 1102 (s), 1054 (s), 925 (w), 800 (w), 657 (w), 570 (w). **Elemental analysis:** calcd (%) for C₉H₁₂N₄O₆: C 37.22, H 3.90, N 21.70; found: C 39.02, H 4.41, N 21.30. **DSC:** melting area: 40-185 °C, point of decomposition: 215 °C.

1-Nitrocellulose-2-(1*H*-tetrazol-1-yl) acetate (NCTA)

1-Cellulose-2-(1*H*-tetrazol-1-yl) acetate (1 g, 3.03 mmol) was dissolved in 3 mL acetic anhydride as well as 1.5 mL nitric acid and stirred at room temperature. After two hours the liquid was emptied into ice water and the product was filtered off. It was obtained as pale yellow glasslike solid. (0.77 g, 65%).

IR $\tilde{\nu}$ / cm⁻¹ (intensity): 3436 (s), 3148 (w), 2963 (w), 1767 (m), 1708 (m), 1645 (m), 1485 (m), 1436 (m), 1384 (m), 1285 (m), 1262 (m), 1230 (m) 1176 (m), 1101 (m), 1063 (m), 1020 (m), 826 (m), 796 (m), 745 (w), 700 (w), 654 (w), 571 (w), 531 (w). **Elemental analysis:** calcd (%) for C₉H₁₀N₆O₈: C 35.89, H 3.68,

N 23.25; found: C 35.36, H 3.25, N 24.14. **DSC**: melting area: 40-200 °C; point of decomposition: 200 °C.

Butylaminocellulose (BAC)

To a solution of tosylcellulose [16] (1 g, 3.16 mmol) in 30 mL *N,N*-dimethylformamide, butylamine (1.87 mL, 18.97 mmol) was slowly added. The suspension was refluxed for three days at 100 °C.

The resulting solution was emptied in water. Because no precipitate was formed, the solvent was removed under reduced pressure and the product was obtained as brown oil. (3.46 g, 94%).

IR $\tilde{\nu}$ / cm⁻¹ (intensity): 3292 (m), 3040 (m), 2957 (m), 2931 (m), 2873 (m), 1627 (vs), 1549 (m), 1496 (m), 1458 (m), 1397 (m), 1264 (m), 1220 (m), 1175 (s), 1121 (s), 1033 (s), 1013 (vs), 816 (m), 740 (w), 711 (w), 680 (vs). **Elemental analysis**: calcd (%) for C₁₄H₂₈N₂O₃: C 61.73, H 10.36, N 10.28; found: C 53.19, H 9.46, N 10.59.

Butylnitraminocellulose (BNAC)

Butylaminecellulose (1 g, 3.67 mmol) was dissolved in 4 mL acetic anhydride as well as 2 mL nitric acid and stirred at room temperature. After two hours the liquid was emptied in water and the product was filtered off. The product was obtained as yellowish solid (0.84 g, 63%).

IR $\tilde{\nu}$ / cm⁻¹ (intensity): 3552 (s), 3477 (vs), 3416 (vs), 2966 (m), 2940 (m), 1721 (m), 1662 (vs), 1619 (m), 1529 (w), 1384 (s), 1281 (s), 1192 (m), 1178 (m), 1072 (m), 1037 (m), 839 (m), 746 (w), 672 (w), 621 (w), 477 (w). **Elemental analysis**: calcd. (%) for C₁₀H₁₈N₂O₆: C 45.80, H 6.92, N 10.68; found: C 39.09, H 5.12, N 11.49. **DSC**: melting area: 107-151 °C, point of decomposition: 151 °C.

Methylaminocellulose (MAC)

To a solution of tosylcellulose [16] (5.00 g, 12.71 mmol) in 250 mL *N,N*-dimethylacetamide, methylamine (40% in H₂O, 37.48 mL, 535.77 mmol) was added. The suspension was refluxed for 48 hours at 60 °C. The resulting solution was emptied in 1L isopropyl alcohol. The formed precipitate was filtered and washed with water. The product was obtained as colorless solid [17] (1.17 g, 49%).

IR $\tilde{\nu}$ / cm⁻¹ (intensity): 3341 (m), 2897 (m), 2361 (m), 2337 (m), 2159 (w), 1986 (w), 1623 (s), 1498 (m), 1415 (m), 1398 (m), 1358 (m), 1266 (w), 1187 (m), 1173 (m), 1058 (vs), 1037 (vs), 1011 (vs), 816 (m). **Elemental analysis**: calcd (%) for C₇H₁₃NO₄: C 47.99, H 7.48, N 8.00; found C 47.62, H 7.60, N 8.09.

