

# High performance SMC matrix for structural applications

T Salard<sup>1,2</sup>, F Lortie<sup>1</sup>, J F Gérard<sup>1</sup> and C Peyre<sup>2</sup>

<sup>1</sup>Ingénierie des Matériaux Polymères, UMR 5223, Institut National des Sciences Appliquées de Lyon, Bât 403, 69621 Villeurbanne Cedex, France

<sup>2</sup>Plastic Omnium-MCR, ZI des Iles Feray, 07300 Tournon s/ Rhône, France

E-mail : thomas.salard@insa-lyon.fr

**Abstract.** Mechanical properties of a common SMC (Sheet Molding Compound) matrix constituted of a vinylester resin and a Low-Profile Additive (LPA) were compared to those of vinylester modified with core-shell rubber (CSR) particles. Valuable properties are brought by CSR, especially high impact strength, high fracture toughness with little loss in stiffness, in spite of the presence of CSR agglomerates in blends.

## 1. Introduction

The automotive industry currently knows an important energetic transition with the development of vehicles which must respond to drastic environmental constraints. In this context, the reduction of overall weight of cars is a key point and a way to perform it is to substitute heavy steel parts by lightweight composite materials.

Sheet molding compounds (SMCs) are a class of composite materials used for a long time in automotive industry because of their low weight, low cost and good mechanical properties [1], [2]. Generally they are constituted of a polymer matrix reinforced by short glass fibers and mineral fillers [1]. The matrix is usually constituted of unsaturated polyester or vinylester resins which own interesting intrinsic properties (high modulus, good solvent resistance, low cost) and which are blended with a thermoplastic low profile additive (LPA) to compensate for polymerization shrinkage.

Up to now SMCs have been mainly found in semi-structural applications like rear closures or rear floors but the possibility to extend their range of use in structural parts is studied. However, it requires to significantly improve their mechanical properties and especially their impact strength with no loss in stiffness. Many techniques have been studied to produce composites with better performances. Among them, several studies describe toughening strategies of thermoset resins (soft toughening agents like reactive liquid polymers, core-shell particles, block copolymers or different kind of inorganic fillers) but most of them are related to epoxy resins or remain at the matrix scale [3], [4].

The present work focuses on the modification of a vinylester resin by core-shell rubber (CSR) particles. Usually, CSR as powder are difficult to disperse in thermosetting precursors and a high level of shear is required to favor a good dispersion. Also, the resulting mixtures are often very viscous and are hardly compatible with the requirements of SMC industrial process for which a low initial viscosity is sought to promote a good impregnation of fibers [5]. Hence, to avoid problems of dispersion and viscosity, the present work investigates the toughening of thermosetting resins by CSR initially pre-dispersed in a carrier resin.



## 2. Experiments

### 2.1 Materials

A vinylester resin VE (in solution in 35 wt. % of styrene) was used for this work. Two grades of CSR, named M1 and M2 were employed. Both of them are liquid masterbatches composed of 40 wt. % of CSR particles (CSR1 for M1 and CSR2 for M2) dispersed in a carrier resin (C1 for M1 and C2 for M2). C1 and C2 are constituted of a vinylester or unsaturated polyester diluted in HPMA (Hydroxypropyl Methacrylate). The properties given by the supplier of the two masterbatches are listed in Table 1. A classic PVAc (Poly(Vinyl Acetate))-based additive (polymer in solution in 57 wt. % of styrene) employed in SMC to compensate for polymerization shrinkage was mixed with vinylester to make a standard SMC matrix, which was compared to VE-CSR blends. MEKP (Methyl Ethyl Ketone Peroxide) and Cobalt Octoate allowed the initiation of the polymerization.

