Macromol. Symp. ***2001,*** *166, 179-187*

Phase Separation in Styrenated Polyester Resin containing a PVAc Low Profile Additive and Metallic Stearates

Christophe Mavon, Alain Chambaudet, Franck Jaffiol*

Laboratoire de Microanalyses Nucléaires, E.A. "Microanalyse des Matériaux" LRC- CEA n° MO7, U.F.R. des Sciences & Techniques, La Bouloie, 16 route de GRAY, 25 030 BESANCON Cedex, France
Tel : 03 81 66 65 17, Fax 65 22, E-mail : cmavon@utinam.univ-fcomte.fr

*PSA, Etudes & Recherches, La Garennes-Colombes, Paris, France

SUMMARY : Unsaturated Polyester Resins(UP) that contain compatible low-profile additives (PVAc) are used in BMC composite materials (Bulk Molding Compound). The general morphology of the UP/PVAc matrix is made up of small polyester nodules embedded in a matrix-rich thermoplastic additives.

An internal mold-release agent (often a Calcium Stearate) is incorporated into the UP/PVAc mixture to facilitate the extraction of the curing materials. Although used in small quantity, this agent does have an effect on the final morphology of the curing mixture. Some of the internal mould-release agents provoke the formation of a polyester rich phase in the form of large spherical globules (roughly 60 micrometers). The formation of the "globular" polyester phase seems to depend largely on the nature of the metallic ion and the solubility (in the styrene) of the mould-release agent. If this phase occurs, most of the internal mould-release agents are trapped inside the polyester globules.

Given its particular affinity for mineral materials, this phase tends to coat filler and glass fibbers. Consequently, this phase strongly conditions the mechanical characteristics of the final composite.

Introduction

Complex composite materials, called hybrid composites, are increasingly used for a number of applications. Their organic matrix can be made up of several phases that link the fibers and fillers. Modifying the composition (even at a minimal level) can sometimes cause a variation, notably in the overall mechanical characteristics of the material; mechanical experiments are thus necessary to test each new formula.

Precise knowledge and understanding of the material's morphology versus the formula make it possible to evaluate the mechanical properties. From there, controlled modifications can be made in order to adapt the material to a specific application.

CCC 1022-1360/00/$ 17.50+.50/0

Materials

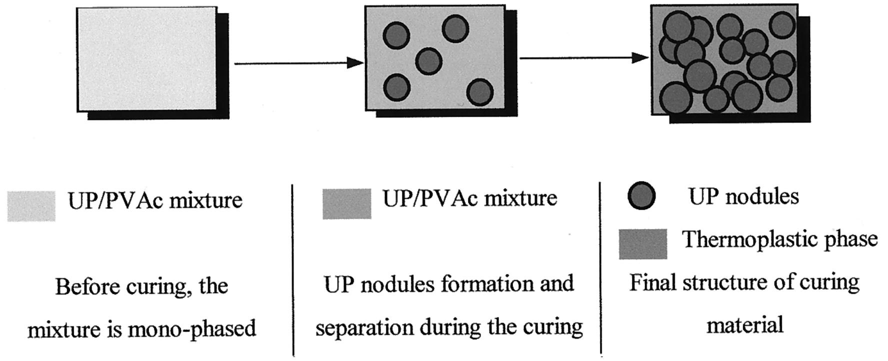
The matrix studied was composed of a standard Unsaturated Polyester (UP) orthophtalic resin (UP + Styrene) with a low-profile additive (LPA) like many of the BMCs (Bulk Molding Compounds). The low-profile agent is a polyvinyl acetate (PVAc). It is thermoplastic compatible with the UP resin. The latter guarantees the dimensional stability of the molded material during curing[1].

The morphology of the polished and broken (in liquid nitrogen) surfaces of the cured materials was examined using a scanning electronic microscope (Jeol 35CF).

Results and discussion

- UP/PVAc reticulation

In general, polyester pre-polymers form microgels that contain a high molecular mass and are non-soluble[2-5]. The polyester nodules (about 1 micron) are precipitated in the UP/PVAc/Styrène mixture[6]. The microstructure of the cured material was a mix of polyester nodules dispersed in a continuous PVAc matrix[7].



