



Phosphonium-based ionic liquids as modifiers for biomedical grade poly(vinyl chloride)

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ABSTRACT

This work reports and discusses the influence of four phosphonium-based ionic liquids (PhILs), namely trihexyl(tetradecyl) phosphonium dicyanamide, $[P_{6,6,6,14}][dca]$; trihexyl(tetradecyl) phosphonium bis(trifluoromethylsulfonyl)imide, $[P_{6,6,6,14}][Tf_2N]$; tetrabutyl phosphonium bromide, $[P_{4,4,4,4}][Br]$; and tetrabutyl phosphonium chloride, $[P_{4,4,4,4}][Cl]$, on some of the chemical, physical and biological properties of a biomedical-grade suspension of poly(vinyl chloride) (PVC). The main goal of this work was to evaluate the capacity of these PhILs to modify some of the properties of neat PVC, in particular those that may allow their use as potential alternatives to traditional phthalate-based plasticizers in PVC biomedical applications. PVC films having different PhIL compositions (0, 5, 10 and 20 wt.%) were prepared (by solvent film casting) and characterised by Fourier transform infrared, thermogravimetric analysis, differential scanning calorimetry, dynamical mechanical thermal analysis, scanning electron microscopy/energy-dispersive X-ray/electron probe microanalysis, X-ray diffraction, transmittance, permeability towards oxygen and carbon dioxide, thermal degradation, contact angle measurement, water and vapour uptake, leachability and biocompatibility (haemolytic potential, thrombogenicity and cytotoxicity). A conventional organic plasticizer (di-isononyl phthalate) was used for comparison purposes. The results obtained showed that it was possible to change the neat PVC hydrophobicity, and consequently its water uptake capacity and plasticizer leachability, just by changing the PhIL employed and its composition. It was also possible to significantly change the thermal and mechanical properties of PVC films by choosing appropriate PhIL cation/anion combinations. However, a specific PhIL may not always be capable of simultaneously keeping and/or improving both physical properties. In addition, ionic halide salts were found to promote PVC dehydrochlorination. Finally, none of the prepared materials presented toxicity against Caco-2 cells, though pure $[P_{6,6,6,14}][dca]$ decreased HepG2 cells viability. Moreover, PVC films with $[P_{6,6,6,14}][dca]$ and $[P_{4,4,4,4}][Cl]$ were found to be haemolytic and thus these PhILs must be avoided as PVC modifiers if biomedical applications are envisaged. In conclusion, from all the PhILs tested, $[P_{6,6,6,14}][Tf_2N]$ showed the most promising results regarding blood compatibility, leaching and permeability to gases of PVC films. The results presented are a strong indicator that adequate PhILs may be successfully employed as PVC multi-functional plasticizers for a wide range of potential applications, including those in the biomedical field.

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1. Introduction

Poly(vinyl chloride) (PVC) is one of the most important and widely used thermoplastic materials, mostly due to its cost effec-

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tiveness, transparency, flexibility, biocompatibility and sterilization performance, haemolytic potential within acceptable limits, biological stability and compatibility with a variety of additives that can improve its mechanical, physical and chemical properties [1–3]. These PVC properties make it valuable for widespread applications in many different fields, from packaging to healthcare devices, toys, construction materials or cloths. The most relevant biomedical applications of PVC are in flexible containers (for blood and blood components, urine or ostomy products) and in tubing applications