

Dedicated to Professor Valer Farcasan
on the occasion of his 95th anniversary

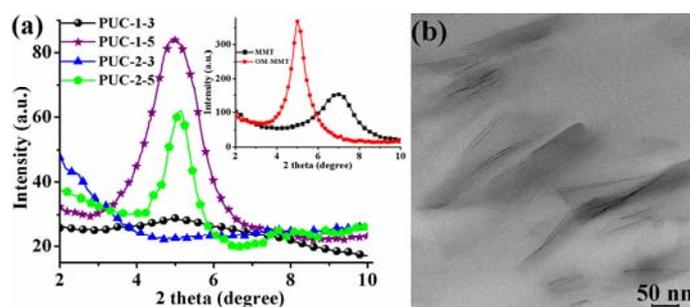
EFFECT OF ORGANOMODIFIED MONTMORILLONITE ON THE PROPERTIES OF SOME PIPERAZINIUM POLYURETHANES

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This study reports the synthesis and characterization of cationic polyurethanes (PUC) containing piperazinium moieties, and their use in the preparation of soft polymeric coatings and hybrid composites with possible antimicrobial activity. Polymers and their composites with 3 and 5 wt.% organically modified montmorillonite (OM-MMT) were examined by employing specific techniques: FTIR, wide-angle X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). The diffraction signals at $2\theta = 2-10^\circ$ of the hybrid composites including 3 wt.% OM-MMT suggested a complete exfoliation of the clay platelets within polycationic matrix, whereas the peaks located around 5° for 5 wt.% OM-MMT reflect rather an intercalated structure, feature confirmed by TEM image. Investigation of mechanical properties of the final materials revealed the role of organo-silicate in the improvement of Young modulus and tensile strength comparatively with the pristine polymers due to the interaction between organic and inorganic phases. A preliminary investigation of the antibacterial activity of these materials against some Gram-positive and Gram-negative bacteria suggested that such cationic PUCs containing quaternary structures are capable to inhibit bacterial growth in film state.



INTRODUCTION

Polyurethanes are linear block copolymers usually assembled of statistically alternating soft and hard segments, possessing a wide range of versatile properties which make them promising candidates for many applications in various areas where tough, durable, and elastomeric materials are required.¹ This class of polymers offers a design freedom not found in other materials due to an unique and broad-ranging portfolio of

characteristics including outstanding abrasion resistance, strength and toughness, chemical and hydrolysis resistance, fungal growth resistance, low-temperature flexibility, clarity, colourability and a large processing window in many plastic procedures. An interesting approach in this field was brought by the insertion of a small amount of ionic functionality into these polymers to yield ionic polyurethanes, usually named ionomers, as first reported by Dieterich *et al.*,² and Cooper and co-workers.^{3,4} Though the polymers contain a

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minority of ionic groups, below 250 meq (per 100 g of polymer) according to Nomula and Cooper,⁵ or a more constrained range between 10 and 120 meq (per 100 g of polymer) according to Dieterich,⁶ their properties are strongly influenced by the presence of ionic charges which tend to aggregate via Coulombic interactions into so-called 'ionic domains' with an effect on phase separation and hard domain cohesion. Depending on the nature of the charge (positive, negative or both) placed within the polymeric backbone, pendant to the chain or only at the chain ends (telechelic systems), all types of ionomers, *i.e.* cationomers, anionomers and zwitterionomers, have received much attention.^{7,8} Considered now one of the most fast-developing and active branches of polyurethane chemistry, such polymers combine the well-known properties of the parent polymers with those derived from the existence of ionic structures in the backbone, offering a unique opportunity to form aqueous dispersions in the absence of any external emulsifier.

