

FUNCTIONALIZED COTTON-BASED NONWOVENS THROUGH THE INCORPORATION OF NANOPHASE MATERIALS**Gajanan Bhat****Prabhakar Gulgunje****University of Tennessee****TANDEC****Knoxville, TN****Rajan K. Vempati****Brittany Lundy****Xiang Hua****ChK Group, Inc.****Plano, TX****Richard Wagner****Phycobiologics, Inc.****Indianapolis, IN****Martin Goldberg****Michael Bennett****Padmakar Kulkarni****UT Southwestern Medical Center****Dallas, TX****Abstract**

Currently, nonwovens are one of the most significant developments of the textile industry. Collaborative studies, involving material chemist, chemist, textile engineer, microbiologist and medical pathologist, are being conducted in our research program to take advantage of nanotechnology to produce functional nonwovens, and to improve their performance. We have demonstrated that by using conventional processes and equipments, one can produce several such products. Nanophase manganese (VII) oxide (NM7O) was shown to be stable and reactive chemical that can neutralize several chemicals and is antimicrobial. Incorporation of NM7O into cotton-based nonwoven fabrics successfully demonstrated the possibility to produce functional nonwovens suitable for a variety of applications. In addition, nanophase NM7O incorporated nonwoven products exhibit excellent destruction (proactive) and/or prevention of algal and bacterial growth. These nonwoven products are suited for applications where antibacterial and odor control is important; such as, in healthcare and hygiene products, diapers, hospital bedding, house hold wipes, sportswear, and water purification membranes.

Background

Over the last couple of years, we are conducting research on the possibility of incorporating nanophase manganese (VII) oxide (NM7O) into selected nonwoven fabrics (Bhat et al, 2007). NM7O is an environmentally friendly material and is a super Lewis acid. It has the capability to destroy Lewis bases; such as, nitrogen, sulfur, oxygen, and phosphorous compounds containing lone pairs of electrons. The characteristics are being further explored to destroy and dispose off mustard gas as well as other harmful chemical warfare agents.

With changing valence of manganese oxide a distinct color is observed from violet with Mn(VII) oxide, brown to black with Mn(IV) oxide, green with Mn(III) oxide, and pink with Mn(II) oxide. Using this unique color changes one can develop a chemical sensor resulting in smart fabrics (Vempati et al., 2006).

This article will discuss NM7O as an antimicrobial agent using E. Coli as a model. Also, incorporation of NM7O into some of the nonwovens will be discussed. Of the several Nonwoven fabrics that can be used as substrates, cotton-based materials have a strong potential because of their unique performance properties, acceptability and biodegradable nature.

Experimental Procedure

Processing

To manufacture NM7O, manganese chloride ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$) from Sigma (#M-9522) was dissolved in de-ionized water and the pH was increased to 9.1-9.2 with 5.2 N sodium hydroxide (NaOH). Then *p*-Phenylenediamine (PDA) was added to the solution in the presence of air; consequently, the pH was brought to 7.2 with 6 N hydrochloric acid (HCl). During the addition of HCl, a color change was observed from a teal green to violet. This violet color signifies the production of NM7O. NM7O is a positively charged oxide, and therefore coating it on a negatively charged substrate will increase the fine particle adhesion/coating. The NM7O-clay coated fabric was made is a slightly different process (Vempati et al., 2006)

An 80gsm needle-punched cotton nonwoven, and a through air bonded cotton/PLA web were used as substrates to coat NM7O. Needled cotton web was supplied by the Cotton Incorporated, Raleigh, NC, and the cotton/PLA thermal bonded webs were produced at the University of Tennessee, Knoxville, TN (UTK). Both these fabrics were produced from renewable resources, and are known to be biodegradable. This makes them suitable in producing sustainable products for many of the desired applications. These webs were either produced to, or cut to the width to process continuously in the Mathis padding drying equipment. All the padding experiments were carried out using the Mathis 2-roll laboratory padder type VFM, 350mm wide, and the padded samples were dried/cured using the Mathis KTF dryer.