Methylnitraminocellulose (MNAC)

Methylaminocellulose (1 g, 5.71 mmol) was dissolved in 4 mL acetic anhydride as well as 2 mL nitric acid and stirred at room temperature. After two hours the liquid was emptied in water and the product was filtered off. The product was obtained as yellowish solid (0.92 g, 59%).

IR $\tilde{\nu}$ / cm^{-1} (intensity): 3553 (s), 3477 (vs), 3415 (vs), 2927 (w), 2031 (w), 638 (m), 1618 (m), 1385 (w), 1277 (w), 1177 (w), 1110 (w), 829 (w), 710 (w), 617 (m), 479 (w). **Elemental analysis**: calcd (%) for $\text{C}_7\text{H}_{11}\text{N}_3\text{O}_8$: C 31.71, H 4.18, N 15.85; found C 29.02, H 3.33, N 15.17. **DSC**: melting area: 141-172 °C, point of decomposition: 172 °C.

Results and Discussion

Polymers based on cellulose containing tetrazole moieties

Tetrazoles are nitrogen rich compounds, covering a wide range of applications, amongst others they are used as pharmaceuticals [18], membranes [19], or as energetic materials [20]. The advantages of tetrazoles include that the tetrazole moiety itself possesses a nitrogen content of 80% along with a combination of high-energetic character with sufficient thermal stability [21]. Therefore, they are often used in gas generators, but can also be useful for an application as energetic polymers. Nevertheless, to date, within the wide range of applied nitrogen rich polymers, compounds containing tetrazole moieties are rare. Therefore these groups were applied to obtain polymers based on cellulose with a high content of nitrogen.

1-(1*H*-Tetrazol-1-yl) acetic acid was introduced to cellulose to obtain 1-cellulose-2-(1*H*-tetrazol-1-yl)acetate (CTA), presuming its high nitrogen content and its high thermal stability. A further advantage of this molecule is the possibility of increasing the nitrogen content of this compound even more by nitration, giving 1-nitrocellulose-2-(1*H*-tetrazol-1-yl)acetate (NCTA).

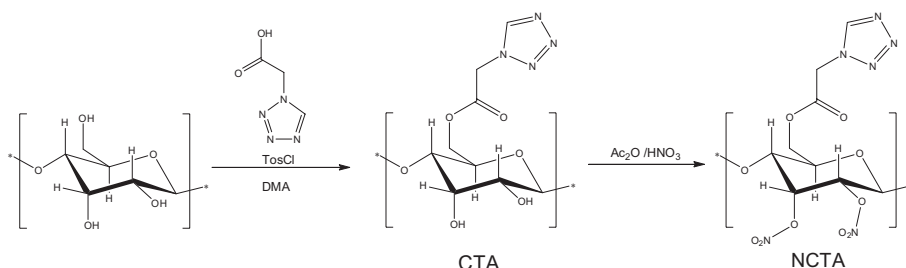


Figure 1. Synthesis of CTA and NCTA.

CTA was obtained in high yields (97%). The degree of substitution was estimated by elemental analysis. Comparing different degrees of substitution, CTA gave the highest conformance with a degree of substitution of 1.2 tetrazole moieties per glucose unit. An explanation of this effect is the higher availability of the methylene hydroxyl group, compared to the hydroxyl groups of the ring system. The comparison of different degrees of substitution, according to the elemental analysis of NCTA, depicted that the carbon and hydrogen content of this compound suited better to a degree of substitution of one nitro group per free hydroxyl group, whereas the nitrogen content fitted better when two hydroxyl groups were substituted by nitrogen groups. Therefore still *N,N*-dimethylacetamide, HNO₃ or NO₂, respectively, are contained.

To analyze the degree of conversion, vibrational spectroscopy is also a useful analytical method. For this reason the comparison of the infrared spectra of CTA and NCTA showed that both spectra still contain unoccupied hydroxyl groups, because of the OH-vibration at about 3400 cm⁻¹. Furthermore the C=O vibration at 1629 cm⁻¹ demonstrates the ester linkage between the cellulose and the tetrazole moiety is formed in CTA and is still present at 1750 cm⁻¹ in NCTA. The infrared spectrum of NCTA shows the expected appearance of vibrations of the nitro groups at 1630 cm⁻¹ and 1342 cm⁻¹, indicating a successful nitration [22].

