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# Arsenic Antibacterial Polymer Composites Based on Poly(Vinyl Chloride)

*Witold Brostow,*[1] *Stevens Brumbley,*[2] *Marina Gahutishvili,*[1,3] *Nathalie Hnatchuk**[1]

**Summary:** New compositions based on arsenic oxide nanoparticles and poly(vinyl chloride) (PVC) were prepared. Sufficient antibacterial activity has been achieved for *Escherichia coli* and *Pseudomonas syringae*. The antibacterial materials so obtained are non-irritant. At the same time, the PVC-based composites have high thermal stability as demonstrated by thermogravimetric analysis and aging of samples; crosslinking enhances thermal stability. Still further, we have determined scratch resistance in a microscratch tester. High scratch resistance has been demonstrated, including strong viscoelastic scratch recovery (the bottom of the groove goes up inside of 2 minutes).

**Keywords:** antibacterial activity; PVC; scratch resistance; viscoelastic recovery

## Introduction

One does not need to argue the importance of providing antibacterial activity to materials. The way it was done earlier was simply using materials which can destroy bacterias. There are immediate problems since some such materials including arsenic are highly toxic; they do destroy bacterias but not only . . . One option which has been used before our project began was using low molecular weight antibacterial agents. This represents progress as compared to 'nude' arsenic or arsenic oxide; however, toxicity is mitigated only to some extent while the service life is insufficient.

Arsenic is one of the few chemical elements that are almost universally recognized by the general public, who associate the material with poison—as evident from the literature. The book by Kathryn Harkup which covers in a scientific way poisons used by Agatha Christie in her novels[1] begins with arsenic with the comment "murder is easy". Many applications of arsenic are controversial – given the high toxicity of its compounds. Arsenic is the most widely used medication for a variety of illnesses, most commonly in the treatment of leukemia.[2,3] The benefit of arsenic was first recognized more than 2400 years ago by Greek and Chinese healers who used arsenic to treat a variety of diseases. The toxicity of arsenic to insects, bacteria and fungi led to its use as a wood preservative. Arsenic is added in small quantities to alpha-brass to make it dezincification resistant. This grade of brass is used to make plumbing fittings or other items that are in constant contact with water. Arsenic is also used for taxonomic sample preservation; for the production of agricultural chemicals (insecticides, herbicides, algaecides, and growth stimulants for plants and animals). Arsenic (III) oxide exhibits antimicrobial and its antibacterial activity against a growing number of organisms has been demonstrated.[4–6] In our approach, we put arsenic (III) oxide into poly(vinyl chloride) (PVC). We investigate several properties of such systems.

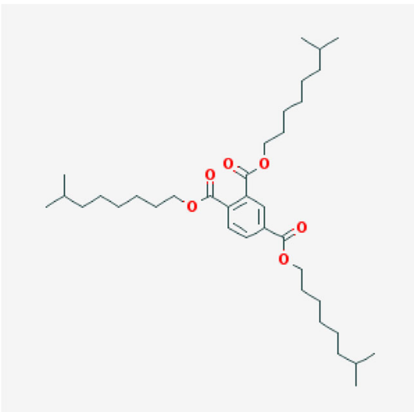
[1] Department of Materials Science and Engineering and Department of Physics, University of North Texas, 3940 North Elm Street, Denton, TX 76207, USA
E-mail: hnatnm@gmail.com
[2] Department of Biological Sciences, University of North Texas, TX 76207, USA
[3] College of Exact and Natural Sciences, Ivane Javakhishvili University, 1 Ilia Chavchavadze Avenue, 0179 Tbilisi, GA, USA

