



# The effects of functional nanofillers on the reaction kinetics, microstructure, thermal and mechanical properties of water blown rigid polyurethane foams

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## ABSTRACT

The use of functional nanofillers to improve the properties of rigid polyurethane (PU) foams has caused the need for a better understanding of how these nanofillers modify the reaction kinetic of the PU system. In this study, different nanoclays and nanosilicas are used as functional nanofillers. Analysis of the kinetic data obtained by *in-situ* FTIR spectroscopy monitoring allows to correlate the isocyanate consumption with the type of nanoparticles. The quantification of urethane and urea, obtained by deconvolution of the carbonyl region absorptions, enables to follow the blowing and gelling reactions during the foaming process. These reactions are correlated to the nature of the chemical groups present on the surface of the nanoparticles added. In addition, the effect of the modification of the reaction kinetics on the density, cellular structure, thermal conductivity and mechanical properties is herein discussed.

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## 1. Introduction

Polyurethanes (PUs) are multipurpose polymers, since they are present in a wide range of industrial sectors, like automotive, medical, construction, furniture, appliances, etc [1]. PUs can be found commercially as solid thermoplastics (known as TPU), coatings, adhesives, sealants, binders, elastomers, and foams [2].

PUs foams are usually classified according to their mechanical behavior as flexible foams (such as those used for furniture, mattresses or automotive seats), or rigid foams (which can be applied for insulation and structural materials) [3]. PU foams represent almost a 50% of the global market of foams, and their use is still substantially growing over the years [4]. Thermal management in buildings and transportation insulation or refrigeration systems are the core applications of rigid PU foams with closed cells [Fig. 1(a)]. These applications have been extensively studied both theoretically

[5–7] and experimentally [8–11].

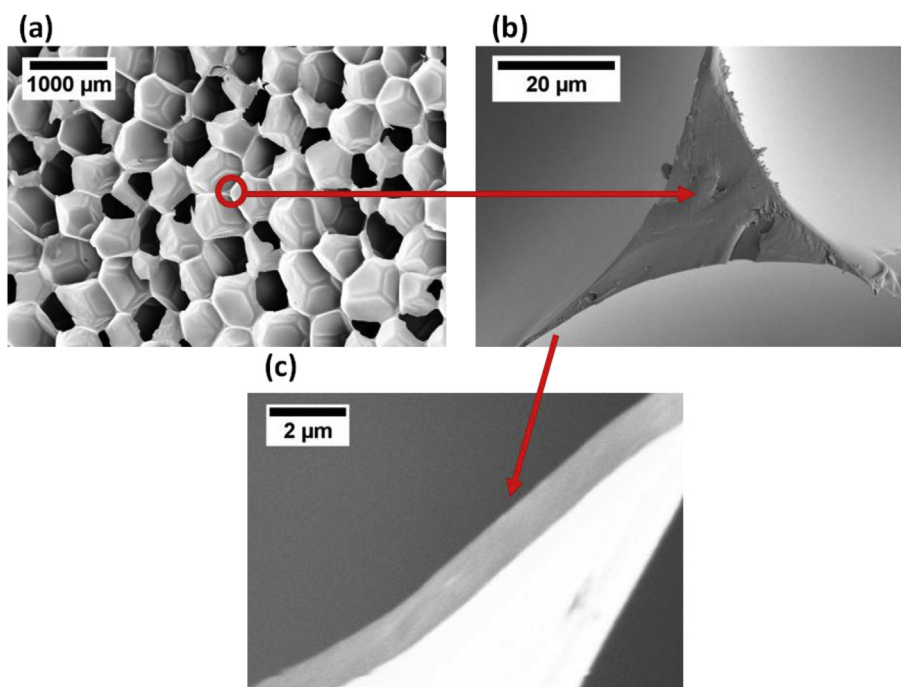
Incorporating additives to the PU formulation is an excellent method to improve the mechanical, thermo-mechanical, or thermal properties of the foam. Nanoscale size fillers are becoming a promising option in order to obtain improved properties [12,13]. For a PU foam with closed cells, with a density of 50 kg/m<sup>3</sup>, the cell wall thickness is usually in the range of 1–2.5 μm [Fig. 1(c)], and therefore the typical sizes of cells and struts are slightly higher [Fig. 1(a) and (b)] [14,15]. These features should be taken into account in order to select an appropriate filler for modifying its physical properties, and a logical approach is adding fillers with at least one of the dimensions clearly below the thickness of the cell walls (i.e. smaller than 1 μm).