In accordance with the expected results, the thermal stability of NCTA, shown in Figure 2 was lower than that of CTA. The melting area of NCTA starts at 40 °C and ends with the point of decomposition at 200 °C. However it has two decomposition points, the first decomposition point at about 175 °C is the decomposition of the nitrate ester, whereas the second one at about 200 °C is the decomposition of the tetrazole ring, which is comparable to that of CTA. This compound has a melting area ranging from 40 °C to 185 °C, whereas the point of decomposition of CTA is at 215 °C.

The sensitivity data was obtained using a BAM [14] drophammer and friction tester. These methods obtained that CTA and NCTA are insensitive against impact of 100 J and friction of 360 N and can therefore be regarded as insensitive. Besides compared to commonly used nitrocellulose (impact sensitivity: 3 J, friction sensitivity: > 353 N) [23], it has a better response to impact and friction, which can be regarded as a clear advantage in terms of safety. The energetic values of the energy of explosion, the explosion temperature, the detonation pressure, the detonation velocity and the gas volume have been calculated using the enthalpies of formation and the EXPLO5 5.04 program [24]. This program also contains the corresponding data of nitrocellulose which has a practical maximum value of nitrogen content of ca. 13.4% [23], and is therefore calculated with a nitrogen content of 13.5%.

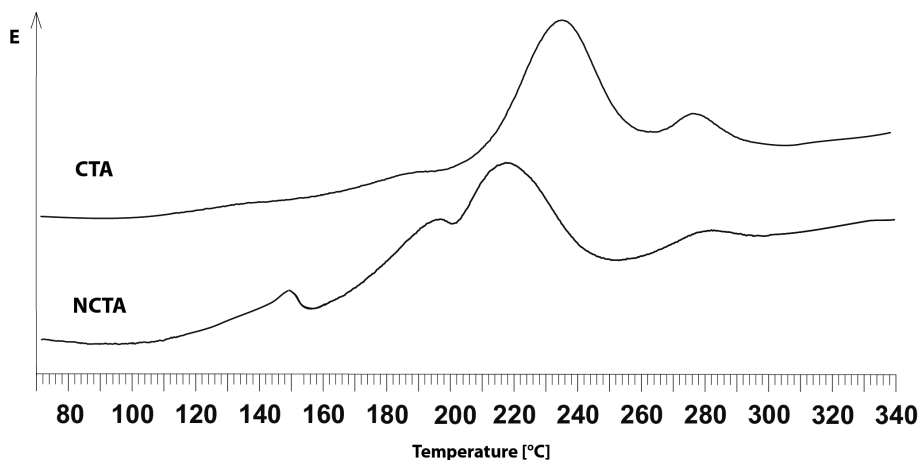


Figure 2. DSC data of CTA and NCTA.

Table 1. Bomb calorimetric data of NCTA

	NCTA	Nitrocellulose (13.5%) ^k
Formula	C ₉ H ₁₀ N ₆ O ₁₀	C ₆ H _{7.26} N _{2.74} O _{10.48}
Molecular mass (g mol ⁻¹)	362.21	285
Density (g cm ⁻³) ^a	1.5 (for calculation)	1.5 (for calculation)
-ΔU _{comb.} (cal g ⁻¹) ^b	2944	-
-ΔH _{comb.} (kJ mol ⁻¹) ^c	1207	-
-Δ _f H _m (kJ mol ⁻¹) ^d	1237	-
Values calculated by Explo5 V5.04		
-Δ _E U _m ^o (kJ kg) ^e	3930	4890
T _E (K) ^f	3216	3933
p _{c-J} (kbar) ^g	66	81
D (m s ⁻¹) ^h	4851	5279
Gas vol. (L kg ⁻¹) ⁱ	725	744
I _s (s) ^l	187	232
I _s (s) ^m (70 % AND)	242	236

^a estimated from a structure determination, ^b experimental (constant volume) combustion energy, ^c experimental molar enthalpy of combustion, ^d molar enthalpy of formation, ^e energy of explosion, ^f explosion temperature, ^g detonation pressure, ^h detonation velocity, ⁱ assuming only gaseous products, ^k obtained from the database of EXPLO5 V5.04, ^l specific impulse (isobaric combustion, chamber pressure 60 bar, frozen expansion), ^m specific impulse containing 70% ammonium dinitramide as oxidizer.

Given that the nitration of the polymer destroyed the cellulose chains, and the right length of the polymer cannot be stated, the calculation was done by calculating with the monomers of the cellulose derivatives.