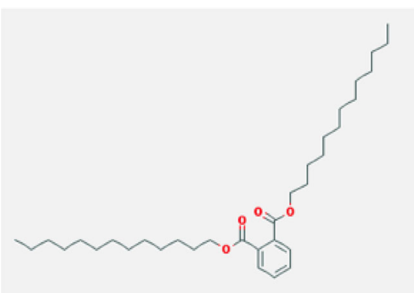
## Experimental Section

### Materials and Sample Preparation

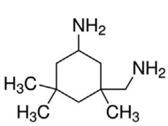
The PVC grade is called SE1300 N provided by Shintech Inc, Houston, TX, USA, and was used as the main polymer matrix. It contains vinyl chloride monomer up to 10 ppm by weight and was used without further purification. Thermal stabilization of our formulation was achieved by incorporating a Ca/Zn commercial salt. The plasticizers consisted of triisononyl trimellitate (TINTM)



plus ditridecyl phthalate (DTDP)



The crosslinking agent was 5-amino-1,2,3-tetramethyl cyclohexane methylamine:




For all samples, the amounts of PVC, Zn/Ca thermal stabilizer, plasticizer and the arsenic (III) oxide were kept constant at 10; 0.1; 2.5 and 0.4 g respectively (Table 1). Plasticizer was separately prepared as TINTM + DTDP with the ratio 60:40 wt.% and preheated up to 60 °C. The control sample did not contain the arsenic trioxide antibacterial agent.

Two different solvents, water and aq. alkaline solution, were used for the preparation of arsenic nanoparticles. 0.19 g of the crosslinking agent was used for preparation of the crosslinked PVC + As composite.

Components were mixed with strong agitation until a homogeneous dispersion was obtained. All samples were processed in a compression molding machine (DAKE, Model 44–250, Grand Haven, MI, USA) at 150°C and 10 tons of compressive force. Four samples of each composition were prepared for antibacterial and thermophysical analysis: discs 2.0 cm in diameter and 0.5 cm in thickness were made. Compositions of the samples studied are listed in Table 1.

### Antimicrobial Assay

Two different bacterial species, *Escherichia coli* DH5α and *Pseudomonas syringae* PV288, were employed. *E. coli* was grown on liquid and solid lysogeny broth (LB) media and maintained at 37 °C whereas *P. syringae* was maintained on the King's B media (liquid and solid) and grown at 28 °C. A King's B medium consists of 10 g proteose peptone #2, 1.5 g anhydrous $K_2HPO_4$, 15 g glycerol and 5 mL $MgSO_4$ (1 M; sterile). We use the diameter of the inhibition zone as the measure of the anti-bacterial activity.

### Liquid Culture Assay

The bacterial strains were streaked on appropriate solid media and single colonies were picked after overnight growth. Each subculture was created by inoculating the single colonies in 10 ml liquid culture media, with or without the PVC samples. A total of 1 mg of the PVC sample was grinded and added to 100 ml of liquid culture media, with the final concentration of the PVC sample of

***Table 1.***
Weight content of components in the composition.

| Composition | PVC [g] | Stabilizer [g] | Plasticizer [g] | Crosslinking agent [g] | Antibacterial agent $As_2O_3$ [g] | Solvent |
|---|---|---|---|---|---|---|
| A (control) | 10 | 0.1 | 2.5 | | | |
| B | 10 | 0.1 | 2.5 | 0.19 | 0.4 | $H_2O$ |
| C | 10 | 0.1 | 2.5 | | 0.4 | $H_2O$ |
| D | 10 | 0.1 | 2.5 | | 0.4 | NaOH |

10 μg/ml. The cultures were allowed to grow for 12 h and optical density of the cell growth was measured at 600 nm. The experiment was performed in triplicates and repeated twice (n = 6).

### Solid Culture Assay

To measure the anti-bacterial properties of the PVC samples, ≈5 mm$^2$ pieces of the samples were used. A clear zone of growth inhibition around the PVC sample is an indication of anti-bacterial activity. A total of 50 μl of the overnight grown bacterial cultures were spread plated on the appropriate solid media; the PVC sample squares were placed in grids demarcated on the culture plates. Observations with regards to a zone of growth inhibition around the PVC samples were made after a lawn of bacterial growth was visible. The experiment was repeated thrice (n = 6).