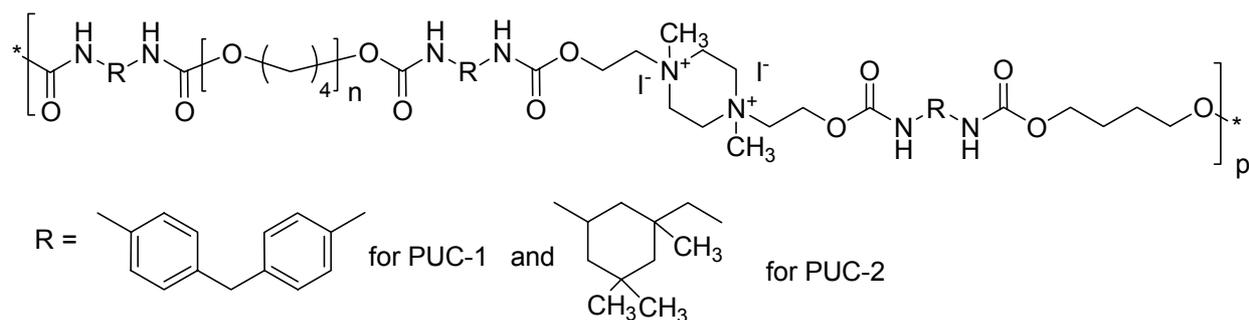
For modern applications, the chemistry of hybrid nanocomposites possessing a novel synergism of properties has been progressively explored to establish if the structural order within the material can be controlled on nanometer/submicron scale.⁹ In particular, the dispersion of nanosized inorganic particles (silver, hydroxyapatite, clay, etc) into a polymer matrix, open the possibility of generating new types of nanostructured materials with designed surface and structural properties, which can be exploited in physical, biological, biomedical, and pharmaceutical applications. It is a well known issue that polymeric composites represent a modern alternative to conventionally filled polymers, since they exhibit markedly improved properties compared to the pure polymers. Therefore, all this information motivated us to extend our previous work on cationic polyurethanes with different (photo)bioactive functions^{10,11} to investigate polyurethane (PU) composites prepared by intimately mixing the cationic polyurethanes with organically-modified montmorillonite, following the final features of the materials comparatively with those of the parent polyurethanes. Encouraged by the antibacterial efficiency of the PU nanocomposites incorporating organophilic silicates as bioactive materials,¹² we report herein a comparative evaluation of the thermo-mechanical and biocidal surface properties of some hybrid

composites, which contain alkyl chain (C12)-modified montmorillonite (OM-MMT) within the cationic PU matrix. Literature data established that natural clay minerals showed no antibacterial effect, but some of them could adsorb and kill bacteria when antibacterial materials were intercalated,¹³ of particular importance being cetylpyridinium (chlorhexidine acetate)-modified MMT or MMT-carrying copper and silver ions that can eliminate bacterial infection.¹⁴

RESULTS AND DISCUSSION

The preparation of cationic PUs with piperazinium moieties was performed through a conventional methodology, that involved a classical polyaddition of the polytetrahydrofuran (PTHF) of 1000 average molecular weight with 4,4'-methylene bis(phenylisocyanate) (MDI) (for PU-1) or isophorone diisocyanate (IPDI) (for PU-2) to form a prepolymer with isocyanate end groups, which is further reacted with a mixture of N,N'- β -hydroxyethyl-piperazine (HEP) and 1,4-butanediol (1,4-BD), the final molar ratio between the partners being 1:3:1:1. In order to achieve polymeric materials with possible antimicrobial activity, the tertiary nitrogen atoms belonging to piperazine residues from the PU backbone were quaternized with methyl iodide, the final idealized structure of the synthesized PUC's being illustrated in Scheme 1.

The titrimetric determination of the ionic iodine content allowed an estimation of the quaternization degree in piperazine rings as being of about 95 %, result that corresponds to a concentration of about 85 meq. ionic groups/100 g polymer, sustaining the framing of such polyurethanes to ionomers class, respectively, PU cationomers. The ionic polymers are soluble in common polar solvents like DMF, DMSO, or dimethylacetamide (DMAc), and by solution casting they give homogeneous films with a typical microstructure to soft urethane elastomers, a good adhesion on a variety of substrates, and high optical quality. To examine the influence of organo-silicate on the properties of the resulting materials, nanocomposites of elastomeric polyurethanes incorporating alkyl chain (C12)-modified montmorillonite (OM-MMT) well dispersed into the polymeric matrix (in proportion of 3 and 5 wt. %, respectively) were prepared.



