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Preparation and Characterization of Monolithic Nitrocellulose-Cellulose Composites*)

Stanisław CUDZIŁO*, Sławomir DYJAK
and Waldemar A. TRZCIŃSKI

Military University of Technology,
Kaliskiego 2, 00-908 Warsaw, Poland
**E-mail: scudzilo@wat.edu.pl*

Abstract: Monolithic nitrocellulose-cellulose composites were prepared by separately cross-linking the mixed precursors (NC + C) with hexamethylene diisocyanate (HDI). The syntheses were optimised according to the component mass ratios, HDI, solvent and catalyst concentration. The concentrations of the reactants and cure catalyst are the most important factors. The general method of synthesis involved dissolving HDI and the catalyst in methylene chloride and then wetting an NC-C mixture with the solution. The resulting mixture was placed in a sealed box for cross-linking at room temperature. Finally the solvent was evaporated at ca. 40 °C. The NC-C composites obtained were characterized using TG/DTA and sensitivity to friction and drop weight impact, and were used as energetic materials in reactive armour elements.

Keywords: nitrocellulose-cellulose composites, reactive armour

Introduction

Shaped-charge warheads are known to pierce thick steel armour walls. However the penetrating effect of a shaped charge jet can be effectively weakened by reactive armour elements fitted on the outside of the armour itself. The reactive armour element is a multi-layer sandwich structure comprising plates made of metal or a composite material and at least one intermediate layer of an explosive or any other energetic material. Upon initiation of the energetic material by the jet, the released gases accelerate the metal plates and displace them away,

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disrupting the jet and weakening its penetrating efficiency.

Four principal groups of reactive armour are known: explosive reactive armour (ERA), self-limiting explosive reactive armour (SLERA), non-explosive reactive armour (NxRA) and non-energetic reactive armour (NERA) [1]. ERA is the most effective protection against both shaped charges and kinetic projectiles but the use of a fully detonable explosive in the element may be problematic as its detonation also affects the protected object. SLERA and NxRA provide reasonable performance, excellent multiple-hit capability (in modular configuration) against shaped charge warheads and substantially reduce the effects on the object structures.

In the present work we tried to provide an energetic material suitable for SLERA or NxRA which fulfils its protective function and simultaneously does not cause any damage to the protected environment. To this end monolithic nitrocellulose-cellulose (NC-C) composites were prepared by separately cross-linking the mixed precursors (NC + C) with hexamethylene diisocyanate (HDI). The NC-C composites obtained were characterized using TG/DTA and sensitivity to friction and drop weight impact, and were used as a packing for model armour elements. Their behaviour after shaped charge jet attack was investigated by the use of X-ray flash photography [2].

Experimental

Materials and test methods

The composites were prepared using commercial grade nitrocellulose (13.13% N) and pure powdery cellulose for TLC chromatography (Whatman, CF 11). 1,6-Diisocyanatohexane (HDI 98%, Aldrich D12,470-2), di-n-butyldilauryltin (DBTL 95%, ABCR GmbH&Co KG, AB106543) and methylene chloride (CH_2Cl_2 99.9%, Chempur) were used for the cross-linking of the polymers.

Simultaneous thermal gravimetric and differential thermal analyses (TG/DTA) were carried out applying LabSys-TG/DTA apparatus (SETARAM). Samples of ca. 1.0 mg in mass were heated from 20 to 400 °C, at different rates (2, 4, 5, 7 and 9 °C/min) in an argon atmosphere at a flow rate of 50 ml/min. Friction sensitivity measurements were made on a Julius Peters apparatus according to the Polish standards (BAM method) [3]. The impact sensitivity was determined by the Fall Hammer Method using a one-kilogram-drop hammer [4].

The model armour element consists of two square (120×120 mm) steel plates separated by a 10-mm layer of NC-C composite. The upper and bottom cover

plates were 4 and 8 mm-thick, respectively. Square rods (10×10 mm) made of Plexiglas were used as a lateral enclosure of the NC-C layer. The diagnostic shaped charge was placed above the upper steel plate at a distance of 70 mm, Figure 1.

