Synthesis and Characterization of Commercial Grade Energetic Materials using Decanted 2,4,6 Tri-nitrotoluene (TNT)

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Summary: 2, 4, 6 Tri-nitrotoluene commonly known as TNT is one of the safest and most widely used energetic material for both military as well as commercial purposes. During Second World War, a huge quantity of TNT was used for filling of various conventional munitions used against adversaries. Resultantly, large numbers of unserviceable munitions were left unused and were either disposed of through conventional disposal techniques such as open burn open detonation, sea dumping, incineration, biological degradation or buried underground without proper disposal. A number of accidents have been reported during disposal of these unserviceable and unwanted munitions. To avoid such a detrimental situation, global efforts were made in the past for re-use of unwanted energetic materials but still a lot more effort is needed in this regard. The present work is aimed at the safe conversion of decanted TNT into commercial grade energetic material which can be utilized for mining, quarrying, underwater blast activities. For this purpose, various materials / ingredients have been used with decanted TNT for the synthesis of newly formed melt cast commercial grade energetic material. This particular sample has further been characterized through Thermo gravimetric/ Differential Thermal Analysis (TG/DTA), Scanning Electron Microscopy (SEM), and X-Ray Diffraction (XRD) techniques for the identification of various aspects. Results show that the newly synthesized sample has a clear, compact and smooth morphology with almost negligible numbers of cracks and pores unlike decanted TNT in unserviceable state. This process of synthesis and reutilization is not only safe and economical but also environment friendly.

Key words: 2,4,6 Tri-nitrotoluene, Nitrocellulose, Aluminium (Al), Methanol, Thermogravimetric/ Differential Thermal Analysis (TG/DTA).

Introduction

Energetic materials vary from low grade initiators to high grade energetic materials depending on their use and potential. Most of the energetic materials are energy rich compounds or elements which can be used in many ways to furnish their optimum utility in both civil and military operations. A lot of efforts have been made in the past to demolish unserviceable (unsvc) or unwanted energetic materials through safest means. But because of the unreliable nature, conventional munitions disposal techniques are still hazardous and pose serious threats to human lives. Similarly, existence of debris of these energetic materials not only contaminates the soil but also creates severe biological effects on living beings [1-3]. Since last few decades, an extensive research and development (R&D) projects have been undertaken for recycling and reutilization of various types of unsvc and unwanted energetic materials. These efforts are still going on globally [4-9]. The present research work is focused on the safe conversion of military grade TNT (a highly energetic material) in unsvc condition into commercial grade energetic material. These efforts will not only negotiate various types of hazards involved in handling and disposal of unwanted energetic materials but will also provide an opportunity for safe conversion of highly energetic materials into usable products. TNT, being one of the most widely used highly energetic materials in military grade munitions since 1870, is considered to be safest in handling [10]. It is a nitro compound having (C, H, N, O) bonds. In order to convert conventional TNT into a commercial grade energetic material, aluminium powder (Al) was used as the main ingredient. Al having high calorific value has widely been used in the past in different energetic materials formulation for both commercial as well as military grades [11-12]. This is because Al particles contribute towards energy level of energetic materials and thus enhance the blast effect of energetic materials [13-14].In the past, it has also been observed that the addition of ingredients other than Al has not produced the desired results required for specific munitions. Initially, Germans applied a conventional technique of dismantling munitions casing into various parts, thereby extracting energetic materials out of the munitions casing and then letting these materials burn in open air. This technique was comparatively easy to implement but produced harmful results mostly due to uncontrollable combustion and emission of toxic gases such as NOx, COx and SOx, etc. into the atmosphere[15].

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Table-1: Material/ ingredients used for synthesis of commercial grade TNT/Al sample.

