# Permanent, Non-Leaching Antimicrobial Polyamide Nanocomposites Based on Organoclays Modified with a Cationic Polymer

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The intercalation of cationic copolymer into a smectic clay, montmorillonite, has been used to produce polymerically modified organoclays. The organoclays of different lamellar morphology and content of quaternary ammonium groups have been prepared by altering the clay/polymer ratio. The organoclays prepared have been explored in the design of antimicrobial materials based on clay/polymer nanotechnology. Polyamide nanocomposites containing organoclays with incorporated cationic polymer showed an antimicrobial activity and improved mechanical properties. The antimicrobial efficiency and the mechanical properties of the nanocomposites were controlled by the variation of the content of the cationic polymer incorporated into the organoclay and organoclay loading.
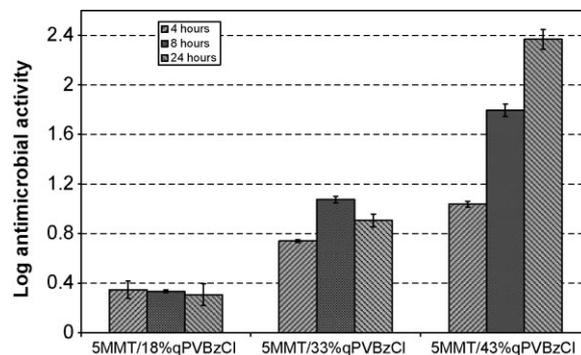
Introduction

The increase in numbers of antibiotic-resistant microbes and related disease outbreaks, the declination of immunity due to population aging and environment pollution, the increase of global human and livestock mobility, require extensive activities in infection control. The old and current practice to combat infections mainly relies on disinfection methods that aim to inhibit the microbial growth on surfaces via special chemical or physical treatments. The disinfectant migration from the surface and the loss of its activity due to various interactions ultimately result in unprotected surfaces.

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Alternatively, biocide-containing materials have been used in various applications as self-sterilizing surfaces.[1–3] The main approach in developing such materials is based on the entrapment of biocide substances into a matrix material. As a result, the material is able to release biocides and thereby to provide antimicrobial, antifungal or antiviral protection. However, biocide release rate decreases with time because of biocide depletion. Therefore, the surfaces can be protected only for a limited period of time. Moreover, the release of low-molecular-weight biocides into the environment, contributes to the development of microorganism resistance against biocides.

Binding biocide molecules onto the surface has the potential to overcome these problems if immobilized antimicrobial agents retain their activity and thereby impart antimicrobial properties to the surface. Recently, permanent rendering of surface biocidal activity (or, at least, for life-term of the material), has attracted growing interest as an alternative approach to suppress cell viability on solid surfaces.[3–5] Significant efforts in developing surface-bound antimicrobials have been focused on

quaternary onium salts.[5–11] Cationic surfactants represent a broad range of organic disinfectants.[12] In addition to low-molecular-weight surfactants, cationic biocides have been further developed as polymer and copolymers containing quaternary onium groups. There are number of evidences that polymeric onium salts are more potent than their low-molecular-weight counterparts in biocidal activities.[13] The early development of polymeric biocides was focused on water or alcohol-soluble substances which could be used in a similar way to the low-molecular-weight surfactants. Over the past few decades, sporadic attempts were undertaken to explore antimicrobial activity of insoluble forms of the polymeric onium salts.[6–8,14–16] More recently, research activities on self-sterilizing surfaces based on polymers containing onium groups have undergone a substantial growth. It is generally accepted that surface-bound polymers containing quaternary onium groups can suppress the viability of cells contacting the materials efficiently. There are strong evidences that the antimicrobial efficiency of a surface-bound polymer with onium groups is higher for the polymeric onium salts, which contain long alkyl chains in a quaternary group.[9,17] The hydrophobic alkyl chains are believed to facilitate polymer penetration through bi-layered cell membrane, compromising its integrity and ultimately causing cell death.[5]

In the past two decades, long-chained quaternary onium salts have become a key element of thriving clay/polymer nanotechnology.[18,19] Cationic surfactants are used to produce organophilic clays through the ion-exchange of the metal cations within the layered silicates. Conceptually, clay modification is intended to intercalate organophilic substances into the interlayer space in order to weaken the interlayer interactions, to increase the interlayer spacing and to improve clay-polymer compatibility. Such effects enable the penetration of macromolecules into the clay interlayer space during processing, leading to the separation of the individual silicate layers and the uniform dispersion of the separated layers in a polymer matrix. Composites produced in this way are filled with particles of nanometer scale and show the improvement of a wide range of physical and engineering properties at relatively low clay content, typically below 5 wt.-%.