To prepare the formulations, resin and additive were mixed for a few minutes in a planetary mixer which prevents from air bubbles. This step was repeated twice by adding first Cobalt Octoate and secondly MEKP. Then, the mixture was poured into a vertical mold (300 x 220 x 4 mm<sup>3</sup>) before gelation occurs. It was first polymerized for 24h at room temperature, and then post-cured during 2h at 90°C, 2h at 120°C and 2h at 150°C. DSC measurements were made to assure that the reaction was complete. By adding the masterbatches M1 or M2 to the vinylester resin, the properties can be modified by the CSR particles and/or by the carrier resin. To discriminate the influence of the carrier resin from that of the CSR particles, blends with carrier resin but without CSR particles were also prepared. The respective compositions of the prepared formulations are given in Table 2.

**Table 1.** Comparison of the CSR grades.

Masterbatch	CSR particles		Carrier resin	
	Core type	CSR size(nm)	Reactive diluent	Nature of the prepolymer
M1	Styrene-butadiene rubber (SBr)	100	HPMA	vinylester
M2	Polybutadiene (PBd)	200	HPMA	polyester

**Table 2.** Prepared formulations.

Formulation name	VE amount (parts)	M1		M2		PVAc-based additive	
		CSR1 amount (parts)	C1 amount (parts)	CSR2 amount (parts)	C2 amount (parts)	PVAc (parts)	Styrene (parts)
ref	100	0	0	0	0	0	0
5M1	87.5	5	7.5	0	0	0	0
5M2	87.5	0	0	5	7.5	0	0
8M2	80	0	0	8	12	0	0
10M2	75	0	0	10	15	0	0
15M2	62.5	0	0	15	22.5	0	0
5C1	87.5	0	7.5	0	0	0	0
5C2	87.5	0	0	0	7.5	0	0
8C2	80	0	0	0	12	0	0
15C2	62.5	0	0	0	22.5	0	0
8PVAc	80	0	0	0	0	8.5	12.5

### 2.2 Methods

The glass transitions of neat resin and CSR-modified vinylester networks were determined using dynamic mechanical analysis on cured samples in three-point bending mode at 1Hz from -120°C to 230°C with a heating rate of 3°C/min.

Compressive tests were performed according to ISO 604 at a testing speed of 1 mm/min on samples with dimensions of 10 x 10 x 4 mm<sup>3</sup> and the compressive yield strength  $\sigma_y$  was recorded.

Three-point bending test were carried out on samples with dimensions of 80 x 10 x 4 mm<sup>3</sup>. The support span and cross-head speed were set at 60 mm and 2 mm/min. The flexural modulus  $E_f$ , flexural strength  $\sigma_f$  and flexural strain  $\varepsilon_f$  were determined in accordance to ISO 178.

The Charpy impact resistance of the blends was measured according to ISO 179-1. The dimensions of the specimens were 80 x 10 x 4 mm<sup>3</sup> and the support span was 62 mm. The hammer employed had an energy of 0,5 J or 1 J according to the energy required to break the samples.

Fracture toughness measurements were made according to ISO 13586 on three-point bending mode with samples with dimensions of 60 x 10 x 4 mm<sup>3</sup> (Single-Edge Notched samples). Specimens were first notched with a saw. Then a razor blade is put in the notch and is tapped until a sharp crack is created. The value of the crack length shall be around the half of the sample width. The plain strain critical stress intensity factor  $K_{1C}$  is calculated using the equation:

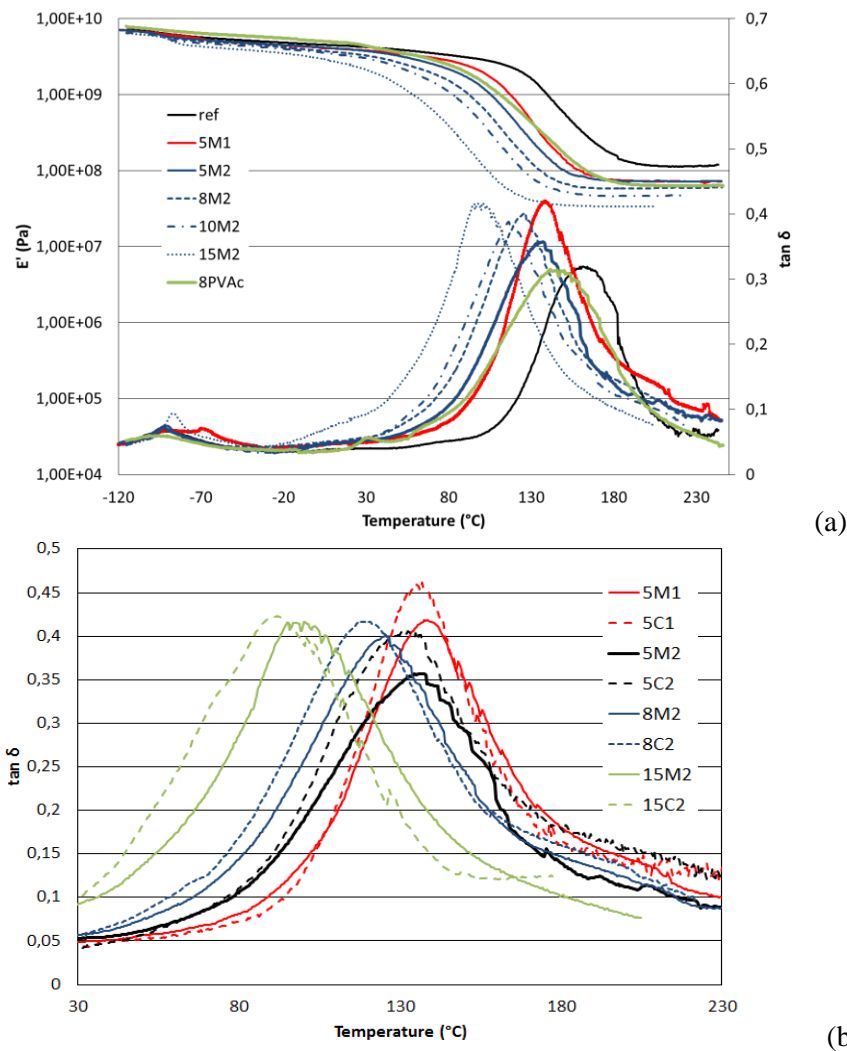
$$K_{1C} = \frac{P}{BW^{\frac{3}{2}}} f\left(\frac{a}{W}\right) \quad (1)$$

Where P is the critical load, B the sample thickness, W the sample width and  $f(a/W)$  a shape factor which depends of the crack length to sample width ratio.

The fracture surfaces of specimens used of  $K_{1C}$  measurements were observed with a scanning electron microscope under an acceleration voltage of 10 kV in order to study the dispersion of CSR particles in the matrix and to analyze the toughening mechanisms encountered in the presence of CSR.

### 3. Results and discussion

Storage modulus  $G'$  and  $\tan(\delta)$  are plotted from DMTA results (Figure 1.a). Values of  $T\alpha$  of materials were chosen from the maximum of the  $\tan(\delta)$  peak attributed to the  $\alpha$  relaxation. A secondary transition at around -90°C ( $\gamma$  relaxation) for the neat resin was attributed to motions of local groups of the polymer chains as reported by others authors [6], [7]. The addition of CSR materbatch to resin leads to a decrease of  $T\alpha$  from 165°C for the neat resin to 100°C for the 15-M2 blend. For CSR blends, the  $\alpha$  relaxation of CSR core is also visible at -65°C for M1 blends (SBr core), and at around -90°C for M2 blends (PBd core), superposed with the  $\gamma$  transition of the vinylester network. Results from Figure 1.b shows that drop of  $T\alpha$  was completely due to the carrier resin which acts as a plasticizer for the matrix since the decrease of  $T\alpha$  was almost identical whether CSR particles are present or not. These observations were confirmed by a decrease of the rubbery plateau modulus when M1 or M2 is added, showing a reduction of networks' crosslinking density. 8PVAc system is bi-phasic with a PVAc-rich phase ( $\alpha$  transition near 30°C) and a VE-rich phase with a  $\alpha$  relaxation lower than that of the neat resin (145°C instead of 165°C) due to a part of solubilized PVAc which plasticizes the phase. This depletion can also be partly attributed to a modification of the ratio of double bonds  $C=C_{VE}/C=C_{styrene}$  by the introduction of styrene brought by the PVAc solution.