No.	Material used	Specifications	Company/ Supplier
1.	Decanted TNT Unsvc	Military Grade	Army field installation
2.	Nitrocellulose (NC)	Military Grade	Government defense sector
3.	Aluminium powder (Al)	Analytical Grade (avg particle size 45 µm)	Panreac
4.	Methanol	Analytical Grade	Sigma-Aldrich (Riedel-de Haen)
5.	Paraffin Wax	Analytical Grade	Merck / MP Biomedicals
6.	Dry Lecithin	Analytical Grade	Expert Scientist/ Germany
7.	Glycerin	Analytical Grade	Scharlau/ Spain
8.	Calcium Carbonate	Analytical Grade	Sigma-Aldrich (Riedel-de Haen)

Experimental

Material and Methods

Decanting of TNT samples

For complete retrieval of decanted TNT from unserviceable munitions, decanting process was carried out. In this process, TNT was extracted from the munitions casing with the help of steam wand. One of the decanting plants already installed in an Army field installation was used for the recovery of decanted TNT. A steam jet was injected through the nozzle of shell filled with unsvc TNT. Melted TNT from munitions casing was then collected in receiving tray and subsequently dried until only 1% of moisture contents remained. The purpose of this drying was to avoid any kind of reaction between water contents and Al during synthesis process at high revolutions per minute (rpm). Dried TNT sample was pulverized into powder form with the help of specially designed mortar and pestle for smooth and uniform mixing with other ingredients/ materials during synthesis process.

Synthesis of Commercial Grade Energetic Material

Required quantity of decanted TNT unsvc was physically processed with a no. of ingredients / materials for safe conversion into synthesized commercial grade energetic material. The synthesis process was conducted in various steps with different materials as shown in Table-1. Melted paraffin wax was added to dry lecithin in a beaker and stirred continuously at selected rpm. Simultaneously, a small quantity of nitrocellulose was mixed with methanol and then poured into wax mixture prepared earlier along with calcium carbonate. After a thorough mixing, the whole blend was poured in an open pan. Lastly, a small quantity of decanted TNT unsvc was melted and subsequently added to the whole blend along with moderately heated free flow wax coated Al. In this step, a beaker containing whole blend of different ingredients was kept in a specially designed container filled with glycerin to serve as an oil bath; the aim being to avoid direct contact of heat with beaker containing decanted TNT and other materials. Percentage of Al was frequently changed during no. of experiments to get an optimum value of synthesized TNT/Al sample. Once the whole mix was thoroughly blended, a small quantity of synthesized TNT/Al samples was used for advanced analysis and characterization.

Analytical Techniques

Four types of samples i.e. Chinese TNT Svc, decanted TNT Unsvc, TNT/ 15% Al and TNT/ 26% Al were used for brief investigation through Scanning Electron Microscope (SEM), Thermogravimetric/ Differential Thermal Analysis (TG/DTA) and X-Ray Diffraction (XRD) techniques.

Scanning Electron Microscope

SEM analysis was carried out to see any kind of apparent changes in the structure and morphology of decanted TNT Unsvc versus Chinese TNT Svc. Four samples were investigated through Scanning Electron Microscope (SEM-6490A JEOL made in Japan. Various magnifications of 250-10000 times were used for brief analysis of samples at different angles.

Thermo Gravimetric / Differential Thermal Analysis (TG/DTA)

Perkin Elmer TG/DTA instrument was used for thermal cum kinetic studies of all four samples. Initially, apparatus was calibrated before samples analysis. Nitrogen gas (N_2) was used as purging gas to produce an inert atmosphere. Small quantities of all four samples were subjected to non-isothermal environment under controlled temperature program. Examination was carried out between temperature range of 25^{o}C - 325^{o}C and at heating rate of 10^{o}C/min.

X-Ray Diffraction (XRD)

All four samples were also characterized by X-Ray Diffraction (XRD made by Theta-Theta (Toe), Germany) instrument for the identification of various parameters such as crystalline phase and orientation, structural properties and lattice parameter etc.

