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LETTER

AFM fracture surface study of vinylester and unsaturated polyester based thermosets

M. A. Mosiewicki · W. F. Schroeder · F. L. Leite · P. S. P. Hermann · A. A. S. Curvelo · M. I. Aranguren · J. Borrajo

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The study and understanding of the structure and properties of styrene/vinylester (St/VE) and styrene/unsaturated polyester (St/UP) cross-linked thermosets has received technologic and scientific attention, because these resins are widely used as matrices in composites formulations, sharing advantages, such as low room temperature viscosity coupled with good mechanical properties and low cost, plus the added chemical resistance in the case of VE. To investigate the morphologies of these systems, scanning electron microscopy (SEM) offers an useful tool at a micron scale, while the atomic force microscopy (AFM) allows to reach the detail of the topography at a nanometric scale and also to determine the nanostructures of the surface [1].

In both systems, the cross-linked reaction occurs by free radical polymerisation where, big molecular structures are formed through connecting St and UP (or VE) unsaturated comonomers by both inter- and intra-molecular reactions. These branched structures tend to form a spherical type structure or ‘‘nanogel particle’’, due to the intramolecular cross-linking among the unreacted C = C bonds located in different pendant chains, with reactive radicals [2]. The microgel morphologies are strongly depending of the cure temperature and the initial composition of the reactive mixture as it has been previously reported [2, 3]. In the present work the relationship between the final morphologies and the St-resin initial ratio is analyzed, and the development of the microstructures resulting from the use of the two different unsaturated resins is compared.

A natural UP resin was obtained from modified linseed oil in two basic steps: glycerolisis and posterior maleinization [4]. The linseed oil used was provided by Grainer S.A. (Entre Rios, Argentine) and was used without further purification. The glycerol used was 99.5% pure and was obtained from Científica Central (Bs. As., Argentine). A commercial soap without additives was used as emulsifier catalyst for this reaction. 2-methyl imidazole was used as catalyst during the maleinization reaction between the glycerol –OH groups and maleic anhydride, both from Fluka A.G Chemical Co.

A low molar mass divinylester (VE) monomer was synthesized from the reaction of an epoxy resin diglycidyl ether of bisphenol-A (DGEBA, DER 332 Dow Chemical Co., epoxy equivalent weight 175 g/eq) with methacrylic acid (Norent Plast S.A., laboratory grade reagent), using triphenylphosfine (Fluka A.G., analytical reagent) as catalyst. The final conversion reached was higher than 97% [5].

Different final materials were prepared varying resin:St ratio in a wide concentration range.

The high stiffness of these materials allows obtaining fragile fracture surfaces like mirror at room temperature.

The general schemes of copolymerization of St/UP and St/VE systems are summarized in Fig. 1. Both synthesis

M. A. Mosiewicki (✉) · W. F. Schroeder · M. I. Aranguren · J. Borrajo
Institute of Material Science and Technology (INTEMA), University of Mar del Plata – National Research, Council. J. B. Justo 4302, 7600 Mar del Plata, Argentina
e-mail: jborrajo@fi.mdp.edu.ar