Despite nearly two decades of development of polymer/clay nanotechnology, it was overlooked that organoclay-based nanocomposites actually contain antimicrobial entity, cationic surfactants, and have potential to be antimicrobial materials. Just recently, several research groups reported antimicrobial activity of clay/polymer nanocomposites based on commercially available organoclays.[20–26] Although the migration of the surfactants from the nanocomposites has been experimentally confirmed, the antimicrobial action of the composites is believed to be dominated by solid surface activity on contact.[20] Surfactant migration from the nanocomposites produced from those commercially available organoclays, not only restricts materials applications, but also can eventually result in the loss of the antimicrobial activity due to biocide exhaustion.

A novel solution has been developed in this study to prevent the migration of antimicrobial modifiers towards developing non-leaching antimicrobial materials via clay/polymer nanotechnology. The strategy applied in this research is to use macromolecular substances containing quaternary onium groups for clay modification. We assume the formation of the multiple ionic bonds between the multi-charged modifiers and one or several clay platelets during the ion exchange. The cooperative interactions are expected to exclude unbound state of the modifier and thereby to prevent polymeric biocide migration from both the organoclays and nanocomposites.

The ability of cationic copolymers to intercalate mineral clays has been proven for several polymer modifiers such as end-capped polymers, ionenes, branched polymers, graft-, block- and random copolymers.[27] The term polymerically modified organoclays was previously used to refer to organoclays with chemically bound polymers. This definition allows distinguishing such materials from the intercalated structures when a polymeric intercalant is not chemically bound to the clay surface. Additionally, polymer-modified and macromolecule-modified organoclays will be used in this paper as equivalents of polymerically modified organoclays. Similar to organoclays with the incorporated low-molecular-weight organic substances, the polymerically modified clays can facilitate the dispersion of clay in a polymer matrix to form nanocomposites. Moreover, compared with cationic surfactants, it is anticipated that copolymers could offer more flexibility in tailoring modifier properties as a compatibilizer between the clay and a targeted polymer matrix.

In this study, poly(vinylbenzyl chloride) (PVBzCl) partially aminated with a tertiary amine containing one long alkyl chain, has been used as an example of antimicrobial macromolecular clay modifier in the development of non-leaching polymer nanocomposites, which are effective against microorganisms by contact. Organoclays with different content of the antimicrobial polymer modifier have been prepared and used to produce polyamide 6 nanocomposites. The antimicrobial activity of the nanocomposites was investigated against *Escherichia coli* and *Staphylococcus aureus* strains. The influences of organoclay composition and content on antimicrobial activity, mechanical properties and morphology of the nanocomposites have been studied.

Experimental Part

Materials

Montmorillonite (MMT) (sodium form) with cation exchange capacity of 0.92 mequiv. · g^{-1} was supplied by the Southern Clay

Products. PVBzCl with molecular weight 55 kDa was purchased from the Scientific Polymer Products (Ontario, NY, USA). *N,N*-dimethylhexadecylamine and tetrahydrofuran (THF) were supplied by Sigma-Aldrich (Loughborough, UK) and were used without further purification. The polyamide-6 studied was Ultramid® B3 purchased from BASF.

Synthesis of Partially Aminated Poly(vinylbenzyl chloride)

The synthesis of a derivatized PVBzCl containing quaternary ammonium groups (qPVBzCl) was carried out by partial amination of the methylene chloride groups with a tertiary amine (Scheme 1). In a round-bottom flask equipped with a reverse condenser, 40 g of PVBzCl were dissolved in 500 mL of THF to produce a polymer solution. 26.5 mL (78.6 mmol) of *N,N*-dimethylhexadecylamine were added to the polymer solution resulting in 3:1 molar ratio of vinylbenzyl chloride units to tertiary amine. The reaction in the mixture was carried out at 60 °C for 24 h under constant stirring. After the reaction, portions of qPVBzCl polymer solution were used directly for organoclay preparation.