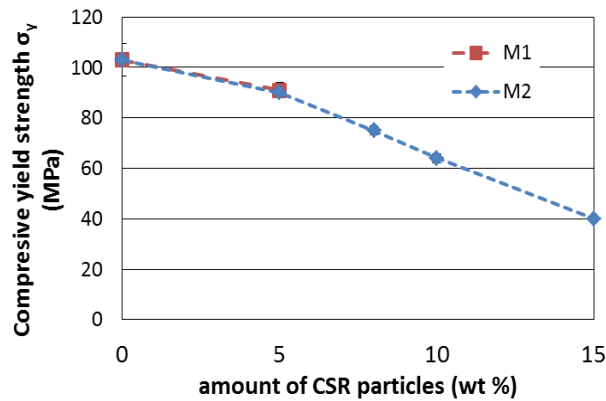


**Figure 1.** DMTA curves : (a) storage modulus and  $\tan \delta$  Vs temperature curves of CSR-blend systems ; (b)  $\tan \delta$  Vs temperature curves of formulations with and without CSR particles.

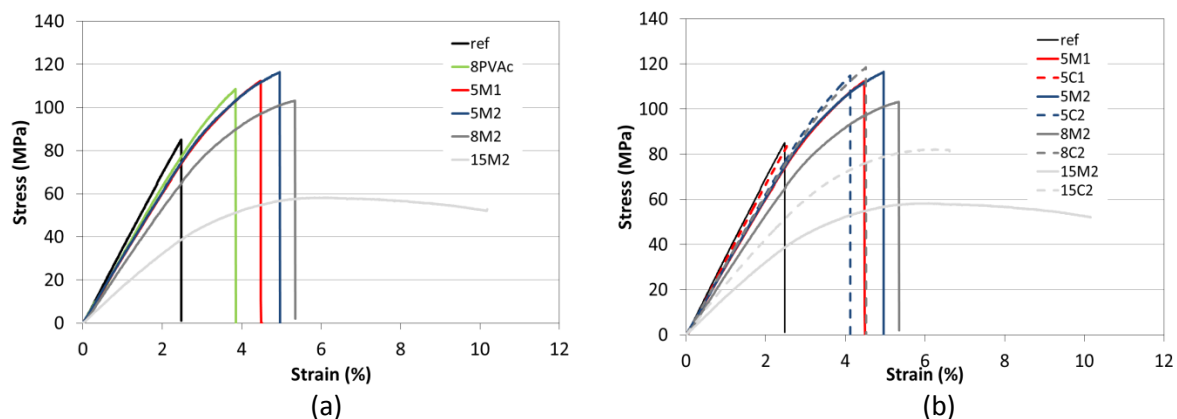
As expected, the compressive yield strength of blends decreases with an increase of the CSR content (Figure 2). This result can be explained by the fact that a part of rigid VE matrix was replaced by low-modulus rubber particles which promote plastic deformation of the material. Others authors reported these observations with thermosets in presence of CSR particles [8], [9]. In our case, the value of  $\sigma_y$  was almost the same for 5M1 and 5M2 proving that rubber fraction may be the main factor determining this value instead of the nature of CSR particles (size and nature of the core).

Stress-strain curves obtained for the materials are shown in Figure 3.a. The flexural modulus decreases with CSR content because of the introduction of a low-modulus phase in the material. Indeed, the modulus is reduced from 3.3 GPa for the neat resin to 1.6 GPa for 15M2 blend. Keeping a high modulus is a key factor for structural materials and the drop in modulus noticed for 10M2 and 15M2 (respectively 2.4 GPa and 1.6 GPa) was considered too high to employ these blends for structural applications. Increasing the amount of CSR leads to blends more ductile because the presence of a soft phase reduces the flexural stress whereas flexural strain keeps rising. Both carrier resin and CSR particles influence flexural properties of materials by improving ductility (Figure 3.b). However, the neat resin possesses low flexural stress and strain (Figure 3.a) because of its important brittleness and its high sensitivity to the presence of flaws. It is noted that there is no difference

between M1 and M2 blends, confirming the predominance of rubber content on others parameters for mechanical reinforcement. As for the 5 wt. % CSR blends, the addition of a soft phase PVAc (8.5 wt. %) improves the ductility of the material and delays the failure of the materials if compared to the neat resin.