F. L. Leite · P. S. P. Hermann
Embrapa Agricultural Instrumentation, São Carlos, São Paulo, Brazil

F. L. Leite
Institute of Physics of São Carlos, University of São Paulo, São Paulo, Brazil

A. A. S. Curvelo
Institute of Chemistry of São Carlos, University of São Paulo, São Paulo, Brazil

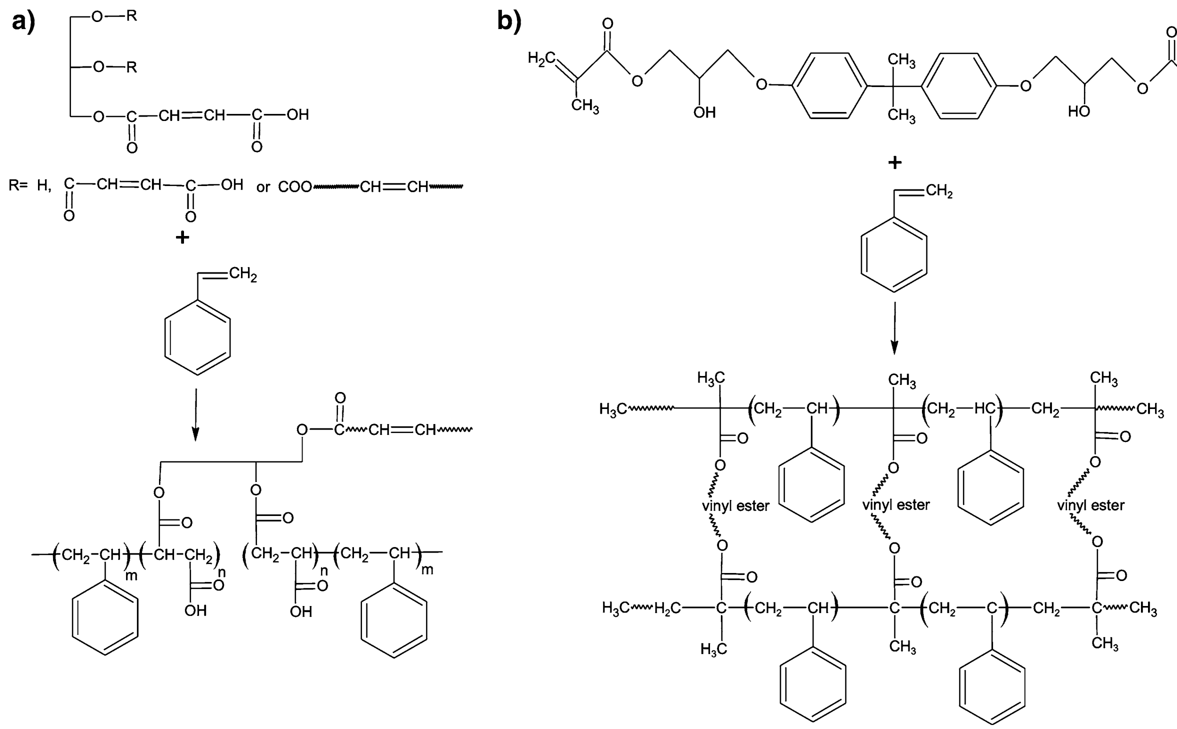

Fig. 1 Chemical structure and copolymerization with St of: (a) UP; and (b) VE systems

products (UP and VE resins) were stabilized with 500 ppm of hydroquinone and analyzed by FTIR, SEC and ^{1}H-RMN techniques [4, 5] in order to characterize their molecular structures. The cross-linked reaction was carried out by the free radical copolymerization of each resin with St using benzoyl peroxide (Lucidol 0.75, Akzo Chemical S.A) as radical initiator. Different final materials were prepared varying resin/St ratio in a wide concentration range.

SEM (Philips SEM 505) was used to obtain photographs of St/UP and St/VE cured materials with different comonomer concentrations. Fragile fracture specimens were observed in a Topometrix TMX 2010 Discoverer AFM using microfabricated Si_3N_4 gold coated cantilevers (V shape) with a nominal spring constant of 0.06 N/m and integrated Si_3N_4 pyramidal tips with curvature radius of 50 nm. All images were obtained in the tapping mode at scan rate of 2Hz and processed by TOPOSPM software.

The cured materials with mass relations St/UP = 40/60 and St/VE = 45/55 were viewed by SEM. For the copolymer formulated with the UP resin, SEM allows observing a particulate structure (Fig. 2a), but without a clear definition at these magnifications (10000×); while the St/VE system presents a surface practically flat in SEM at 15000×, (Fig. 2b).