Scheme 1 – The proposed structure for the cationic polyurethanes with piperazinium groups.

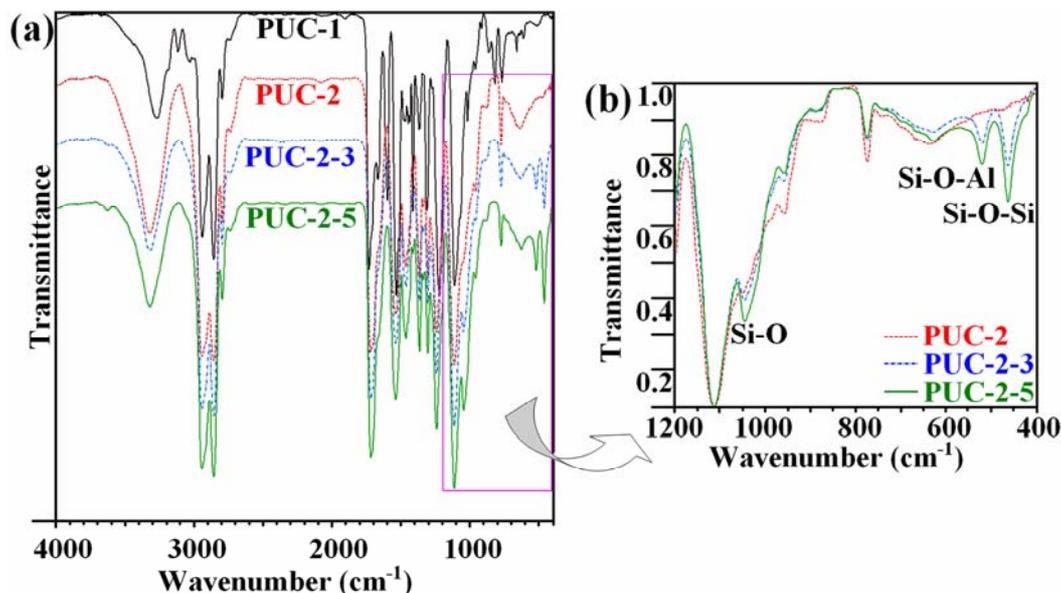


Fig. 1 – FTIR spectra for cationic polyurethanes PUC-1 and PUC-2 and for the composites PUC-2-3 and PUC-2-5 (a), and detail of the region 400-1200 cm^{-1} for PUC-2 series (b).

The intended structures for the synthesized polymers were confirmed by ^1H NMR and FTIR spectroscopy. The FTIR spectra of cationic polyurethanes (Fig. 1, a) exhibited specific absorption bands attributed to urethane NH groups ($3270\text{--}3325\text{ cm}^{-1}$), carbonyl units (CO) (1720 cm^{-1}), the vibrations of the CH_2 groups ($2858\text{--}2945\text{ cm}^{-1}$), amide II absorption ($1535\text{--}1540\text{ cm}^{-1}$), while the C-O-C linkages determined the appearance of the characteristic ester vibrations at 1114 and $1225\text{--}1240\text{ cm}^{-1}$, respectively. For the hybrid composites, the presence of C12-modified MMT particles induced the formation of characteristic bands associated with the stretching of Si-O (1046 cm^{-1}) and Si-O-Al (520 cm^{-1}), and bending of Si-O-Si at 463 cm^{-1} , as shown in Fig. 1, b.