**Figure 2.** Compressive yield strength of CSR blends.

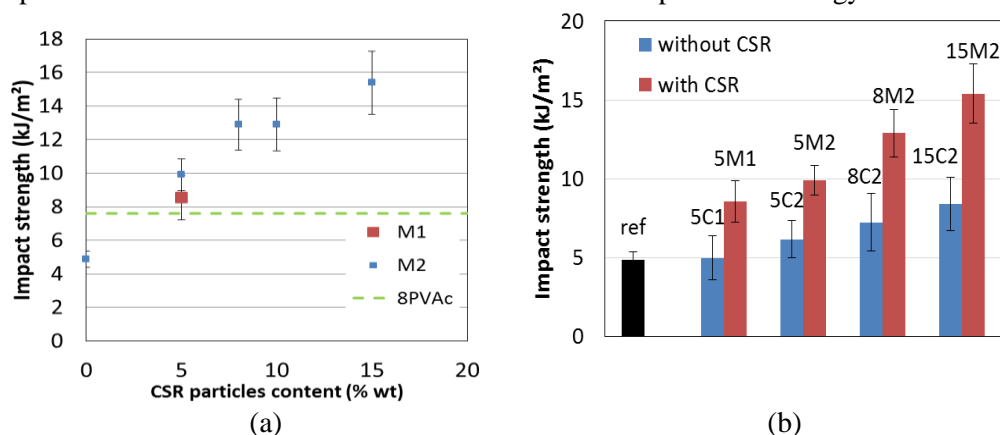


**Figure 3.** (a) Flexural stress-strain curves of different blends; (b) Comparison of stress strain curves of blends with and without CSR particles.

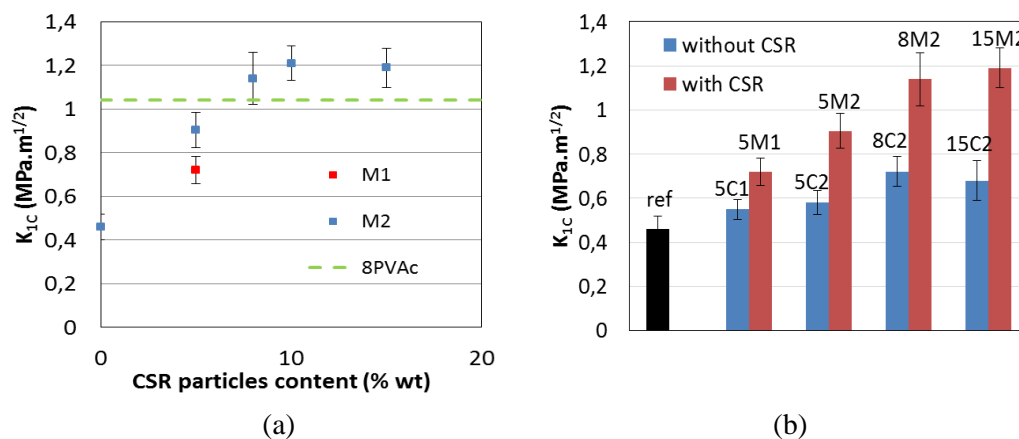
The effect of masterbatches M1 and M2 on impact strength of materials was studied (Figure 4.a). Adding M1 or M2 to the neat resin leads to an outstanding increase of the impact strength from 4.9 kJ/m<sup>2</sup> for the neat resin to 15.4 kJ/m<sup>2</sup> for 15M2 blend, i.e. an improvement higher than 200%. 5 wt. % of CSR is high enough to reach performances surpassing the ones of standard SMC matrix 8PVAc. As for static tests, differences between 5M1 and 5M2 are small considering standard deviations. Even if toughening may be partly brought by the carrier resin, the major part of the improvement seems to come from CSR particles or from a synergistic effect between carrier resin and CSR (Figure 4.b). Toughening mechanisms will be discussed later but an increase in impact strength could originate from the absence of large defects which could promote the initiation of cracks in materials. It can be deduced that CSR particles are probably macroscopically well-dispersed in the matrix.