AFM technique allows observing the surfaces at higher magnifications presenting a better definition. Figures 3 and 4 show the morphologies of the St/UP and St/VE systems, respectively; obtained by AFM. As it can be observed, both

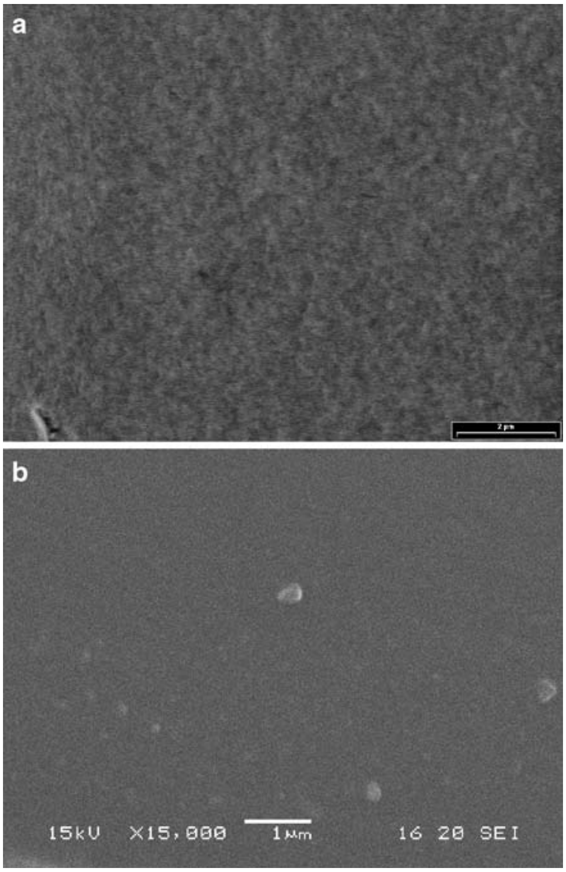

Fig. 2 Micrographs obtained by SEM for: (a) UP/St = 60/40 wt.% (10000×), (b) VE/St = 55/45 wt% (15000×)