Further, the X-ray diffraction (XRD) analysis was performed to establish the formation and structure of polymer/clay composites at microscopic level, and to estimate the significant changes appeared in the diffraction patterns

through the organic modification of montmorillonite, as well as through the specific interactions filler/filler and filler/matrix during the dispersion process. XRD study of the organically modified MMT suggested that 2-hydroxyethyl-N,N,N-dimethyldodecyl ammonium bromide (DDAB) is an efficient organic modifier of the silicate, increasing basal spacing from 1.26 nm in unmodified MMT up to 1.76 nm in the OM-MMT (Fig. 2, a, inset).

Concerning the polymer composites, the XRD diffraction pattern at $2\theta = 2\text{--}10^\circ$ recorded for PUC-1-3 and PUC-2-3 composites with 3 wt. % OM-MMT indicated the absence of any diffraction peaks (Fig. 2, a), confirming hence the almost complete exfoliation of the clay platelets inside the polyurethane matrixes. This implies that the separated interactions between polymer chains, on one hand, and the clay lamella, on the other hand, are strong enough to disrupt the order of the parallel clay structure, resulting in an exfoliated

silicate system. In the case of composites with 5 wt. % organoclay (PUC-1-5 and PUC-2-5) the presence of peak at about 5° (1.77 nm) in the diffraction spectra is a clear indicative of the incomplete exfoliation of the OM-MMT into the polymeric environment, and this reflects most probably an intercalated structure of the formed hybrid materials. Such finding is supported by the TEM image of microtomed thin film based on PUC-1-5 (Fig. 2, b), where the dark lines represent individual clay layers, whereas the bright area is given by the polymer matrix.¹⁵ Moreover, the TEM micrograph shows that ordered intercalated or exfoliated assembled layers of clay are well dispersed in the polyurethane matrix, confirming thus the X-ray data.

To date, the good mechanical parameters of some polyurethane coatings are considered to be important in both biomedical and industrial applications. Consequently, we have determined the Young modulus, maximum tensile strength and elongation at break for the polyurethanes and their

composites (Fig. 3). By comparing the results, it can be observed that polyurethane PUC-2 with an elongation at break of 840% proved to be more flexible than PUC-1, which exhibited an elongation at break of 450%. This behavior can be mainly ascribed to the structural dissimilarities between the two polymers, knowing that the elasticity of polyurethanes is easily enhanced by using an aliphatic diisocyanate instead of aromatic diisocyanate.¹⁶ Therefore, the more restricted structure of the hard segments introduced by means of aromatic rings from diisocyanate determined a higher Young modulus for PUC-1 (1.72 MPa), while in the case of PUC-2, the aliphatic nature of the hard segment led to a Young modulus of only 0.75 MPa. For the hybrid composites, the same tendency was maintained, so that the composites derived from PUC-1 presented higher Young modulus compared to the PUC-2 based composites. Giving this visible difference, the role of the OM-MMT in upgrading the mechanical properties is thus confirmed.

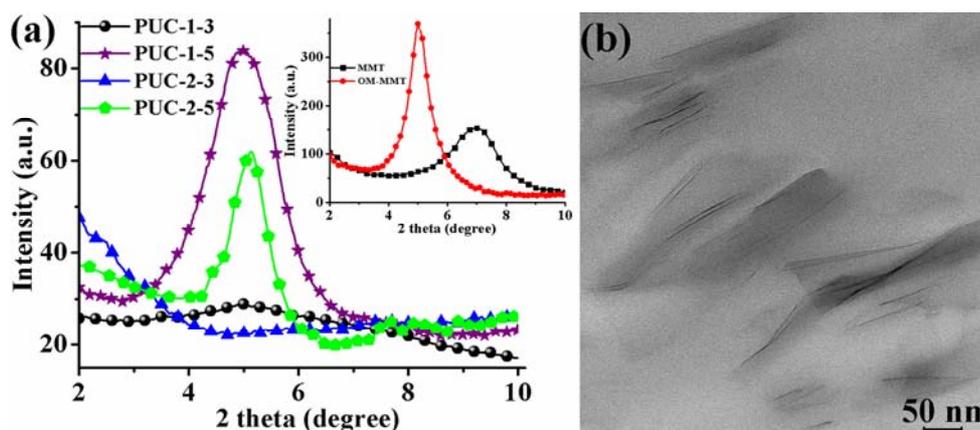


Fig. 2 – X-ray diffraction patterns of unmodified/modified MMT's (a, inset) and for the hybrid composites PUC-1-3, PUC-1-5, PUC-2-3, PUC-2-5 with 3 and 5 wt. % OM-MMT (a) and TEM image of PUC-1-5 hybrid polyurethane composite (b).

