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Development of new high-throughput screening method to compare and to detect efficient catalysts for adhesive materials

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ABSTRACT: Organotin compounds particularly dibutyltin dilaurate, are commonly used as catalysts in coatings or adhesive materials to crosslink silyl modified polymers. However, environmental concerns should lead before 2020 to ban organotin compounds due to their high toxicity. Thus new catalysts must be developed. According to the different types of catalytic systems, i.e. acid, basic or metal containing catalysts, a large variety of candidates should be tested. Thus a high-throughput screening (HTS) method could be an interesting tool for the detection of new efficient catalysts to substitute organotin compounds. We report a global HTS method, compatible with organic amino or acid catalysts libraries, as well as with metal-containing libraries.

KEYWORDS Silyl modified polymers, Cross-linking, High-throughput screening, catalysts.

1. INTRODUCTION

Silyl modified polymers (SMP) are key materials, applied in many applications such as binders for elastic adhesives [1,2], composites [3,4], electrolytes [5] or for coating [6,7] applications. These hybrid polymers are also becoming increasingly common in aeronautical and aerospace applications [8]. They can be used in several other applications due to their adjustable properties [9] such as Young's modulus, tensile strength, thermal, gas barrier and photonic properties. Cross-linking of silyl modified polymers takes place with alkoxy silane groups attached to the ends of polymer chains by hydrolysis and polycondensation with moisture [10,11]. The hydrolysis and condensation reactions occur almost simultaneously and they are in competition with each other. Organotin compounds such as dibutyltin dilaurate (DBTDL) are widely used as catalysts to accelerate the cross-linking of silyl modified polymers with moisture [12]. However, in recent years, the high toxicity of organotin compounds has been proved and the environmental concerns should lead before 2020 to ban organotin catalysts. Thus, several studies were performed in basic or acidic conditions allowing cross-linking of silyl modified polymers without tin catalysts. Indeed, strong acids like $\text{CF}_3\text{SO}_3\text{H}$ [13] or HCl [14] efficiently accelerate the process of hydrolysis. Under basic conditions to deprotonate water, hydroxyl OH^- ions attack the most positively charged atom by nucleophilic reactions [15]. Thus super-bases, like DBU or TBD amines are very efficient to accelerate the reaction and to increase the density of cross-linking. Metal alkoxide catalysts were also reported, in order to generate different cross-linked matrix by comparison with acid or basic organic catalysts.

In all of these studies, the discovery of efficient catalysts has always been obtained by an iterative approach. Each potential catalyst is tested one per one and sometimes at different time scale. This can be time-consuming and does not allow comparison of a large number of catalysts in the same time period, for instance for the same batch of starting material. This classical iterative method has already been described by Bostik [16] for different applications. On the other hand, the high-throughput

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