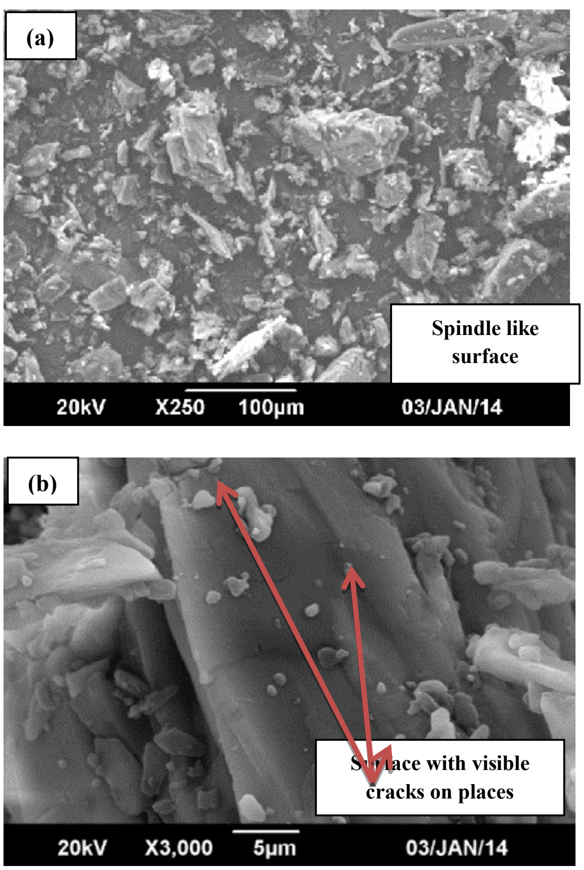
Results and Discussion

Scanning Electron Microscope Analysis

Chinese TNT Svc

In Fig. 1, a small sample was analyzed for an in-depth morphology. Closer observation reveals that Chinese TNT Svc has a flake-type microstructure with few tiny pores and cracks on its surface. These voids may be linked to the filling, handling and processing defects. Energetic materials are mostly classified with regards to their various physical and chemical characteristics including shape, size and density of powder particles along with its thermal and kinetic properties. Therefore, minor defects in filling and formulation processes or inappropriate handling while in storage may give rise to an untoward situation.

Chinese TNT Svc



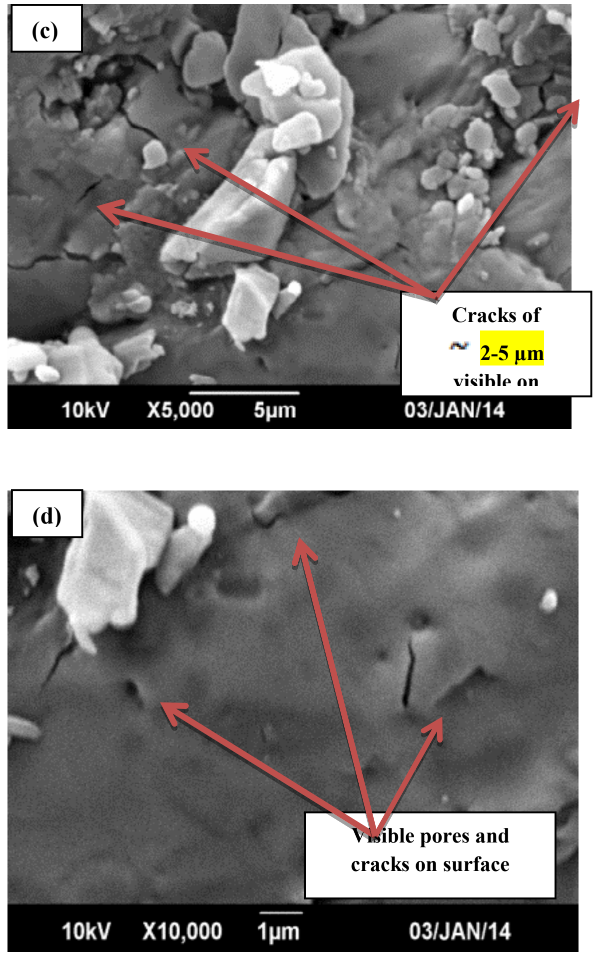


Fig. 1: SEM images of Chinese TNT Svc sample at various magnifications of (a) 250; (b) 3000; (c) 5000; (d) 10000.