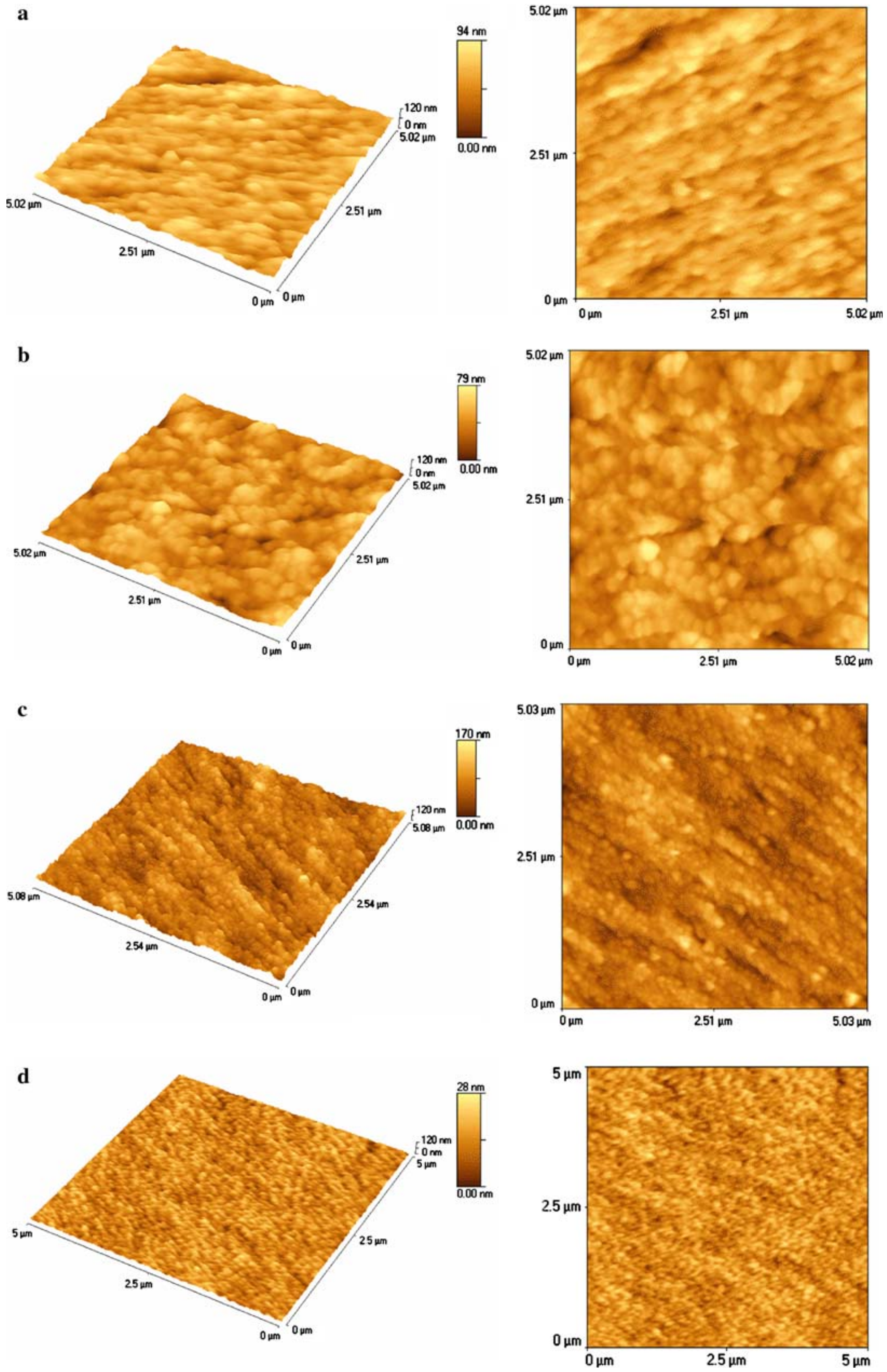

Fig. 3 AFM images for UP system with different St content by weight: (**a**) 80, (**b**) 60, (**c**) 40 and (**d**) 20