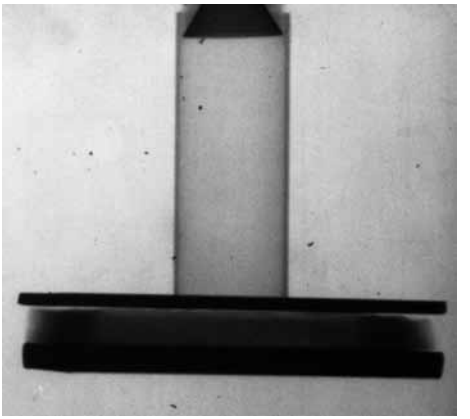

Figure 1. X-ray photograph of the experimental setup.

The charges were made of pressed phlegmatized HMX (21.5 g) and had sintered copper liners (14 g) with a cone shape angle of 60° and base diameter of 32 mm. The jet velocity was determined on the basis of images taken using X-ray flash photography (SCANDIFLASH) at various times after the initiation of detonation of the shape charge. The estimated jet velocity was 5755 m/s. The jet reached the tested armour element within ca. 20 μs after firing the shaped charge. The placements and shapes of plates at different time delays were recorded by the use of X-ray flash photography.

Composition and preparation

The NC-C composites were prepared in a two-stage process. Firstly, nitrocellulose and cellulose were mixed in a water suspension. After separation and drying (under reduced pressure), the mixtures containing 20, 30 or 50 wt% of cellulose were wetted with a solution of HDI and DBTL in methylene chloride. The resulting paste-like material was placed either in a container or directly in the armour element and placed in a sealed box for cross-linking at room temperature (for 72 h). Finally the solvent was evaporated at ca. 40 °C. The final formulations contained ca. 90% of the NC/C mixture and ca. 10% of the cross-linking agent (HDI/DBTL = 2.5, by mass). The average density of the composites was ca. 0.35 g/cm^3.

Friction and impact sensitivity

The friction and impact sensitivities of the pure nitrocellulose was found to be 170 N and 1.0 J, respectively. The values are the minimal pistil load and impact energy, respectively, at which one reaction was recorded in six consecutive trials. These figures did not change after cross-linking pure NC with HDI/DBTL, but increasing the concentration of cellulose in the formulations resulted in a substantial decrease in their sensitivity – from 3.0 J for the composition containing 20% of cellulose (NC20C+HDI) to 7.5 J in the case of the composition with 50% of cellulose (NC50C+HDI).

Non-isothermal kinetics analysis

Typical TG/DTA curves of pure NC and NC30C+HDI composition (recorded at a heating rate of 5 °C/min) are shown in Figure 2. From the thermograms it follows that nitrocellulose (NC) and cellulose decompose separately and that the presence of HDI/DBTL does not significantly influence the thermal decomposition of nitrocellulose.

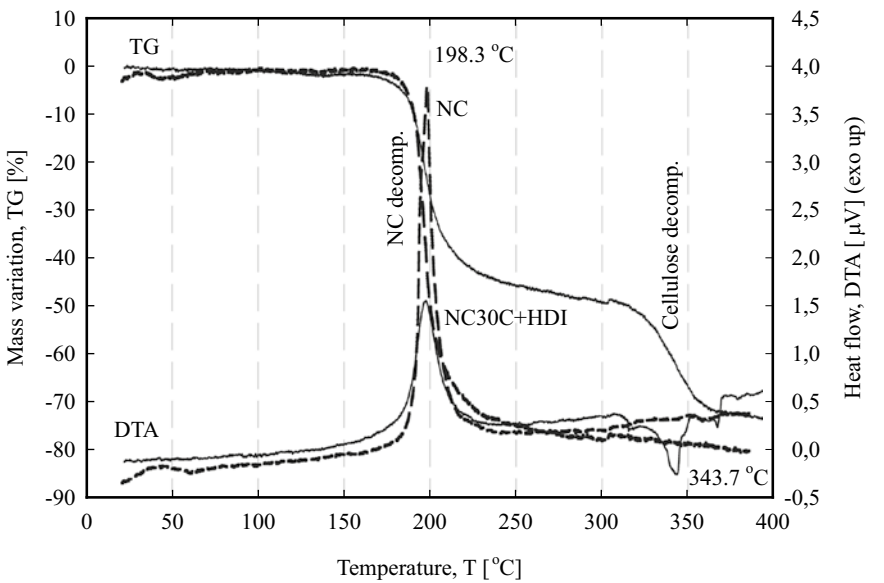

Figure 2. TG-DTA thermograms of NC and NC30C+HDI in the temperature range 20-400 °C.