According to the calculated values, the temperature of explosion of NCTA is lower than that of nitrocellulose. Therefore, it diminishes the erosion when applied. The detonation pressure and the detonation velocity of NCTA are slightly lower, too. However, by addition of an oxidizer, like ammonium dinitramide (ADN), the specific impulse is higher than that of nitrocellulose and hence predicts a good performance.

Polymers based on cellulose containing nitramine moieties

Butylamine was introduced to cellulose to increase the nitrogen content of the derivative. Furthermore, this product has the advantage of the possibility being oxidized to butylnitraminocellulose (BNAC), which has higher nitrogen content than butylaminocellulose (BAC) and should be more stable and more energetic than nitrocellulose. To further increase the nitrogen content, methylamine was introduced to cellulose, as well, to achieve methylnitraminocellulose (MNAC) by further nitration and therefore obtaining a highly energetic and nitrogen rich polymer.

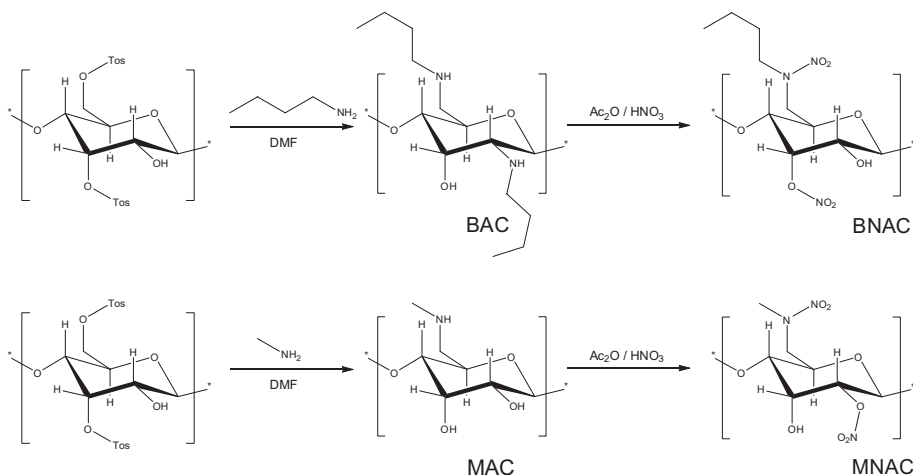


Figure 3. Synthesis of BAC, BNAC, MAC and MNAC.

Infrared spectroscopy as a valuable instrument to analyze the degree of conversion during the synthesis, was performed. The comparison of the infrared spectra of BNAC and MNAC shows the expected appearance of the

vibrations of nitro groups at roughly 1600 cm^{-1} (A) and nitramino groups at about 1200 cm^{-1} (B)³. The OH-vibration at 3400 cm^{-1} (C) of both spectra indicates that not all hydroxyl groups of cellulose were nitrated [22].

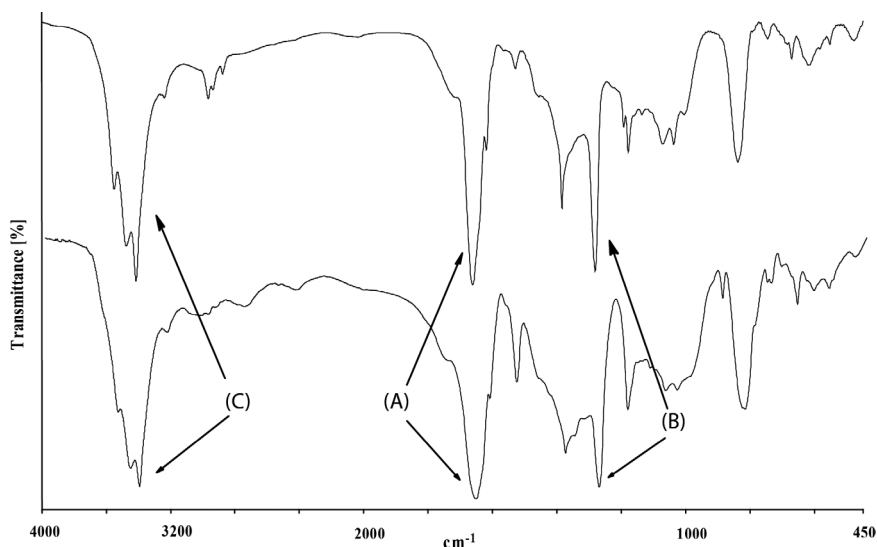


Figure 4. Infrared spectrum of MNAC.