### Thermal Stability and Aging

A PerkinElmer TGA (thermogravimetric analysis) 7 instrument permits the measurement of weight changes in PVC + As composites as a function of temperature. Weight changes resulting from chemical reactions, decomposition, solvent and water evolution, and oxidation in sample materials are thus determined. The technique is well described by Menard.[7]

The second series of thermal stability measurements dealt with aging. We placed samples in a thermal chamber at 75 °C for a time exceeding one week and determined weight changes daily.

### Scratch Resistance Determination

We have used a microscratch tester from Anton Paar. The technique is described for instance in.[8] The indenter was a Rockwell diamond tip with a 200 μm radius. Progressive load tests consisting of 5 scratches for each sample were performed and the averages calculated. The scratch length was 5.0 mm, and scratching speed was 5.33 mm min$^{-1}$; samples were tested in the load range from 0.03 N to 20.0 N.

For each scratch, first the penetration depth $R_p$ (instantaneous depth of penetration by the indenter) was measured and recorded. Because of the viscoelastic nature of polymers, there is a recovery or healing of the scratch groove.[8] The scratch remains with a shallower depth called the residual or the healing depth $R_h$; the recovery process is completed inside of 2 minutes. The extent of healing depends on the load and the properties of the material. The percentage of recovery (healing) f is defined as

$$f = \left[\left(R_p - R_h\right)/R_p\right] \cdot 100\% \qquad (1)$$

We recall that high values of f correspond to low values of brittleness; an equation relating the two quantities has been derived.[9]

## Antimicrobial Assay Results

Selected results are displayed below. The zones of growth inhibition are shown on the left for *E. coli* and on the right for *P. syringae*. In both cases number 4 pertains to the control sample without the antibacterial agent.

We see in Figure 1 that, in both liquid and solid media, all the PVC + $As_2O_3$ samples display anti-bacterial activity.


***Figure 1.***
Antimicrobial assay results

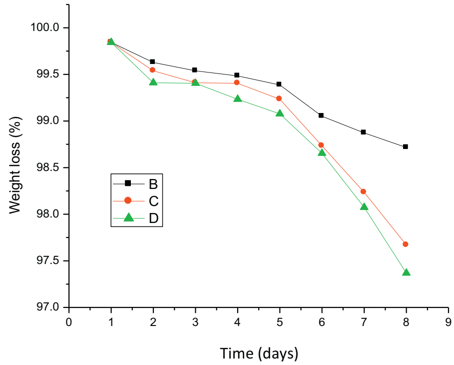



***Figure 2.***
Aging results.

## Thermogravimetric Analysis and Aging Results

TGA scans have been performed from 50 °C to 700 °C at a rate of 20 °C per minute, in a nitrogen environment. The results are summarized in Table 2, including the symbols B, C and D defined above in Table 1.

We now consider aging. Several diagrams of weight changes caused by aging as a function of time in days are displayed in Figure 2.

Figure 2 as well as Table 2 tell us that the crosslinking agent in material B enhances the thermal stability. We see in Table 2 that the degradation start is some 20 °C higher for sample B than for the remaining ones. As for aging, we see in Figure 2 that the same sample B has the lowest weight loss at 75 °C over a week. Thus, results of one-time TGA runs coincide with the results of the aging tests.

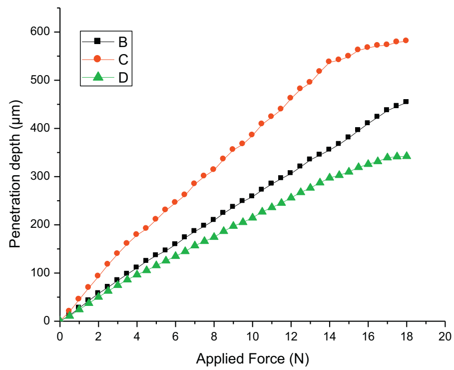



***Figure 3.***
Penetration depth results as a function of the applied force.

## Scratch Resistance

As noted in Section 2.6, measurements were made in a progressively increasing load mode. Penetration depth $R_p$ results are presented in Figure 3, residual depth $R_h$ results in Figure 4. Viscoelastic recovery f as defined by Eq. (1) is displayed in Figure 5.