Kissinger's method [5] was applied to study the decomposition kinetics of the composition containing 30% of cellulose (NC30C+HDI). The sample mass was kept small (ca. 1.0 mg) in order to minimize temperature gradients within

the sample. The DTA thermograms of NC30C+HDI at different heating rates (β = 2, 4, 5, 7 and 9 °C/min) are presented in Figure 3.

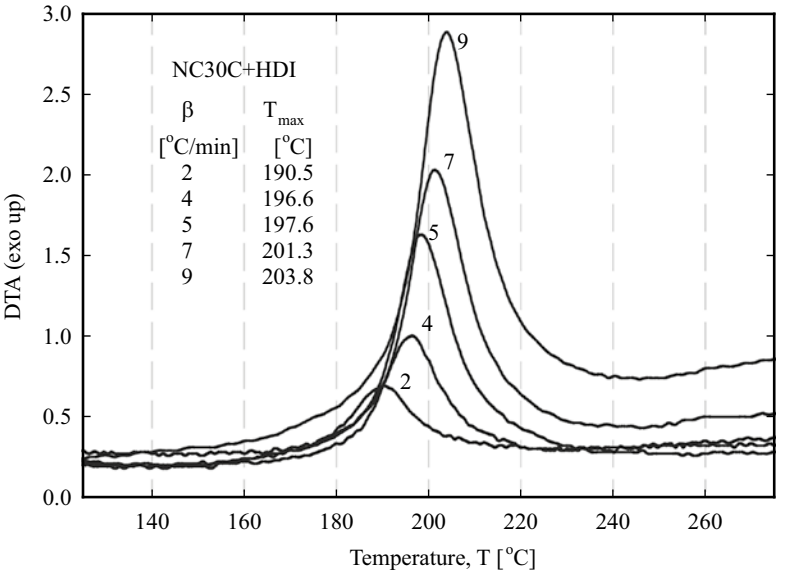

Figure 3. DTA curves of the NC30C+HDI composition at different heating rates.

As can be seen, the temperature of the exothermic maxima T_{max} increases with increasing heating rate, and this enables the kinetic parameters of the thermal decomposition to be determined by applying the model-free, non-isothermal Kissinger method.

Using the main exothermic peak temperatures, the apparent activation energy E_a and the pre-exponential factor A were estimated to be 201.2 kJ/mol and $4.3976 \cdot 10^{17}$/s, with the correlation coefficient $r^2 = 0.993$. The Arrhenius equation can be expressed in E_a/R and ln$A$ as follows:

$$\ln k = 40.625 - 24198.35 \frac{1}{T}. \quad (1)$$

This equation can be used to calculate rate constants k at different temperatures T and to assess the potential of the material for thermal explosion. The high value of the activation energy indicates good thermal stability of the composition.

Reaction to shaped charge jet impact

In order to evaluate the influence of the energetic material composition on the motion characteristics of the model reactive armour elements, X-ray photographs of the operative armour were taken (after jet attack). The energetic materials tested included NC+HDI, NC20C+HDI and NC30C+HDI composites. The photographs were recorded 100 and 200 μs after the firing of the shaped charge. The plates were driven for ca. 80 and 180 μs, respectively, as the jet reached the armour upper plate within ca. 20 μs.

Figure 4 shows pictures recorded after 200 μs from the firing of the shaped charge (i.e. ca. 180 μs from the jet impact). The energetic material layers were made of composites containing 20 and 30% of cellulose (NC20C+HDI and NC30C+HDI).

From a simple comparison of these pictures, it follows that the NC20C+HDI formulation has a higher performance, because the plates travelled a much longer distance within the same time interval (i.e. 180 μs).