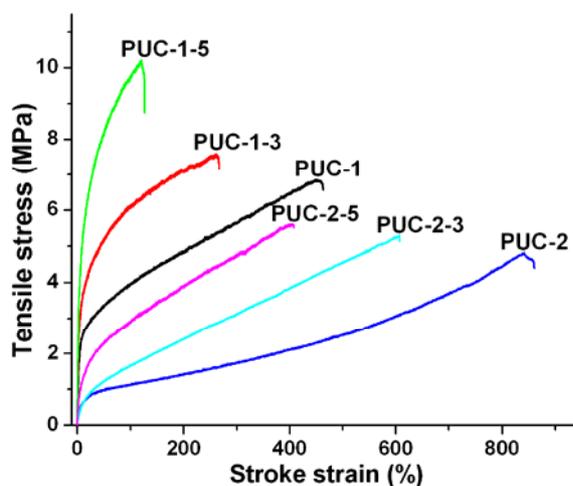


Fig. 3 – Stress-strain curves for the polyurethane cationomers PUC-1 and PUC-2 and composite films with different clay contents.

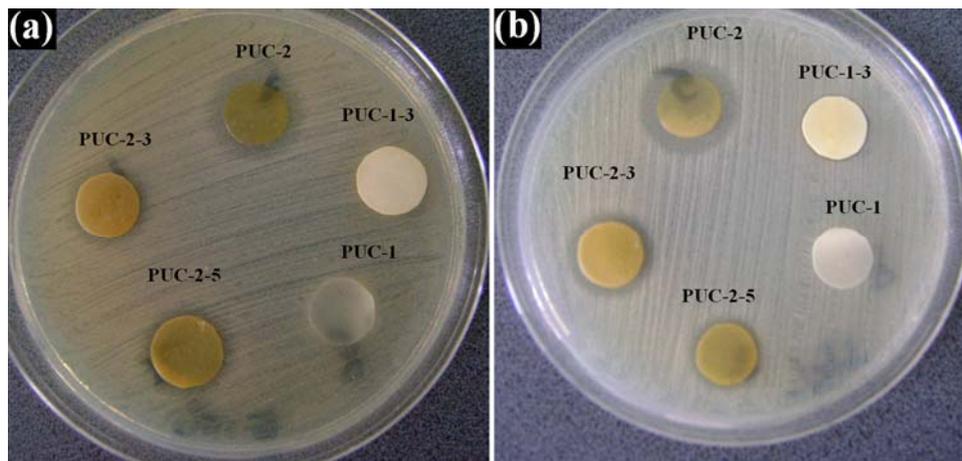


Fig. 4 – Antibacterial activity results for polyurethane films and composites against *E. coli* (a) and *S. aureus* (b).

The antibacterial properties for these cationic polyurethanes in film state were evaluated in the presence of Gram-negative or Gram-positive bacteria namely, *Escherichia coli* and *Staphylococcus aureus* (Fig. 4 a, b).