Decanted TNT Unsvc

In Fig. 2, small quantity of decanted TNT Unsvc sample was examined at varying magnifications. SEM images show that the sample has an irregular granular-type shape with comparatively more pores and cracks visible on the surface of microstructure [16]. As decanted TNT Unsvc was treated with steam jet during decanting process, therefore the no. of pores and cracks were observed to have increased. Resultantly, impurities in the decanted TNT Unsvc sample have increased manifold. Presence of such a large no. of pores and cracks are prone to affect the sensitivity and thermal characteristics of energetic material.

Decanted TNT Unsvc

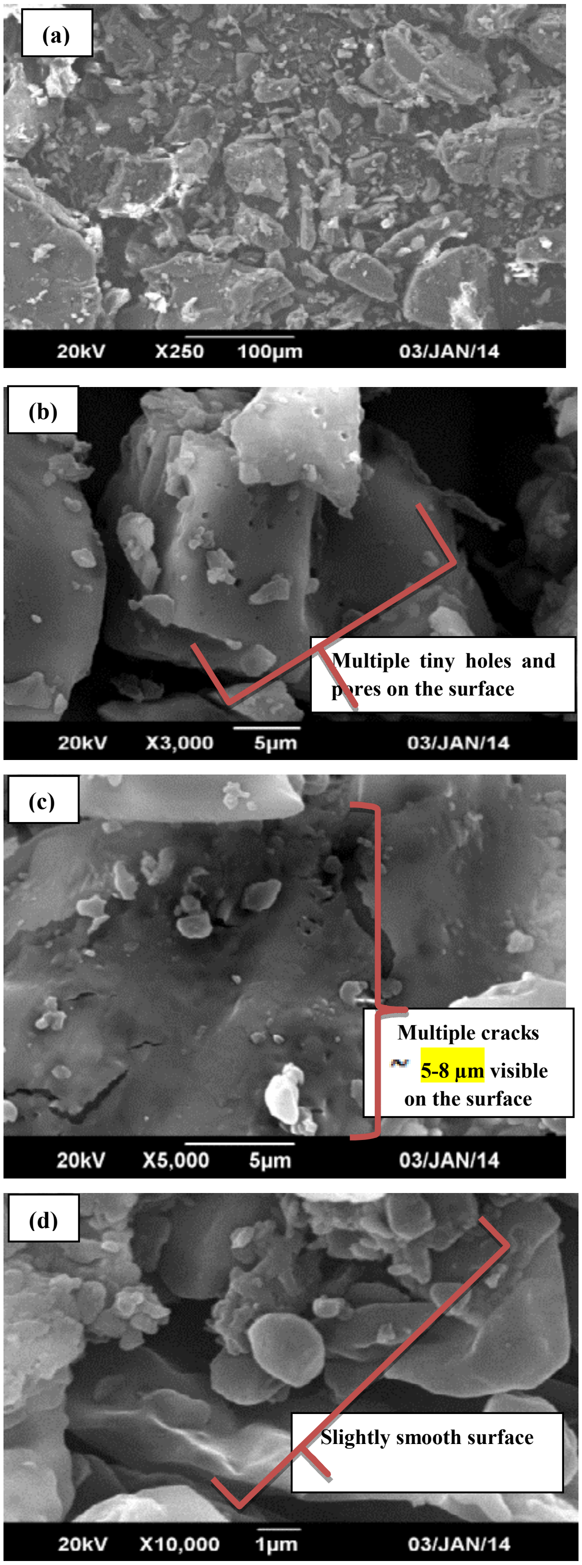
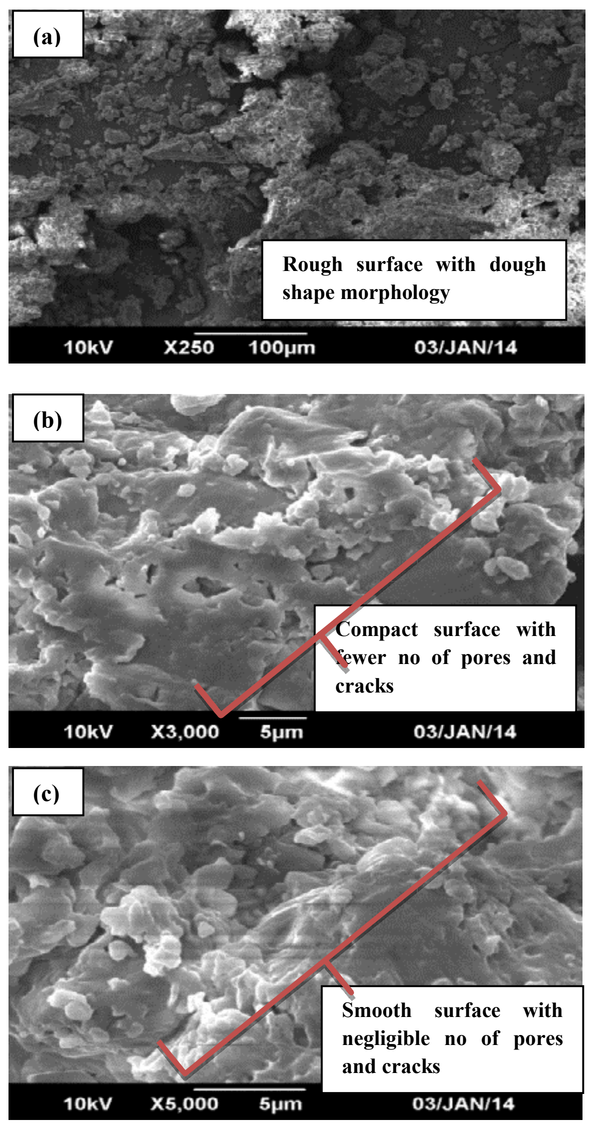