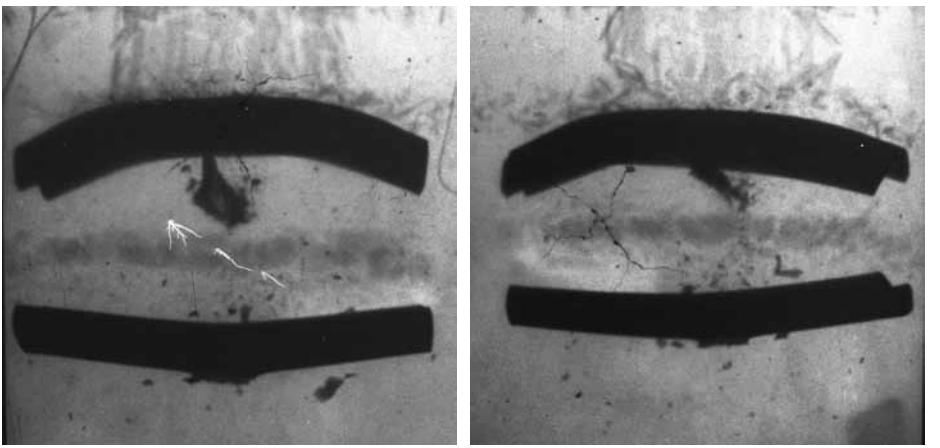

Figure 4. X-ray photographs of reactive armour plates driven by the explosion of NC20C+HDI (on the left) and NC30C+HDI (on the right) compositions taken after 200 μs from the firing of the shaped charge.

Profiles of the plates driven by the explosion of the composites containing 0, 20, and 30% of cellulose after 180 μs from jet impact, are shown in Figure 5 (x_c = 0, 20, and 30%). Knowing the armour element displacements and the times of their motion, it was possible to calculate the average velocities of the elements in various armour structures and configurations.

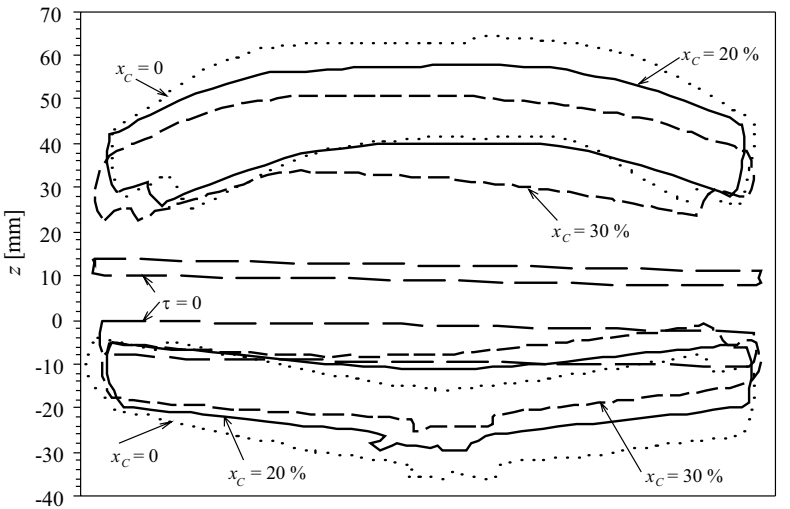

Figure 5. Profiles of steel plates driven by the explosion of composites containing 0, 20 and 30% of cellulose (NC+HDI, NC20C+HDI and NC30C+HDI) after 200 μs from the firing of the shaped charge.

The mean velocity of the upper and bottom plates of the armour comprising a layer of NC+HDI composite, within a recorded time interval of 100-200 μs, was found to be 320 and 160 m/s, respectively. The upper armour plates propelled by explosion of NC+HDI, NC20C+HDI and NC30C+HDI within 180 μs move at an average velocity of ca. 305, 260 and 220 m/s, respectively.

The plates were more deformed when the more energetic material was used as the armour intermediate layer, but they were never fragmented. This fact and the comparatively low initial velocities of the armour plates indicate that the NC-C composites tested explode or deflagrate under the experiment conditions.

Conclusions

Nitrocellulose-cellulose monolithic composites, obtained by cross-linking of nitrocellulose-cellulose mixtures with HDI/DBTL in methylene chloride, turned out to be real tuneable reactive materials, as their mechanical properties, sensitivity and performance can be easily changed by changing the mass ratio of nitrocellulose to cellulose.

The X-ray pictures of the interaction of the shaped charge jet with the model non-explosive reactive armour, taken at different time delays, make it possible

to determine the time-space characteristics of the armour motion. They can be used for the validation of the numerical models applied for simulation of the behaviour of NxRA elements after jet impact.

Acknowledgments

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