Fracture toughness is also significantly improved in presence of masterbatches (Figure 5.a).  $K_{IC}$  values go from 0.45 MPa.m<sup>1/2</sup> to 1.2 MPa.m<sup>1/2</sup> for 10M2 and 15M2 blends. It appears that M2 masterbatch is more efficient than M1 comparing 5M1 and 5M2 even if deviations must be taken into account. Like for impact strength measurements, it was noticed that carrier resins contribute in improving  $K_{IC}$  values of matrices but the main toughening effect is noticed when CSR particles are present. Many authors described the role played by CSR particles in thermoset toughening [4], [10],

[11]. Around a crack tip, the cavitation of the rubbery core of CSR particles leads to a reduction of the hydrostatic component of the stress field and allows the transition from a triaxial stress state (plane-strain) to a plane-stress state, initiating deformation of the matrix by shear-banding which contributes to toughen materials. The reduction of compressive yield strength due to CSR particles can also facilitate plastic deformation of the matrix which is able to dissipate more energy.



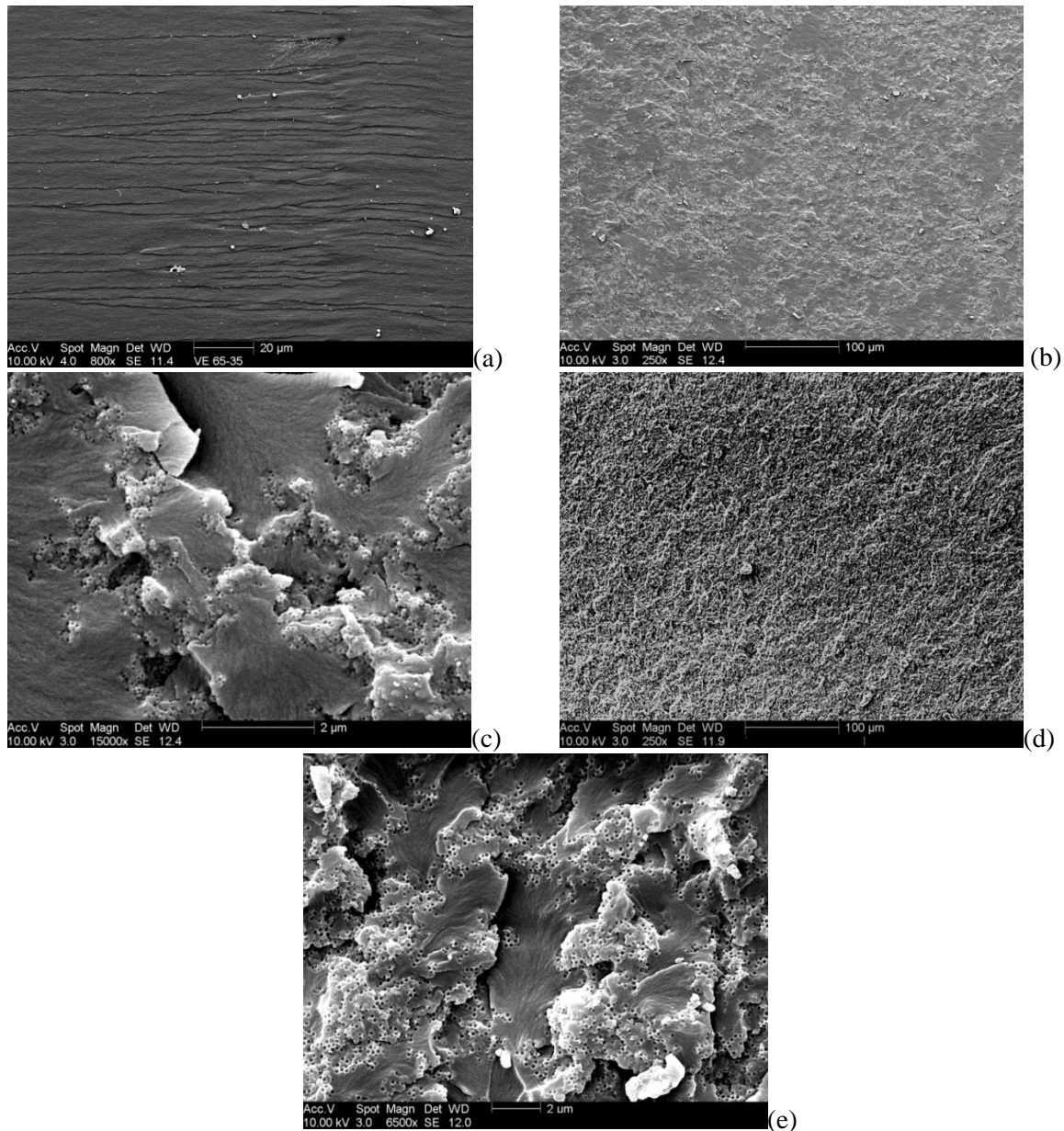
**Figure 4.** (a) Impact strength of different formulations with M1, M2 and PVAc ; (b) Influence of both CSR particles and carrier resin on the increase of the impact strength.