▨ UP/PVAc mixture

Before curing, the mixture is mono-phased

▨ UP/PVAc mixture

UP nodules formation and separation during the curing

● UP nodules

▨ Thermoplastic phase

Final structure of curing material

Fig. 1 : Curing of UP/PVAc mixture

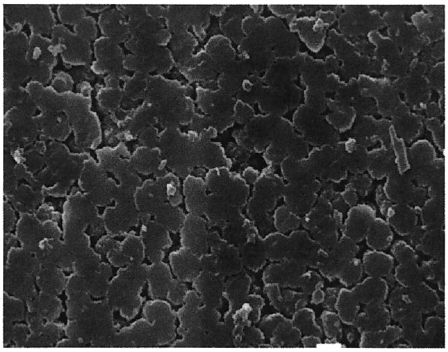
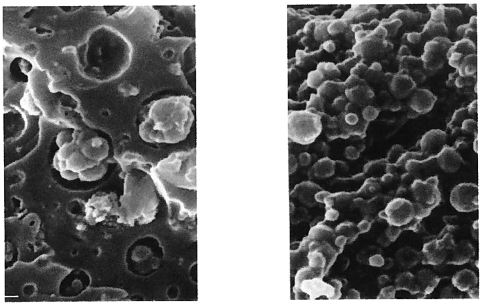


Fig. 2 : Polished surface of the curing matrix - scale : 1 micron.

In general, the organic matrix's structure is specific with a UP/PVAc ratio of 60/40 (weight - the proportions were optimized to guarantee no polymerization shrinkage). The matrix was made up of scattered polyester nodules in a PVAc continuous matrix (Fig 2).

The microvides appeared during the cooling stage. These microvides resulted from the shrinkage of the UP phase and the thermal contraction of the PVAc[4].

The distribution of the phases depended on their respective quantities[8]. If this proportion is modified, the hardened mixture's morphology would also vary (Fig. 3).



UP/PVAC ratio : 80/20
The continuous matrix is
UP in nature

UP/PVAC ratio : 40/60
The UP nodules are very
spread out in the PVAc

Fig. 3 : Cryofractography of curing matrix (SEM) - Scale : 1 micron

A previous study showed that the behaviour of the phase separation, and consequently, the final microstructure of the cured material can be modified by a small quantity of calcium stearate.

For this study, the UP/PVAc ratio (60/40) remained constant and the morphological modifications of the organic matrix were obtained by adding different internal mold release agents (stearate) in the mixture UP/PVAc.

- Mold release agent effects (UP/PVAc organic matrix)

Many types of mold release agents were tested to understand their effects on the UP/PVAc mixture's morphology. Here, we present the changes of the UP/PVAc morphology obtained by using a different metallic stearate (M St).

The UP/PVAc/M St mixture was mixed for five minutes at 20°C. The curing was carried out at 105°C for nine minutes with 1% Methyl Ethyl Ketone Peroxyde.

These physical characteristics are presented in Table 1.

Table 1 : Used mold release agents.

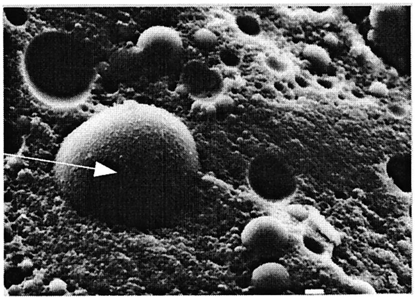
Nature	Symbol	Cation	Solubility*
Calcium Stearate	Ca St	Ca^{2+}	0.52 g
Lead Stearate	Pb St	Pb^{2+}	3.60 g
Magnesium Stearate	Mg St	Mg^{2+}	1.10 g
Aluminium Stearate	Al St	Al^{3+}	"Gel"
Zinc Stearate	Zn St	Zn^{2+}	"Gel"
Potassium Stearate	K St	K^{+}	2.52 g

*The solubility of the stearates is the quantity of the solubilized product in 100 g of styrene at 105 °C during nine minutes.

- Ca St effect

The Calcium Stearate is the common mold release agent used in the industrial mixture.

With a quantity of 4 % weight, this agent strongly modifies the microstructure of the curing material (Fig. 4).



Large
spherical
"globules"

Fig. 4 : Morphology of cured UP/PVAc/Ca St mixture -Cryofractography - scale: 1 micron.

Initially made up of polyester nodules (1 micron) dispersed in a thermoplastic continuous matrix, the microstructure of the cured matrix showed that when the calcium stearate was added, large spherical "globules" (60 microns) appeared.

Infra-Red spectroscopy showed that this phase was mostly made up of polyester pre-polymers. The elements' composition measurements (electronic microprobe) showed that the majority of the internal mold release agent (Ca atom) was placed inside the polyester globules.

- Other used mold release agents effects

All the other mold release agent were incorporated into a UP/ PVAc mixture and cured at 105°C. The samples were broken in liquid nitrogen, and these broken surfaces were observed using SEM. The following morphological observations were obtained (Table 2) :

Table 2 : Morphological observations of the mixtures.

Nature	Globules	Size
Pb St	Yes	20-100 µm
Mg St	Yes	10-40 µm
Al St	No	/
Zn St	No	/
K St	No	/

These observations have enabled us to establish the two following facts : Under these mold conditions (P. atm, Temp. : 105 °C, Curing 9 min) the UP phase appears as if : First, the mold release agent has a low solubility, and, second, the metallic cation must be bi-valent.
Remark : the spherical form of the globules indicates that they are formed when the mixture is still liquid or viscous.