The gained product was also analyzed by elemental analysis. The comparison of different degrees of substitution had the best agreement for BNAC with a degree of substitution of one nitramino and one nitro group per glucose unit. An explanation of this effect is, according to CTA and NCTA, the higher availability of the methylene hydroxyl group, compared to the hydroxyl groups of the ring system. However, one butylamine group was probably split of and substituted by a hydroxyl group, whereas the hydroxyl group at the 3C was nitrated, giving a nitramine group. The elemental analysis of MNAC gave the greatest convenience with one nitramine and one nitric ester formed. It also verifies the fact, already indicated by infrared spectroscopy, that not all hydroxyl groups were nitrated [22].

To analyze the energetic properties of BNAC and MNAC, the energy of combustion (ΔU_c) was measured using bomb calorimetry. Using these values, the enthalpy of formation was calculated by applying the Hess thermochemical cycle, as reported in literature [25]. The heats of formation of H_2O (l) and CO_2 (g) -286 kJ mol^{-1} and -394 kJ mol^{-1} were obtained from literature [26] and the combustion reaction of BNAC is given in Figure 5.

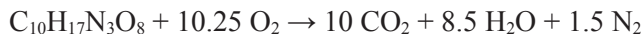


Figure 5. Combustion reaction of BNAC.

These measurements produced the following data of BNAC and MNAC that are specified in Table 2 and are herein compared to nitrocellulose, containing a nitrogen content of 13.5%.

Compared to nitrocellulose, the temperatures of explosion of BNAC and MNAC are lower, thus they diminish the erosion when applied. The detonation pressure and the detonation velocity of BNAC are slightly lower, whereas the detonation pressure of MNAC is comparable with nitrocellulose, whilst the detonation velocity is even higher. However, the specific impulse of BNAC and MNAC are lower than that of nitrocellulose, whereas by addition of an oxidizer, like ammonium dinitramide (ADN), it is higher than that of nitrocellulose.

Table 2. Energetic properties of BNAC and MNAC.

	BNAC	MNAC	Nitrocellulose ^k
Formula (monomer)	$\text{C}_{10}\text{H}_{17}\text{N}_3\text{O}_8$	$\text{C}_7\text{H}_{11}\text{N}_3\text{O}_8$	$\text{C}_6\text{H}_{7.26}\text{N}_{2.74}\text{O}_{10.48}$
FW (g mol ⁻¹)	307	265	285
Density (g cm ⁻³) ^a	1.5 (for calculation)	1.5 (for calculation)	1.5 (for calculation)
$-\Delta U_{\text{comb}}$ (cal g ⁻¹) ^b	4367	3544	-
$-\Delta H_{\text{comb}}$ (kJ mol ⁻¹) ^c	752	8514	-
$-\Delta_f H_m$ (kJ mol ⁻¹) ^d	787	9002	-
Values calculated by Explo5 V5.04			
$-\Delta_E U_m^\circ$ (kJ kg ⁻¹) ^e	4676	3559	4479
T_E (K) ^f	3347	2464	3933
p_{C-J} (kbar) ^g	74	55	81
D (m s ⁻¹) ^h	5096	4502	5279
Gas vol. (L kg ⁻¹) ⁱ	768	740	744
I_s (s) ^l	200	172	232
I_s (s) ^m (70 % ADN)	249	246	236

^a estimated from a structure determination, ^b experimental (constant volume) combustion energy, ^c experimental molar enthalpy of combustion, ^d molar enthalpy of formation, ^e energy of explosion, ^f explosion temperature, ^g detonation pressure, ^h detonation velocity, ⁱ assuming only gaseous products, ^k obtained from the database of EXPLO5 V5.04, ^l specific impulse (isobaric combustion, chamber pressure 60 bar, frozen expansion), ^m specific impulse of a mixture containing 70% ammonium dinitramide as oxidizer.

The comparison of the different mixing ratios of BNAC, MNAC and nitrocellulose (13.5% nitrated) with ADN as an oxidizer, depicts that by the

addition of smaller amounts of the cellulose derivatives, those compounds have a better performance than nitrocellulose, which is generally used in amounts of 12 to 14% nitrogen.