These reasons have encouraged the research on the incorporation of nanofillers into a variety of materials and foams [16,17]. These works have allowed concluding that the properties on the final composite depend, among other aspects, on the nanofiller chemical composition and on the size and shape of the nanoparticles [18,19].

So far, the reinforcing inorganic materials probably more

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**Fig. 1.** SEM micrographs of the microstructure of a closed cell rigid PU foam: (a) Microstructure formed by closed cells. The components of closed cells are (b) struts, and (c) cell walls with thickness in the range of 1–2.5  $\mu\text{m}$ .

extensively used are layered nanoclays, especially those based on montmorillonite,  $[(\text{Na,Ca})_{0.33}(\text{Al,Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}]$ . This is due to their cation exchange capacity, high surface and reactivity, and adsorptive properties. The structure of montmorillonite is based on a central octahedral sheet of alumina, sandwiched between two external silica tetrahedral sheets. The interlayer galleries (of about 1 nm in thickness and 100 nm in width and length) are occupied by cations (usually  $\text{Na}^+$  and  $\text{Ca}^{2+}$ ). The presence of these cations in the interlayer spaces makes montmorillonite hydrophilic, which is the main reason for its poor compatibility with organic polymers. Thus, metallic cations must be substituted by hydrophobic organic cations (alkylammonium or -phosphonium quaternary salts) in order to both enhance a better layer separation, and to improve compatibility with the polymer matrix. Introducing nanoclays based on montmorillonite into PUs allows overcoming some of the weaker aspects of these foams, such as their relatively poor thermal stability, or their low gas-barrier properties. Thus, these type of PU-montmorillonite composites have been studied [14,20–22], and many investigations have been focused on their methods of preparation, structure, hydrogen bonding, degree of clay dispersion or exfoliation, microphase morphology, rheology, mechanical properties, thermal stability, flame retardancy, water sorption, or barrier properties [23].

On the other hand, the number of papers describing polymers reinforced with dispersed silica nanoparticles is also high [24,25]. Nanosilica surface is hydrophilic due to the presence of hydroxyl groups, which generate hydrogen bonding and therefore significant interactions between particles. For this reason, nanoparticles tend to agglomerate, what should be precluded in order to favor the dispersion of nanoparticles into the polymer matrix. The degree of nanoparticles dispersion and the interfacial adhesion are important drawbacks to obtain appropriate materials [26], and surface modification is the best way to reduce the preference for agglomeration of nanosilica particles [27]. Thus, the replacement of silanol groups by non-polar silyl groups removes the active hydrogen bonds on the surface, and changes the hydrophilicity of the filler

surface into hydrophobic. The studies carried out on PU/nanosilica composites reveal that the addition of surface modified nanosilicas can improve the thermal, rheological, mechanical, and adhesion properties of PUs [17].

The properties of composites resulting from the addition of either nanoclays or nanosilicas to PU foams have been studied to some extent [21,24], but most of the reports are mainly focused on the production and characterization of the foams, paying particular attention to the nanoparticles dispersion. However, the effect of these additives on the chemical reactions occurring during foaming has been very scarcely explored. PUs are obtained when isocyanate react with active hydrogen containing compounds, such as the hydroxyl groups of long polyether or polyester chains (polymerization or gelling reaction), or water (blowing reaction) to give urethane or urea linkages respectively. These two simultaneous processes should be adequately controlled in order to obtain a polymer foam with the desired cellular structure and physical properties [3,28,29]. The presence of additives such as nanofillers may modify the kinetics of these chemical reactions, by increasing or decreasing reaction ratios leading to a modification of urethane and/or urea linkages, thus affecting the foaming process and the final morphology of the PU matrix, and consequently the properties of the final foam. The modification of the reaction kinetics, microstructure and physical properties of PU systems containing nanofillers is a topic which depends on many interconnected factors, and therefore requires a high degree of systematization.

The aim of this work is to study systematically the effect of different nanoparticles on the reaction kinetics of rigid PU foams formation, and to analyze how these modifications affect the cellular structure and physical properties of the foams.

## 2. Experimental

### 2.1. Reactants

A commercial, bi-component formulation of rigid PU foam from

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