From the above figure it can be observed that the PUC-2 polymeric film coming in contact with bacteria induced a reduction of colonies growth at the interface between material and bacteria, but it does not reach distant areas from the material. In the case of PUC-1, the antibacterial activity was not detected around the film surface and this result may be connected to the mobility of biocidal moieties from the PU hard block that has impact on cell behavior at the contact interface. As argued,¹⁷ the polyurethanes with non-leaching quaternary ammonium functionality on their surface can kill *S. aureus* after 30 min of contact, the intensity of this contact depending not only on the concentration and the distribution of biocidal functions permanently fixed to the polymer surface through covalent binding, but also on the interaction between bacteria and a positively charged surface. Unlike these polymers, a similar effect could not be seen for the non-ionic polyurethanes. Therefore, the existence of ammonium groups attached to the PU backbone was effective in preventing bacterial growth. As reported by others, in the literature there are polymers with tertiary amine groups converted into quaternary ammonium salt through quaternization with iodomethane (polyurethanes, polymethacrylates, hybrid composites), which presented good antibacterial activity ascribed to both the cationic structure and increased hydrophobicity.¹⁸⁻²⁰ Analyzing then the effect of nanocomposites loaded with C12-modified MMT

on biological interactions, the final result confirmed preservation of bioactivity of the PUC-2 against *E. coli* and *S. aureus*, but it is attenuated around hybrid surface. In contrast with the hydrophilic feature considered earlier, the response of PUC-2-5 seems less effective against the same bacteria, probably owing to the content of ammonium moieties migrated to the surface of the film during the film-formation process, as important factor in antimicrobial contact.²¹ This finding would be also consistent with the absence of antibacterial component capable to diffuse through composite in agar medium. Therefore, our preliminary test anticipates a further study to give evidence that the antibacterial activity was based on contact mechanism rather on any biocidal leaching considered responsible for the local inhibition zone and implicitly, to assess the role of unreacted residual monomer released from the polyurethane film.

An identification of the surface charge density in our materials can be achieved by XPS analysis. Figure 5 displays N_{1s} core-level XPS spectra for PUC-2 (a) and its hybrid composite PUC-2-3 (b), where the expected energy peaks due to N_{1s} , and N^+ were collected and evaluated. The first peak located at 398.9 eV belongs to N_{1s} from the urethane groups, while the second at 401.6 eV is assigned to N_{1s} in quaternized nitrogen from piperazinium moiety. Therefore, the appearance of the latter peak in the spectra confirmed the quaternization of the piperazine ring in the non-ionic PU by iodomethane. We can therefore assume that the changes in surface chemistry that are observed in the XPS spectra of the hybrid composite are most likely due to organo-MMT/cationic polyurethane interactions within the functionalized hard segment domain.

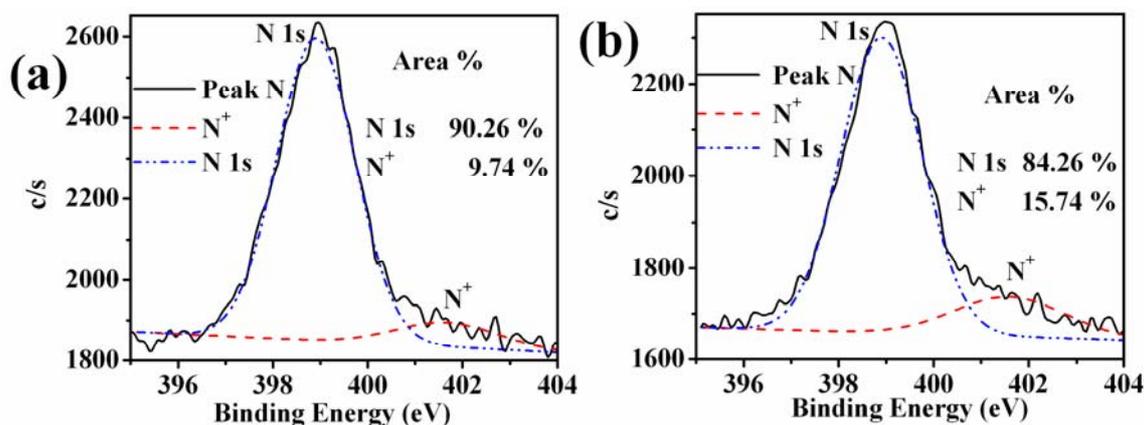


Fig. 5 – N_{1s} core-level XPS spectra for (a) PUC-2 and (b) PUC-2-3 composite.