Fig. 2: SEM images of Decanted TNT Unsvc sample at different magnifications, (a) 250; (b) 3000; (c) 5000; (d) 10000.

TNT/15%Al sample

Fig. 3, shows SEM images of laboratory synthesized sample. Various experiments were conducted at laboratory scale for synthesis of some commercial grade energetic material using decanted TNT Unsvc and other ingredients listed in Table 1. SEM analysis of the synthesized sample was done primarily to see the effects of addition of different ingredients to decanted TNT sample. SEM images of TNT/15% Al sample shows that the structure of the sample is spindle like having smooth, uniform and homogeneous surface. More precisely the synthesized sample has fewer no of pores and cracks and its surface is clean and clear. Thus addition of various ingredients to decanted TNT Unsvc has positive impact on its structural morphology.

TNT/ 15 % Al



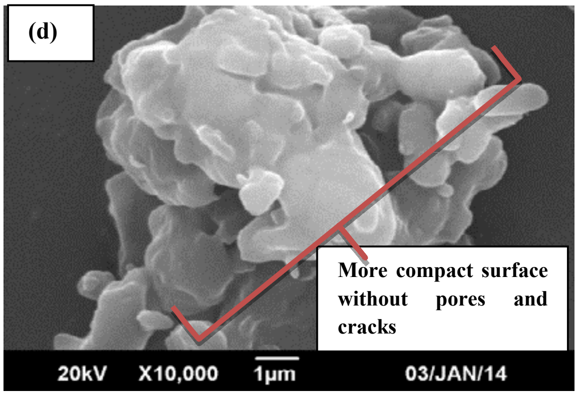
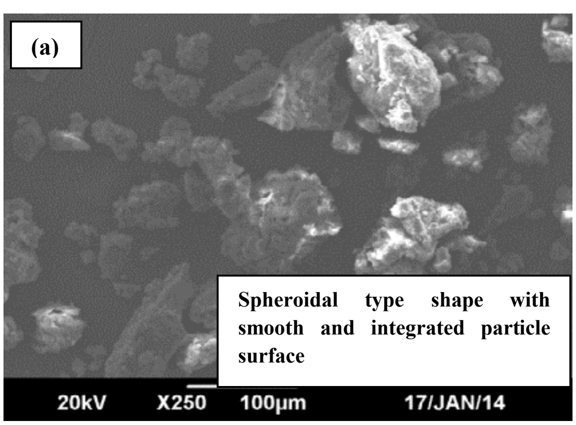


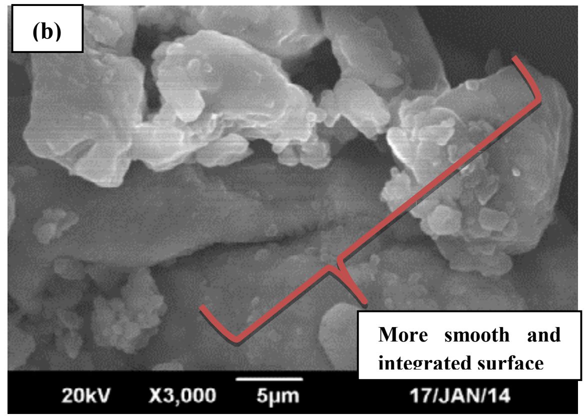
Fig. 3: SEM images of TNT/15%Al sample at magnifications of (a) 250; (b) 3000; (c) 5000; (d) 10000.

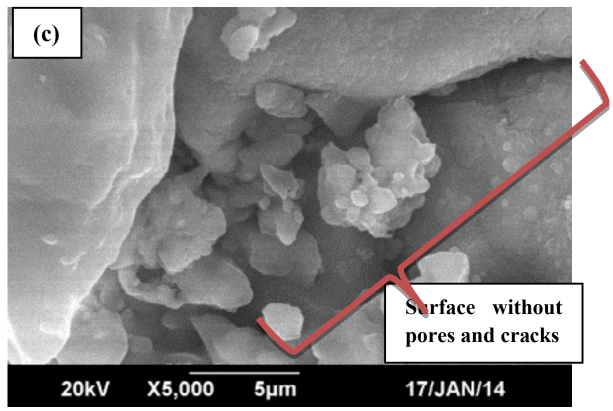
TNT/26% Al sample

Fig. 4, shows SEM of decanted TNT sample synthesized with 26% Al. The percentage of Al was increased with a view to observe its impact on morphology and physical characteristics of synthesized TNT/26% Al sample. Again the SEM images were taken at varying magnifications set for previous sample investigation. It was revealed during SEM analysis that the synthesized TNT/26% Al sample has spheroidal type shape with smooth and integrated particle surface. SEM images of the two newly synthesized TNT samples with addition of 15%Al and 26%Al show remarkable changes in their surface morphology with improvement in reduction of no. of pores and cracks besides giving clear, compact and homogeneous particle surface. Since, increased no of pores and cracks tend to elevate no. of chances of energetic materials degradation during prolonged storage and shelf life.

