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Effect of moisture content on curing kinetics of agglomerate cork

L. Moreira *, V.A.F. Costa [1], F. Neto da Silva

Departamento de Engenharia Mecânica, Universidade de Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

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ABSTRACT

The curing process of Toluene 2,4-DiIsocyanate (TDI) pre-polymer with granulate cork is significantly affected by the cork moisture content since the reaction of isocyanate is highly sensitive to water. Two types of moisture are considered: the moisture contained inside the granulate cork, *residual moisture*, and the moisture intentionally sprayed over the granules of cork, *added moisture*. This study analyses the curing kinetics of TDI and granulate cork mixtures containing added moisture using Differential Scanning Calorimetry (DSC), and the reaction rate increase associated with the added moisture content (AMC). The underlying objective of this work is to reduce the time needed to obtain agglomerate cork stoppers through AMC increase.

1. Introduction

Cork agglomerate stoppers are obtained from granulated cork and an adhesive. Cork is a material with the adequate properties for stoppers manufacture (elasticity, homogeneity, internal resilience and impermeability), and the granulate stoppers have the advantages of the cork stoppers but not their disadvantages (strong non-homogeneity, porosities which may contain materials contributing to a degradation of the wine quality, and strong anisotropy, between others). The most relevant properties and characteristics of cork, considering many of its possible applications, are detailed in [1,2].

Many studies can be found in the literature concerning the mechanical performance of agglomerate cork. Examples are the work by Castro et al. [3] where the cork agglomerates are presented and discussed as ideal core materials in lightweight structures, the work by Fernandes et al. [4] where the impact response of agglomerate cork is analyzed following a numerical approach, the work by Anjos et al. [5] is analyzed the effect of density on the compression behavior of cork, in the work by Oliveira et al. [6] is studied the variability of the compression properties of cork, in the work by Sanchez-Saez et al. [7] is analyzed the dynamic crushing behavior of agglomerate cork, and in the work by Lakreb et al. [8] is studied the mechanical behavior of multilayered sandwich panels of wood veneer of Aleppo pine and a core of cork agglomerates, where it is observed that the cork agglomerate provided a high performance under perpendicular compression. In the work by Teixeira et al. [9] is studied the influence of the wetting properties of polymeric adhesives on the mechanical behavior of cork agglomerates, where the surface tension and contact angle of the polymeric liquids deposited on cork substrates were measured.

Applications of agglomerate cork in stoppers have its own specificities, and some works related with this topic can also be found in the literature. In the work by Six et al. [10] is investigated the mechanism of migration from agglomerate cork stoppers using electron spin resonance, in the work by Sendón et al. [11] is detected the migration of phthalates from agglomerate cork stoppers using HPLC–MS/MS, and in the work by Abdallha et al. [12] is studied the effect of surface treatment in cork reinforced composites. Taking into consideration the agglomerate cork stoppers and the wine interactions, work by Six and Feigenbaum [13] analyze a safety assessment criteria of agglomerate cork stoppers for champagne wine cork producers, for users and for control laboratories, and the work by Jiang et al. [14] searches for the contamination source of butyltin compounds in wine in the presence of agglomerate cork stoppers. By its own turn, Standard UNE 56922: 2004 [15] dictates the test methods and specifications of agglomerate cork stoppers for still wines.

An adhesive is needed to consolidate the granulate cork stopper and also to fill the voids between the cork granules. Typically, a mixture with 100 g of granulate cork contains between 10 and 20 g adhesive for rough grain (size between 2 and 8 mm), and between 20 and 30 g adhesive for fine grain (size between 0.5 and 2 mm).

* Corresponding author.
E-mail addresses: leandro.moreira@ua.pt (L. Moreira), v.costa@ua.pt (V.A.F. Costa), fneto@ua.pt (F. Neto da Silva).
[1] Tel.: +351 234370829.

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The typical used adhesive in agglomerate cork stoppers is toluene 2,4-diisocyanate pre-polymer, a polyurethane adhesive, as it leads to good results in terms of elasticity and flexibility of the stoppers, and due to its compatibility when used in contact with foods and drinks, being approved by the Food and Drug Administration (FDA) for this purpose [16]. It must also be referred that pre-polymer TDI-based polyurethanes are usually more flexible than methylene bisphenylisocyanate (MDI)-based polyurethanes, and this feature is crucial for the cork stoppers [13]. This kind of resins gives to the agglomerate the needed high cohesion and impermeability and ensures final physical and mechanical properties of the agglomerate stoppers. Hence, agglomerate cork stoppers become similar to natural cork stoppers (including color and appearance), while the usual problems associated with the natural cork stoppers are avoided. Additionally, the affinity shown by polyurethane resins to the reactive compounds existing in cork, such as moisture and hydroxyl groups (thus establishing a chemical bond between the cork and the resin), makes polyurethane resins a very attractive choice for this application, ensuring a better cohesion for the stopper. Furthermore, polyurethane resins give stoppers the mechanical features they need (elasticity, homogeneity, internal resilience and impermeability) along with a very low or almost absent porosity. Finally, polyurethane resins give stoppers the high durability and the reliability they need to resist attacks by other physical and chemical, synthetic or natural, agents [17,18].