On the other hand, the area ratio of N^+/N^0 estimated from the curve-fitted N_{1s} core-level spectrum for PUC-2 was 0.108, whereas in the hybrid composite this ratio was 0.187. In fact, we found that the area ratio of N^+/N^0 is less than the theoretical ratio used in synthesis (0.33). Given the quantitative surface composition obtained by this technique, it seems reasonable to correlate the antibacterial effect of the polymeric films with the concentration of ammonium groups oriented toward the surface region, which play a crucial role in direct contact of the organism with the antimicrobial entity.

EXPERIMENTAL

Materials. Polytetrahydrofuran (PTHF, $M_n = 1000$) was purchased from BASF, 4,4' methylene bis(phenylisocyanate) (MDI), isophorone diisocyanate (IPDI), N,N' - β -hydroxyethyl-piperazine (HEP), 1,4-butanediol (1,4-BD), methyl iodide and 2-hydroxyethyl- N,N,N -dimethyldodecyl ammonium bromide (DDAB) were purchased from Sigma Aldrich Chemical Co. and used without further purification. The unmodified sodium montmorillonite (MMT) Cloisite® Na^+ was purchased from Southern Clay Products Inc.

Polyurethane synthesis. For the preparation of elastomeric PUs with quaternizable moieties enclosed in the main chain (PU-1, PU-2) the same method was employed, which is why the synthetic details given below are refers only to the obtaining of one of them. Thus for PU-1, 5 g (5 mmol) PTHF were degassed under vacuum for 2 hours and then, were treated with 3.75 g (15 mmol) MDI. The polyaddition was carried out in the presence of dibutyltin dilaurate and in a dry nitrogen atmosphere at 60 °C for 6 hours. Further, a mixture of 0.87 g (5 mmol) HEP dissolved in 15 mL anhydrous dimethylformamide (DMF) and 0.45 mL (5 mmol) 1,4-BD was left to react for other 10 hours at 60 °C. The course of the reaction was followed through the infrared absorption of the isocyanate stretching band at 2260 cm^{-1} , the reaction being considered completed after the disappearance of the NCO band from the spectrum. The resulting nonionic PU was collected by precipitation in methanol and the removal of the residual solvent under vacuum. The quaternization of tertiary

nitrogen atoms from HEP with methyl iodide was carried out in dry DMF at 35 °C for 72 h. The formed polycation (PUC-1) was precipitated in diethyl ether and dried for 48 h at 50-55 °C under reduced pressure. Similarly, by using isophorone diisocyanate, PU-2 and its cationic form (PUC-2) was prepared.

PUC-1, 1H NMR (DMSO, δ ppm): 8.54, 9.49, 9.65 (6 H, m, NH); 7.11, 7.35 (m, 24H, aromatic); 4.5-3.98 (12H, m, $-CH_2-CH_2-OCONH-$); 3.81 (6H, m, Ph- CH_2 -Ph); 3.34 (72H, m, $-O-CH_2-(CH_2)_2-CH_2-O-$, protons from the piperazinium rings and N^+-CH_3); 1.5 (58H, m, $-O-CH_2-(CH_2)_2-CH_2-O-$); η_{red} : 0.2 dLg^{-1} ; M_w (GPC): 23700.

PUC-2, 1H NMR (DMSO, δ ppm): 7.96, 7.06, 6.93 (6 H, m, NH); 4.01-3.92 (12H, m, $-CH_2-CH_2-OCONH-$); 3.34 (72H, m, $-O-CH_2-(CH_2)_2-CH_2-O-$, protons from the piperazinium rings and N^+-CH_3); 1.5 (58H, m, $-O-CH_2-(CH_2)_2-CH_2-O-$); 1.24-0.8 (protons from the isophorone ring). η_{red} : 0.61 dLg^{-1} ; M_w (GPC): 36900.