TNT/26%Al sample







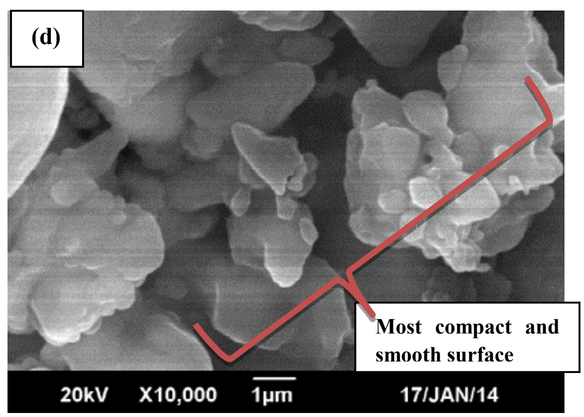


Fig. 4: SEM images of TNT/26%Al sample at similar magnifications of (a) 250;(b) 3000; (c) 5000; (d) 10000.

Thermo Gravimetric / Differential Thermal (TG/DTA) Analysis

TG Curves of Chinese TNT Svc, Decanted TNT Unsvc, TNT/15% Al and TNT/ 26% Al samples

In Fig. 5, all four samples were examined with the help of Perkin Elmer-TG/DTA instrument. It was revealed from TG curves of all energetic material samples including pure and synthesized TNT/Al that the weight loss of all the energetic material samples started near 165°C. Weight loss remained almost constant till 180°C but became rapid between 180-245°C due to thermal decomposition of TNT. Thermal decomposition of all four samples over controlled temperature range of 180-245°C was found to be 86%. TG curves also indicated a single stage reaction for thermal decomposition of all the samples under investigation.

TG curves for Chinese TNT Svc, Decanted TNT Unsvc, TNT/15% Al and TNT/ 26% Al samples

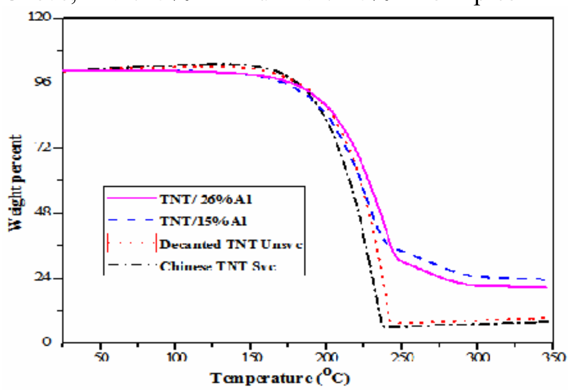


Fig. 5: TG Curves of four types of TNT samples.

DTA curves of Chinese TNT Svc, Decanted TNT Unsvc, TNT/15% Al and TNT/ 26% Al samples

For thermal analysis of all four samples, DTA curves of Perkin Elmer-TG/DTA instrument were used as shown in Fig. 6. The results show that DTA curves (Heat flow curve) of Chinese TNT svc and decanted TNT Unsvc give two distinct sharp peaks which are endothermic in nature. The 1st one sharp peak near 80±1°C corresponds to melting of TNT samples which is in quite agreement with available literature data [17-19]. Similarly, next endothermic peak around 240±5°C correspond to thermal decomposition of TNT samples. However, in case of synthesized TNT/Al samples, small peaks prior to the melting of TNT have been observed which can be attributed to the melting point of paraffin wax near 52°C. Since synthesis process was carried out in open atmosphere, therefore, slight variations in thermal decomposition peaks for synthesized TNT/Al samples were observed. It has also been observed that decanted TNT Unsvc sample melted earlier than Chinese TNT svc but its thermal decomposition took place later than Chinese TNT svc. These variations in thermal behaviour may be linked to the various types of impurities present in the decanted TNT Unsvc sample. However, in case of synthesized TNT/Al samples results show that both the samples melted earlier but decomposed later than pure TNT samples. Similarly, elevation of curves in case of synthesized TNT/Al samples on the heat flow axis is most probably due to the slow oxidation of Al metal which is an exothermic process [20].