Preparation of Polymerically Modified Organoclays

Sodium-montmorillonite (Na-MMT, 8 g) was vigorously stirred in 400 mL of distilled water using a magnetic bar in order to produce a clay suspension. The suspension was stirred at ambient temperature overnight. A portion of qPVBzCl solution was diluted by 200 mL of THF. Clay suspension was added to the diluted polymer solution with vigorous stirring. Copious precipitates were formed immediately after clay introduction. A further 50 mL of water was used to insure the complete MMT transfer into the reaction mixture. The slurry was stirred at ambient temperature for 24 h and followed by repeated centrifugation and washing with 50:50 water/THF mixture and distilled water three times with each solvent system. After the final washing and centrifugation, the organoclays containing the polymer modifier were dried using freeze drying. Three types of organoclays were prepared using 25, 40 and 55 g portions of qPVBzCl solutions. The content of the polymeric modifier in the organoclays was determined by thermal gravimetric analysis (TGA) and shown in the Table 1 with the corresponding material coding. TGA was performed on a Perkin-Elmer Pyris 1 TGA by increasing temperature from 40–800 °C at a rate of $10 °C \cdot min^{-1}$ under a constant nitrogen flow of $20 mL \cdot min^{-1}$. The content of polymer modifier was determined as weight loss during sample heating from 120 °C (after water evaporation) and 800 °C.
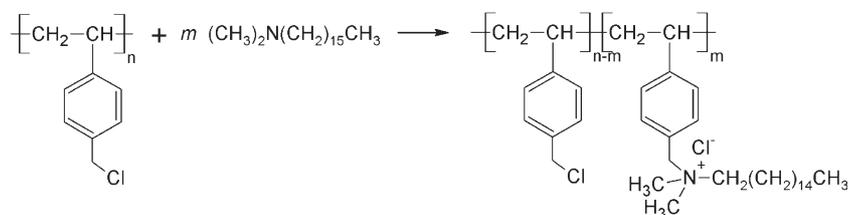
Table 1. Composition and coding of the prepared materials.

Clay	MMT	qPVBzCl	Polyamide 6 nanocomposite	Clay[a]
	wt.-%	wt.-%		wt.-%
18qPVBzCl	82	18	5MMT/18qPVBzCl	5
33qPVBzCl	67	33	2.25MMT/33qPVBzCl	2.25
			4MMT/33qPVBzCl	4
			5MMT/33qPVBzCl	5
43qPVBzCl	57	43	5MMT/43qPVBzCl	5

[a]Based on unmodified MMT.

Nanocomposite Preparation

Polyamide/clay nanocomposites were prepared by melt extrusion using a 16 mm twin-screw extruder. The extrusion was carried out under the condition of temperature 240 °C, L/D (length/diameter) ratio 24:1, screw speed 400 rpm and feeding rate 20%. Two series of nanocomposites were produced using pre-dried and pre-mixed formulations of polyamide/clay. One series contained 5 wt.-% of each type of polymerically modified organoclay prepared (18qPVBzCl, 33qPVBzCl and 43qPVBzCl). The second series was produced using the organoclay with 33 wt.-% of qPVBzCl and contained 2.25, 4 and 5 wt.-% of the organoclay. The composition of the polyamide nanocomposites and their corresponding codes are shown in Table 1. The extruded strands were pelletized and dried in a vacuum oven at 80 °C for 10 h before molding into bone-shaped coupons ($5 \times 3 mm^2$) for tensile test, bars ($9 \times 3 \times 50 mm^3$) for dynamic mechanical analysis (DMA) or square samples ($25 \times 25 \times 1 mm^3$) for antimicrobial and XRD tests using injection molding. The temperature applied in the injection molding was 270 °C.

XRD Characterization of Organoclays and Nanocomposites

The X-ray diffraction (XRD) characterization of the organoclays and nanocomposites was carried out using a Philips XPert Pro XRD (PANalytical, USA) with Cu K_α radiation source at 40 kV and 30 mA. The samples were scanned at a scan rate of 1 degree per minute with the step size of 0.008 degrees.

Mechanical Tests of Nanocomposites

The tensile strength of the nanocomposites was measured according to ASTM D638 using a Monsanto tensiometer with a cross-head speed of $0.25 mm \cdot s^{-1}$. Since the limitation of sample size, it was difficult to fit strain gauge or extensometer to the sample during tensile loading. Therefore only strength data was reliable. The stiffness and other mechanical properties were studied using dynamic mechanical testing. The storage modulus (*G'*),

■ *Scheme 1.*

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