Characterization

The treated fabrics were characterized for their performance properties using the procedure suggested by standard test methods. These tests included the determination of basis weight, thickness and air permeability. These fabrics were targeted for antibacterial applications, so studies were conducted with *E. Coli* bacteria as a model at the UT Southwest Medical Center, Dallas, TX. All investigations were conducted using a competent cell line of *E. coli* called XL1-Blue. A 1:100 dilution of bacterial with lysogeny broth (LB) grown overnight revealed the exponential growth phase at 2 hours. This was conducted by recording the optical density at 600 nm every 15 minutes to determine the time point in which the OD was 0.5 to 0.6. Five mL of LB (Fischer Scientific #DF0446-17-3) was inoculated with the frozen stock of XL1-Blue and grown overnight in a culture tube (Fischer Scientific #14955127) on an orbital shaker. In the morning, the culture tube contents were transferred into a 500 mL Kimax Heavy-duty Erlenmeyer flask (Fischer Scientific #S34088-1) with 50 mL of pre-warmed LB and remained on the orbital shaker for 2 hours.

Concentration experiments were conducted following the two hour incubation in order to allow bacteria to reach the exponential growth phase. The following amounts of NM7O were added separately to each 10 mL vial of bacteria: negative control of no NM7O, 1 μL of NM7O, 10 μL of NM7O, 100 μL of NM7O, and 1 mL of NM7O. After 30 minutes of incubation on the orbital shaker, 100 μL of the samples were plated with Genlantis EZ-Spread Plating Beads (Fischer Scientific #C400100) on LB agar (Fischer Scientific #DF0445-17-4) in 10^{-4} , 10^{-5} and 10^{-6} dilutions and placed in the incubator overnight. Colonies were observed and counted the following morning and analyzed.

The time course experiments were conducted in the same manner as the concentration experiments; however, the incubation period was changed to one to three hours with 30 minute intervals and the amount of NM7O added was constant. When coating NM7O on the clay substrate, the amount of NM7O in solution was 10% of the solution without clay. Therefore, 100 μL of NM7O was added to each 10 mL microbial solution, while 1 mL of NM7O-coated clay was added to each 10 mL microbial solution during the time course experiment. This was in order to normalize total NM7O in solution.

Results and Discussion

From the sample weight before and after padding, it was obvious that there was significant amount of MN7O incorporated in the nonwoven samples ranging from 7 to 114 %. However, add on values were different for various fabrics, although similar padding conditions were used. This is due to the differences in the fabric composition as well as the padding conditions. Multiple passings through the padder helped incorporate more additives. Also, thorough washing removed some of the entrapped nanoparticles, further changing the weight gain.

Figure 1 depicts the effect of purified NM7O concentration with the percentage of colonies killed. An unusual phenomenon is observed with 15.32 μM of NM7O; the addition of this concentration has a decrease in the death rate and was observed in both purified and unpurified samples. Figure 2 describes the effect of purified NM7O coated clay concentration with the percentage of colonies killed. The growth phenomenon observed in Figure 1 is not observed when clay is present as seen in Figure 2. Table 1 gives a head to head percentage killed by both purified NM7O and NM7O coated clay after a 30 minute incubation. NM7O coated clay has a significantly higher killing capacity with the 15.32 μM concentration of NM7O, with an average killing percentage of 94.28 vs. 52.84.