DTA curves of Chinese TNT Svc, Decanted TNT Unsvc, TNT /15% Al and TNT/ 26% Al samples

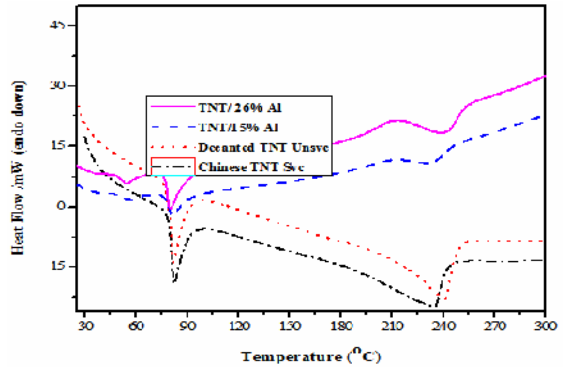


Fig. 6: DTA Curves of four types of TNT samples.

XRD Pattern of Chinese TNT Svc, Decanted TNT Unsvc, TNT /15% Al and TNT/ 26% Al samples

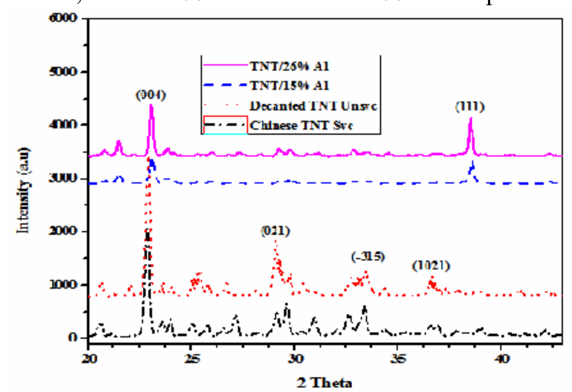


Fig. 7: XRD Pattern of four types of TNT samples.

XRD Analysis

For crystallographic studies, XRD analysis was used for all four samples in the range of 20 to 43^{0} angles as shown in Fig. 7. The results from XRD pattern shows four distinct diffraction peaks for Chinese TNT svc as well as decanted TNT unsvc sample which are very similar to pure TNT peaks available in literature. However, in case of synthesized TNT/Al samples, additional diffraction peaks for Al crystals were also observed. Miller indices have been marked on XRD peaks with h, k, l values of (004), (021), (-315) and (1021) for TNT and (111) for Al crystals. The results also show that TNT in all crystalline states of four samples exist in monoclinic form which is considered to be more stable than orthorhombic form which is metastable at room temperature [16]. It was also revealed that TNT samples belong to space group C2/c and space group number 15 [21]. Peaks with h, k, l value of (004) seemed to be more intense due to higher value of TNT crystallinity as compared to other peaks. Similarly XRD pattern for synthesized samples shows that Al exist in cubic crystal system with h, k, l value of (111) having space group Fm-3m and space group number 225.

Conclusion

After brief investigation through various instrumental techniques, it has been observed that decanted TNT Unsvc sample has lost some of the characteristics values needed for its military applications. Most noteworthy is the earlier decomposition of the sample with lower activation energy (Ea). This may lead to increase in chances of premature ignition and sensitivity to shock and impact of energetic materials due to the presence of impurities. The synthesized TNT/Al samples have got increased level of energy contents required due to addition of Al, which are visible in DTA curves for the samples bearing exothermic elevation. Additionally, it has been noticed that the presence of multiple pores and cracks in the microstructure of synthesized TNT/Al samples have reduced to an appreciable limit. Thus the synthesis of commercial grade energetic material from decanted TNT unsvc is one of the most viable solutions for the safe disposal of unwanted and undesirable munitions. These new conversion techniques are not only much economical, but will also help a lot in safeguarding human beings from environmental pollution and health hazards. However, handling of energetic materials is always a risky affair and needs prompt measures and adherence to the strict Standard Operating Procedures (SOPs) regarding filling, formulation and disposal of energetic materials.

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