**Figure 5.** (a) K<sub>1C</sub> values of different formulations with M1, M2 and PVAc ; (b) Influence of both CSR particles and carrier resin on the fracture toughness.

SEM observations on fracture surfaces after fracture toughness measurements were performed on different formulations (Figure 6). Fracture surface of neat resin is smooth and reveals the brittle nature of thermosetting polymers like vinylester (Figure 6.a). Feather like marks are visible, associated with fast crack growth showing that cracks propagated on several planes. For CSR blends, SEM pictures macroscopically show that, CSR are well dispersed (Figure 6.b,d). But at higher magnification (Figure 6.c,e), SEM pictures present areas more or less rich in CSR particles, like a co-continuous microstructure, proving a CSR reorganization probably taking place during polymerization of the matrix. Even if CSR particles were not well dispersed, the resulting morphology seems to enhance mechanical properties. CSR blends exhibit rougher surfaces if compared to neat resin, indicating that more energy was absorbed during the propagation of the crack. Many voids are visible and could result from core cavitation of CSR or CSR debonding from the matrix. Further investigations like TEM or OM analyses will be carried out to deeper identify toughening mechanisms. SEM

observations (not shown here) were also realized on CSR-free blends (with carrier resin) and fracture surfaces look like neat resin one. Thus, roughness of fracture surfaces of CSR blends is solely attributed to the presence of CSR particles.



**Figure 6.** SEM pictures of : (a) neat resin ; (b),(c) 5M1 system ; (d),(e) 10M2 system.

#### 4. Conclusion

A vinylester resin was modified with masterbatches of CSR dispersed in carrier resins and blends were compared to a common SMC matrix. Results demonstrated an interesting improvement in impact strength and fracture toughness in presence of CSR. In order to give access to structural applications, it is important to get a matrix which exhibits a good compromise between stiffness and toughness. That is why 10M2 and 15M2 systems are not suitable candidates because of the too important loss in modulus. However, 5M1, 5M2 and 8M2 systems are really interesting especially thanks to their

impact strength significantly higher than that of standard SMC matrix 8PVAc, and their rigidity not sacrificed. These blends will be tested in SMC formulations and the effect on mechanical properties will be determined. Complementary analyses like TEM and OM experiments on DN-4PB samples particularly described by Sue [12], will be led on matrix systems in order to identify toughening mechanisms related to CSR particles.

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