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Study of the film formation and mechanical properties of the latexes obtained by miniemulsion co-polymerization of butyl acrylate, methyl acrylate and 3-methacryloxypropyltrimethoxysilane

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ABSTRACT

Miniemulsion polymerization offers several advantages over conventional emulsion polymerization to co-polymerize alkoxysilane monomers, which easily undergo premature hydrolysis and condensation reaction into the polymer particles. The premature hydrolysis and the subsequent condensation reaction can lead to colloidal instability. Furthermore, the premature intra-particle cross-linking will reduce the capability of the latex particles to form films. In this paper we discuss the miniemulsion co-polymerization of the butyl acrylate, methyl acrylate and 3-methacryloxypropyltrimethoxysilane BA–MA–MEMO. The latexes features have been characterized and a compressive explanation of the features has been given. Finally, the work focussed on the study of the latex film formation, and mechanical properties by using nanoindentation trials to measure the superficial properties of the film, and also stress–strain curves have been produced.

1. Introduction

Water-based emulsion polymers are used in many applications such as latex paints, paper coatings and adhesives. Thermoplastic polymers are commonly selected because these kinds of materials can easily deform, coalesce and form coherent films. These films usually have low performance levels because, high glass transition temperature (Tg) (high cross-linking degree) polymer particles do not produce coherent films at room temperature (the coalesce and polymer chain interdiffusion is restricted due to the high cross-linking degree), and low Tg (low cross-linking degree) polymer particles do not produce hard and strong films. Therefore, high performance films based on waterborne thermoplastic polymers synthesis still remains a challenging issue. For many applications, the mechanical properties can be increased by the introduction of cross-linking chemistry into latex-based coating [1,2]. Thus, the latex particles still have a relatively low cross-linking degree in the dispersion but undergo the cross-linking once they have formed the coating on the substrate. Among the different alternatives, the incorporation of alkoxysilanes into latex particles is an interesting purpose [3–7].

The general formula for alkoxysilane shows two different kinds of chemical groups attached to the silicon atom (Fig. 1). One is a non-hydrolyzable organic group which provides the functional group that reacts with the monomers commonly used in the coating formulation, and the second one represents the alkoxy moieties, which can react with hydroxyl groups and liberate methanol or ethanol. The incorporation of alkoxysilane to the latex particles can be via co-polymerization of the methacrylic group or by hydrolysis and condensation of the hydrolysable groups.

The alkoxy moieties provide the self-cross-linking ability to the copolymer. The steps involved in the film cross-linking are shown in Fig. 2. After the film formation, the hydrolysis and condensation reaction of the alkoxysilane moieties, at room temperature, will lead to the film cross-linking (Fig. 2) [7]. Thus, premature hydrolysis and the subsequent cross-linking must be avoided during the latex synthesis in order to obtain the desired cross-linking degree after the film formation. Several strategies can be utilised to reduce the premature cross-linking: thus, the use of sterically hindered alkoxysilane will produce a reduction in the hydrolysis rate, besides, good pH control is required since the lower hydrolysis rate occurs at neutral pH [8,9]. Furthermore, several authors have studied the influence of the type of initiator, surfactants and the rest of experimental parameters in the hydrolysis rate, amount of coagulum and the kinetic of the reaction [3,6,7]. Taking into account these studies it can be concluded

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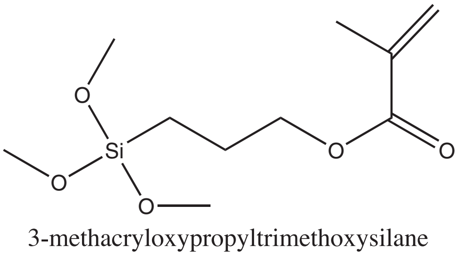

Fig. 1. Chemical structure of the alkoxysilane.

that organic initiators and ionic surfactants are the most effective compounds in reducing the premature hydrolysis and to promote the latex stability. On the other hand, the selection of an adequate polymerization technique can be a powerful tool to avoid the premature cross-linking, thus semi-continuous addition of the alkoxysilane in the late states of polymerization reaction would avoid the prolonged contact between the alkoxysilane and water and therefore the hydrolysis can be efficiently avoided. One different approach is to carry out a miniemulsion polymerization [10] instead of conventional emulsion polymerization [11]. Miniemulsion polymerization consists on the polymerization of a stable dispersion of monomer droplets in the aqueous phase. The dispersion is formed by using an appropriate dispersion device [12] in order to break down the monomer droplets and reduce their size to the required value, usually below 500 nm. In properly formulated miniemulsion, the alkoxysilane monomers are protected from the aqueous phase by a waterproof oil droplet, therefore the hydrolysis reactions can be dramatically reduced [3,13].