Composites preparation. The organophilic clay modified with C12 alkyl chain (OM-MMT) was obtained according to a method described elsewhere.²² Composites were prepared using the solution intercalation technique. For each composition, 1 g of ionic PU was dissolved in 10 mL DMF. Clay suspensions (< 0.1 wt %) were obtained by dispersing the well-dried OM-MMT in a separate beaker of DMF and further sonicated for 30 min with an Ultrasonic Processor GEX-500 probe sonicator at room temperature. The organoclay dispersion was mixed with PU solution and stirred at 50 °C for 3 h. The resulting mixture was then cast on a glass surface and kept in a desiccator for controlled evaporation of the solvent. Homogenous composite films were obtained and subsequently dried at 80 °C under vacuum for 2 days. The amount of inorganic material enclosed in the polymeric matrix is 0, 3 and 5 wt. %.

Measurements. Fourier transform infrared (FTIR) spectra were recorded using a Bruker Vertex 70 FT-IR instrument. Analyses were performed in the transmission mode in the range 400–4000 cm^{-1} at room temperature with a resolution of 2 cm^{-1} . The 1H NMR spectra were recorded on a BRUKER Avance DRX 400 spectrometer, using DMSO- d_6 as a solvent. Wide-angle X-ray diffraction patterns for unmodified MMT, organically modified MMT and hybrid composites were recorded via X-ray diffraction (Bruker D8 Advance), using $Cu(K\alpha)$ radiation ($\lambda = 0.154$ nm) at 40 kV and 30 mA with a scan rate of 1° min^{-1} . The diffraction angle ranged from 2° to 10°. OM-MMT/polyurethane nanocomposites were characterized by transmission electron microscopy (TEM) using a Philips

CM20 instrument with a LaB6 cathode operating at 200 kV. Ultrathin sections were obtained cutting the samples with an ultramicrotome equipped with a diamond knife. For the X-Ray photoelectron spectroscopy investigations, a Physical Electronics PHI-5000 VersaProbe XPS system with a monochromatized Al(K α) radiation ($h\nu = 1486.6$ eV) was used. The take-off angle of the photoelectrons was 45°. All the XPS peak positions in the survey spectra were calibrated with respect to the C 1s peak at 284.6 eV. The stress/strain curves were recorded on a Shimadzu AGS-J deformation apparatus at ambient temperature and at a rate of deformation of 10 mm/min with a load cell capable of measuring forces up to 1 kN and a sample film of 25 mm \times 5 mm \times 0.3 mm. For each data point, five samples were tested, and the average value was taken.

For the determination of the antimicrobial properties of polymers and composites in film state, the agar disc diffusion method was employed.²³ The bacteria (*S. aureus* ATCC 25923 or *E. coli* ATCC 25922) were subcultured to nutrient agar and incubated overnight at 37 °C. Then, the cells were dispersed in the same medium to reach 10⁴-10⁵ CFU/mL. The agar plates were streaked with a sterile swab moistened with the bacterial suspension. The ionic PU/composite films (diameter: 8 mm, thickness ~ 0.15 mm) previously sterilized by UV irradiation, were also placed on the surface of the agar plates and then incubated overnight at 37 °C. Bacteriostatic activity was determined by the ability of the cationic PU/composite films to inhibit bacterial growth on the agar surface in contact with it. Triple replica was used to determine a mean value for each sample.

CONCLUSIONS

In summary, novel materials based on cationic PUs with hard segments containing piperazinium groups were prepared and used for obtaining hybrid composites with 3 and 5 wt.% C12-MMT dispersed into the polymer matrix. The formation of polymer-based hybrid composites was confirmed by spectral methods, and the results derived from thermal, mechanical, morphology, and bioactivity tests may be exploited in designing generation of flexible coatings for applications in the biomaterials field, and not only. Supplementary study needs to be achieved in order to better understand the bacteria-polycation interaction.

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