Production of agglomerate stoppers at the industrial level can be made through individual molding process or continuous extrusion process. Individual molding process allows a better quality control at the individual stopper level since each cork is produced individually in a mold cavity. However, its major drawbacks include the need to use heavy metallic molds and low production rates. The continuous extrusion process requires lighter equipment and allows higher production rates, but it is not so effective in what concerns quality control of each individual stopper. The production rate is conditioned not only by the equipment itself, but also by the curing rate of the resin used in the agglomerated stoppers.

During the manufacturing process granulated cork, with some residual moisture content, is mixed with resin and additional moisture can be used to shorten the curing process. This mixture, which can be preheated in order to accelerate the curing process, is then retained for a given time inside a heated mold cavity with the stopper configuration. Once consolidated, the agglomerated cork is then extracted from the mold cavity. The curing process is finished exposing the stoppers to ambient air without any mechanical restrictions. The obtained stoppers are then subject to finishing operations, which essentially comprise mechanical operations such as cutting and polishing, in order to acquire the smooth surface and the required geometry and dimensions. The reaction between polyurethane pre-polymer and granulated cork occurs as shown in Fig. 1.

The hydroxyl groups in cork may react with isocyanate (NCO). The polymerization of TDI pre-polymers is initiated by the residual moisture of cork granules (usually around 4%) (Fig. 1). However, as the intentionally added moisture is fully distributed over the surface of the granules it is much more easily chemically combined with the resin, which is also distributed over the surface of the granules, thus increasing the curing rate due to the catalytic effect of water on the polyurethane cure reaction. In order to obtain the adequate cork granulate agglomeration as indicated in Fig. 1, industrial practice indicates that the pre-polymer should have between 2% and 5% NCO content. The time required for agglomerated cork stoppers processing is mainly conditioned by the duration of the cure reaction of the resin in the mixture of granulated cork and resin. The duration of the cure process can be reduced through the intentional increase of the cork moisture content (intentionally added moisture content), taking advantage of the catalytic effect of water on the polyurethane cure reaction. However, no studies or results were found in the literature concerning the influence of the AMC on the duration of the agglomerate cork stoppers cure and consolidation.

Kinetic studies allow a better understanding and quantification of reaction characteristics and mechanisms. In order to increase the knowledge of the cork/isocyanate reactions characteristics, the cork/isocyanate reactions at different cork moisture contents were analyzed using Differential Scanning Calorimetry (DSC), the most widely used technique for monitoring and analysis of the curing process of thermosets [19].

2. Experimental details

2.1. Samples preparation

TDI pre-polymer was supplied by Flexpur® (Esmoriz, Aveiro, Portugal). The granulated cork was supplied by Sedacor (Oleiros, Portugal) and was integrally obtained from Portuguese cork. The polyurethane pre-polymer was added to granulated cork at proportion of 16.7% of total weight, for a cork granulometry between 0.5 and 2 mm (fine grain, Fig. 2). Only the fine grain was considered due to the capacity (volume) limitation of the samples container which is 60 μL for DSC analysis. The initial (residual) moisture content of granulated cork is close to 4% (dry basis), and the AMC considered (spraying distilled water over the cork granules) is 2%, 6%, 8% and 12% (dry basis). Samples' moisture content (dry basis) was obtained from two weight measurements, the first one for the wet sample and the other for the (same) sample dried through a stage of 45 min at a temperature of 120 °C.

The granulated cork (including moisture) and TDI pre-polymer mixtures, with 16.7% of resin (total weight basis), were prepared by mechanical stirring during 5 min at a rotational speed of 300 rpm at ambient temperature. The TDI pre-polymer was stored in a completely filled small container to avoid reaction with air humidity before the DSC measurements.

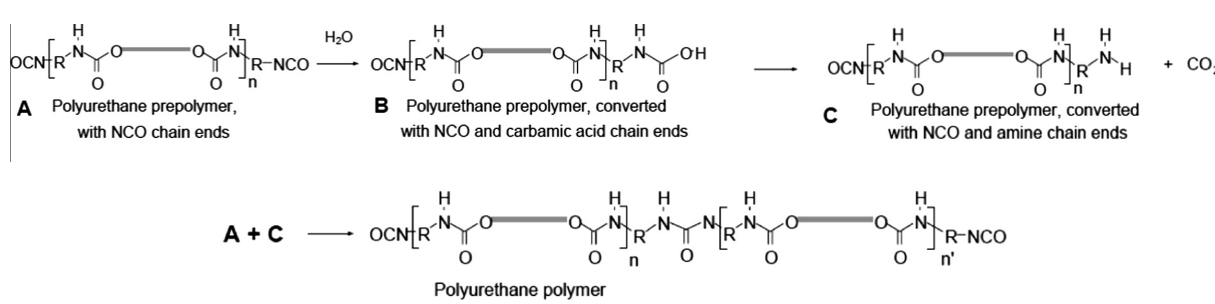

Fig. 1. Polymerization of the polyurethane pre-polymer initiated by water (cork moisture) (adapted from [13]).