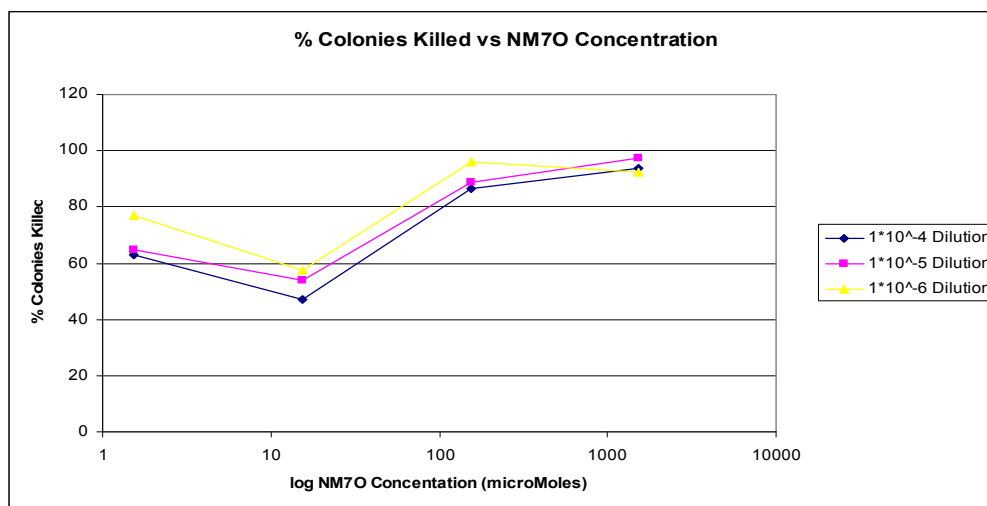


Figure 1. Percent Colonies Killed vs. NM7O Concentration in logarithmic scale.

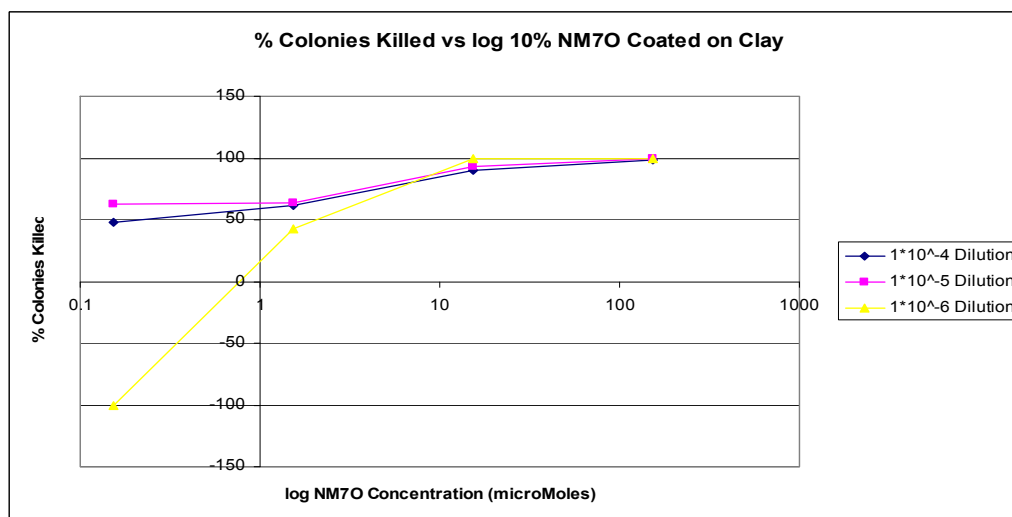


Figure 2. Percent Colonies Killed vs. NM7O Coated Clay Concentration in logarithmic scale.

Table 1. Percent Kill Rate Comparison of NM7O vs. NM7O Coated Clay with 30 Minute Incubation.

| NM7O(μM) | Dilution 10 ⁻⁴ | | Dilution 10 ⁻⁵ | | Dilution 10 ⁻⁶ | | Average | |
|-----------------------|---------------------------|-----------|---------------------------|-----------|---------------------------|-----------|---------|-----------|
| | NM7O | NM7O-clay | NM7O | NM7O-clay | NM7O | NM7O-clay | NM7O | NM7O-clay |
| 1.53 | 63.17 | 61.35 | 64.54 | 63.48 | 76.92 | 42.31 | 68.21 | 55.71 |
| 15.32 | 46.94 | 89.56 | 53.90 | 93.26 | 57.69 | 100.00 | 52.84 | 94.28 |
| 153.24 | 86.58 | 98.67 | 88.65 | 99.29 | 96.15 | 100.00 | 90.46 | 99.32 |

Conclusions

This study showed that NM7O-coated clay is successfully embedded into fabric matrix. The NM7O incorporated matrix in the study was a needle-punched cotton nonwoven, and a through air bonded cotton/PLA web. The maximum coating was observed in the double coated through air bonded cotton/PLA web. The air permeability data indicates that these webs have good permeability and permeability values did not change because of the incorporation of NM7O. The unexpected bacterial growth at 15.32 μ M concentration is inexplicable; therefore, this experiment will be repeated. Overall, clay-coated NM7O showed slightly higher killing rate than the pure NM7O, due to the availability of higher surface area. The applications of this technology include: antibacterial wipes for healthcare and hygiene products, diapers, hospital bedding, house-hold wipes, sportswear, and water purification membranes.

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