We see large differences between the penetration depth and the recovery depth results. Material C, prepared from water

***Table 2.***
Thermal stability of composites.

| | Temperature [°C] | | | |
|---|---|---|---|---|
| Composition | Degradation start | First peak | Second peak | Third peak |
| B | 262 | 343 | 499 | – |
| C | 240 | 331 | 478 | – |
| D | 246 | 329 | 497 | 620 |

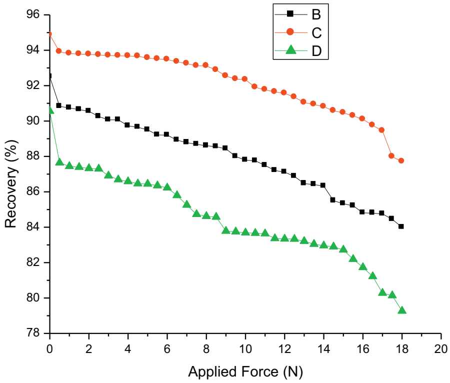



***Figure 4.***
Residual (healing) depth results as a function of the applied force.

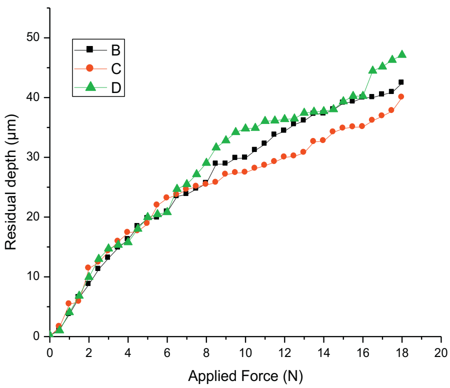



***Figure 5.***
Viscoelastic recovery calculated from Eq. (1).

and without a crosslinking agent, shows the highest penetration depth but the lowest residual depth. The same material shows also the highest viscoelastic recovery.

Needless to say, there is no simple connection between scratch resistance and thermal stability; we recall that in the latter case B was the best material.

## Conclusion

This work presents a new approach for developing PVC + As nanocomposite materials. We have demonstrated that addition of arsenic (III) to PVC provides antibacterial activity. A separate problem is that of separation of arsenic compounds from those of antimony. In Georgia there are mineral ores containing oxides of both. Using a mixed solvent consisting of 1-butanol and n-hexane, followed by azeotropic distillation involving also water, these two oxides can be separated.[10]

Our antibacterial polymers have the additional advantages that they are non-volatile, insoluble in water, chemically and thermally stable. Therefore, they can reduce losses associated with volatilization, photolytic decomposition, and transport – with prospects to be used as disinfectants. Handheld water filters, surface coatings and fibrous disinfectants deserve also to be mentioned in this context.

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[1] K. Harkup, *A is for Arsenic: The poisons of Agatha Christie*, Bloomsbury Press, London **2015**.
[2] F. Ravandi, E. Estey, D. Jones, et al., *J. Clin. Oncol.* **2009**, *27*, 504.
[3] B. L. Powell, B. Moser, W. Stock, et al., *Blood* **2010**, *116*, 3751.
[4] K. Senior, *Drug Discov. Today* **2002**, *7*, 156.
[5] M. J. Park, I. C. Park, I. J. Bae, et al., *Int. J. Oncol.* **2004**, 2, 1271.
[6] F. M. Uckun, X.-P. Liu, US Patent 6, 191,123 B1, **2001**.
[7] K. P. Menard, "Thermal Transitions and Their Measurement", Ch. 8, in *Performance of Plastics*, W. Brostow, Ed., Hanser, Munich – Cincinnati **2000**.
[8] W. Brostow, V. Kovacevic, D. Vrsaljko, J. Whitworth, *J. Mater. Ed.* **2010**, 32, 273.
[9] W. Brostow, H. E. Hagg Lobland, M. Narkis, *J. Mater. Res.* **2006**, *21*, 2422.
[10] W. Brostow, M. Gahutishvili, R. Gigauri, H. E. Hagg Lobland, S. Japaridze, N. Lekishvili, *Chem. Eng. J.* **2010**, *159*, 24.