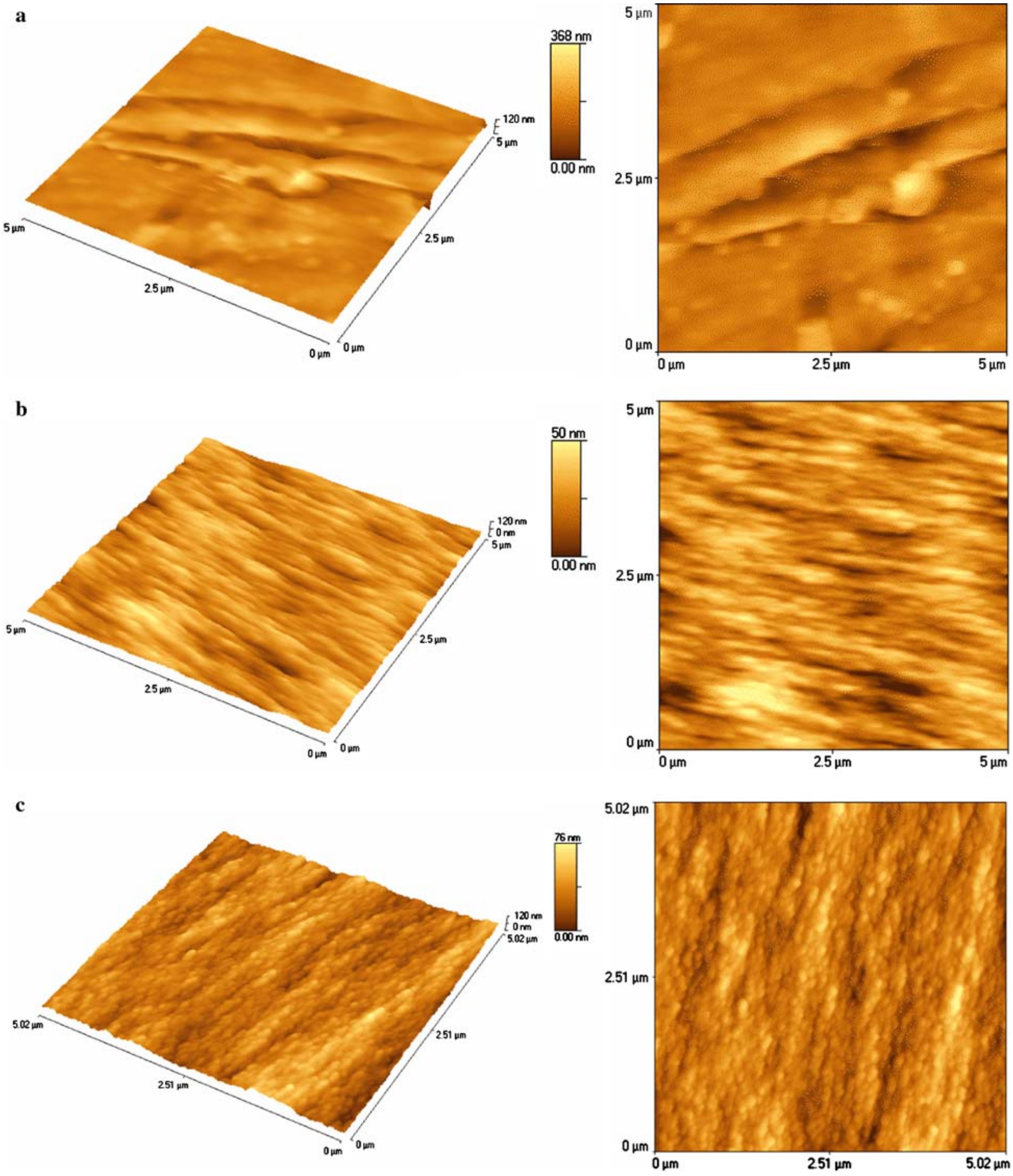

Fig. 4 AFM images for VE system with different St content by weight: (**a**) 15, (**b**) 45, and (**c**) 70

systems present nodular type morphologies although the differences in the UP and VE molecular structures (Fig. 1). These nodules can be assigned to nano and microgels, as it was reported by other authors [2, 3, 6]. In the other hand, it is interesting to note that depending on the concentration of St monomer in the initial mixture, the morphologies of the reacted resins are clearly different. Due to that in these systems the UP and VE, provide the crosslinking points; at low St concentration or high nanogel content, the nanogels are closely packed together, so that no individual nanoparticle can be observed (Figs. 3a and 4a). At high St concentrations, the few formed nanogels are connected by longer St-St chains. Reduced coalescence of the nodules leads to a microstructure formed by smaller more separated particles (Figs. 3d and 4c). The morphologies of the intermediate composition materials (Figs. 3b–c and 4b) present nodular structures with coalescence grades between those of the extreme composition materials.

In spite of the differences in the molecular structures and in the final properties, the same tendency can be observed in the St/UP (Fig 3a–d) and the St/VE (Fig. 4a–c) fracture surfaces with the variation in the St concentrations. This can be attributed to the same behavior in the initial steps of cured reaction, where the nodular particles highly cross-linked are formed, as it was mentioned above.

It is interesting to note that the St/VE fracture surfaces seem to indicate more coalescence between nodules that those of the similar composition St/UP final materials on whole the concentration range analyzed. This can be specially observed between Figs. 3d and 4c. The differences mentioned in the coalescence grade in both systems allow explaining the differences observed in the SEM micrographs. The higher agglomeration of nodules in VE system drives to a smooth surface by SEM while the UP system, with less coalesced nodules, allow to observe microstructure by SEM.

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