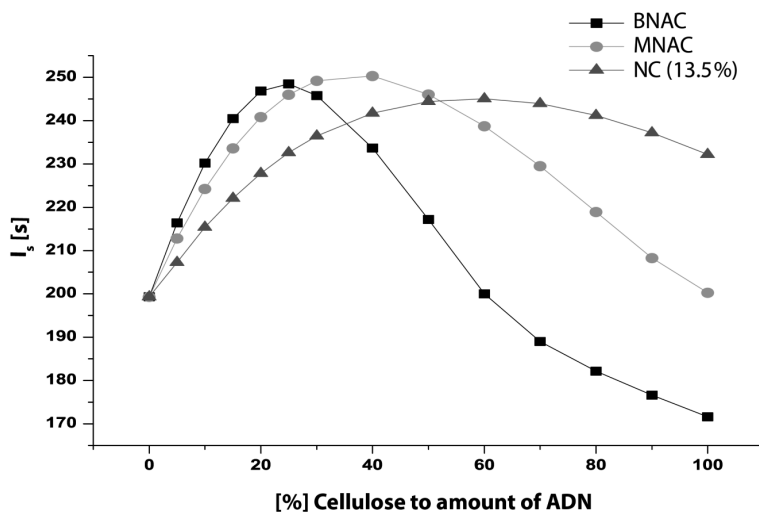


Figure 6. Comparison of the specific impulse of BNAC and MNAC with nitrocellulose (13.5% nitrated) by the addition of ADN, calculated by EXPLO5 V5.04.

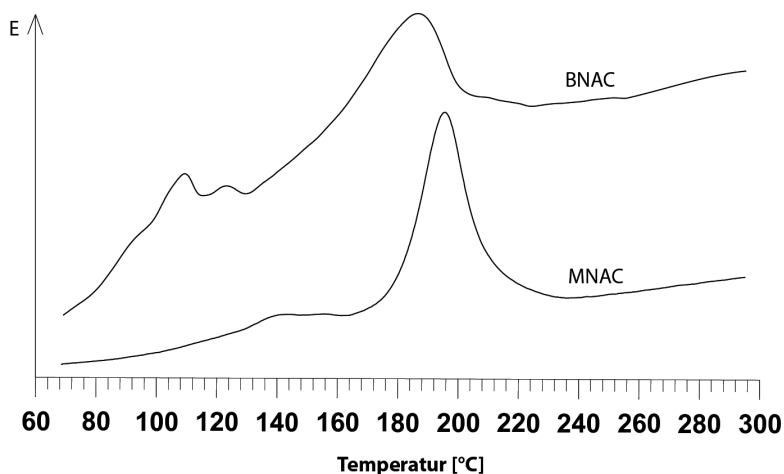


Figure 7. DSC spectrum of MNAC and BNAC.

The melting area of BNAC starts at 107 °C and ends with the point of decomposition at 151 °C, as proven by DSC measurements. MNAC has a better

thermal stability, as suggested by its decomposition point of 176 °C, which is also the end of the melting area that starts at 141 °C.

Sensitivity testing of the compounds using standard BAM tests [27], revealed an impact sensitivity of 10 J as well as a friction sensitivity of 120 N for MNAC, whereas BNAC displayed an impact sensitivity of 35 J and a friction sensitivity of 360 N. As a result BNAC can be regarded as less sensitive in terms of impact and insensitive in terms of friction according to literature [14]. Whereas MNAC should be considered as sensitive, although compared to commonly used nitrocellulose (impact = 3 J, friction > 353 N) [23] it has a better response to impact, which is a clear advantage in terms of safety.

The sensitivity data was obtained using a BAM [14] drophammer and friction tester. These methods obtained that CTA and NCTA are insensitive against impact of 100 J and friction of 360 N and can therefore be regarded as insensitive. Besides compared to commonly used nitrocellulose (impact sensitivity: 3 J, friction sensitivity: > 353 N) [23], it has a better response to impact and friction, which can be regarded as a clear advantage in terms of safety.

Conclusions

In this work, several approaches were presented to synthesize equally or even more energetic nitrogen rich polymers than nitrocellulose. The goal was to fully exploit the possibilities that a natural polymer like cellulose offers, with all its advantages of biocompatibility, low cost acquisition, economical friendliness and moreover the possibility of a biological degradation, due to the fact, that cellulose itself is a biological product.

Finally, some of the materials described in this paper might hold promise for application as the low detonation temperature of MNAC and BNAC renders these polymers a valuable alternative of nitrocellulose, as they also reach higher performances than nitrocellulose by adding an oxidizer, like ammonium dinitramide. Consequently, both MNAC, that also has a good thermal stability, and BNAC, should perform better as a propellant than nitrocellulose, which has been established as propellant and binder in pyrotechnical and explosive compositions. In addition even NCTA has a detonation velocity only slightly lower than nitrocellulose and a better response to impact and friction.

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