This work is focused on the miniemulsion copolymerization of butyl acrylate, methyl acrylate and 3-methacryloxypropyltrimethoxysilane. The influence of the experimental parameters in the latex synthesis will be evaluated. These latexes will be used to protect natural stone against external physical and chemical attacks; therefore the mechanical properties of the latexes film will be measured.

Furthermore, emphasis will be placed on assessing the mechanical properties the mechanical properties of the coating.

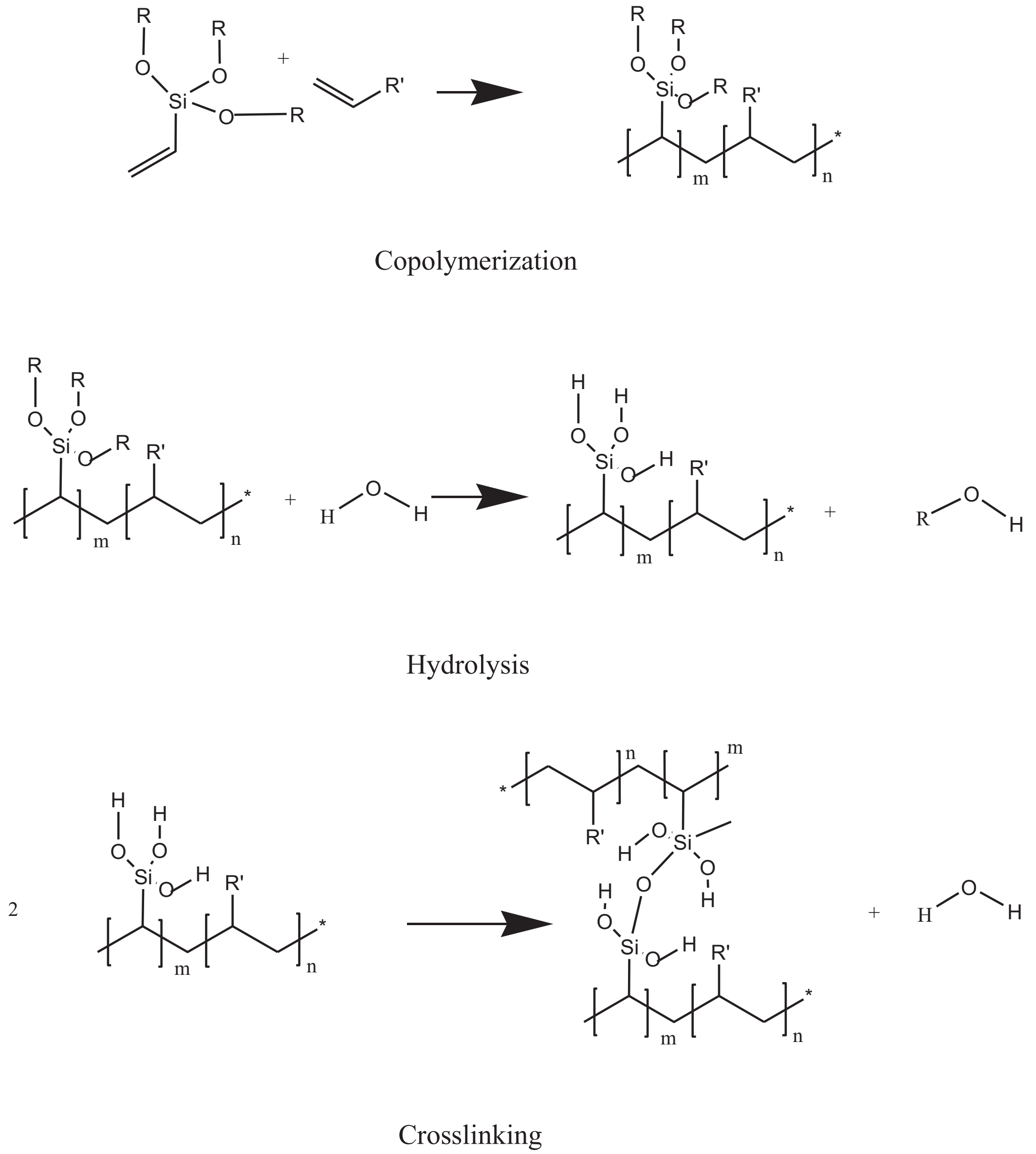

Fig. 2. Chemical reaction involved in the film cross-linking.