- Mold release agent effects on the filled and reinforced composite

The UP/PVAc/Sty mixture can be classified as a composite material with mineral charges and fibers. A powder's Calcium carbonate (Millicarb) is the common filler in the industrial formulation. The composite is reinforced by short E glass fibers (13 mm).

Without a mold release agent, a small quantity of filler or fibers can change the global composite morphology. When the polyester globular phase is present (with Ca St, Mg St or Pb St), the strong wettability of this phase induces the coating of the additive minerals ; see Figures 5 (Calcium carbonate) and 6 (glass fiber).

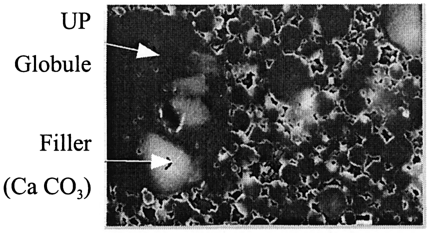


Fig. 5 : Polished surface of the shrunk mixture with St Ca + 10% charges after the MEK attack. Scale : 10 microns.
(MEK attack is used to eliminate the PVAc thermoplastic phase in order to observe the thermoset UP phase only).

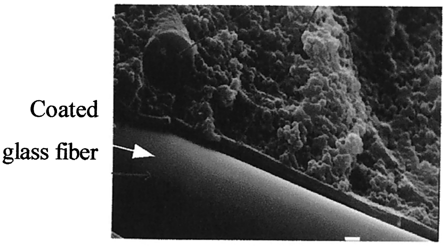


Fig. 6 : Cryofractography of UP/PVAc matrix + St Ca + glass fibres. Scale : 1 micron.

For weaker quantities of mineral charges or glass fibers, the continuous matrix was made up of PVAc (thermoplastic), which conditioned the mechanical characteristics of the composite. With an elevated rate of additive minerals, the glass fibers, or coated mineral charges, moved closer together, often touching. The continuous matrix, initially made up of PVAc, became progressively like a polyester ; this forms a thermosetting network in the composite (Fig. 7).

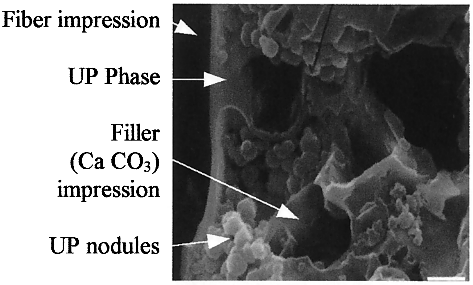


Fig. 7 : Cryofractography after MEK and HCl solubilizations. Scale : 5 µm.

Consequently, the formed polyester network greatly increased the mechanical characteristics of the material (notably the rigidity and temperature resistance).

Conclusion

- UP phase formation

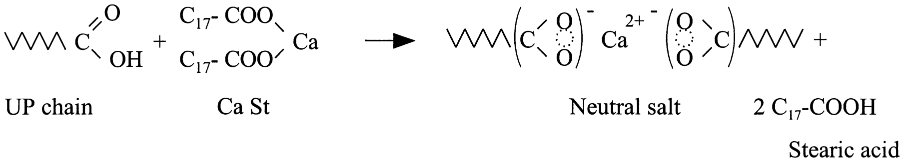
The *Suspene* and *Coll*9) show, along with the ternary diagram studies of UP/PVAc mixtures, that the high molecular weight of the UP prepolymer are less soluble than the low molecular weight UP prepolymer. They also precipitate sooner in the liquid mixture during curing.

The used resin (standard orthophtalic UP resin) contains many carboxylic groups on the end of the UP prepolymers chains (acid level : 23 mg_{KOH}/g). These groups can react with hydroxides, oxides or salts like, for example, the magnesium oxide (MgO) used for the manufacturing of SMC semi-products[10)].

For our materials, the increase in the quantity of bivalent stearate and notably the calcium stearate, led to an increase in the mixture's viscosity. This was not the case for the stearates whose metallic ions were monovalent. Moreover, the increase in Calcium stearate in the mixture induced a linear increase in the quantity of the UP globular phase (until about 12 % in weight). Afterwards, the UP phase quantity remains constant.

The formation of the UP globular phase during the cure can be explained by the following mechanism :

On the Calcium stearate particle (or other bivalent stearate with a bad solubility), the free carboxilic groups of the UP resin can react to form salt.



During the curing, the salt formation tends to increase the UP polydispersity. Next, this phase tends to precipitate by styrene consummation to form spherical UP globules.

- Perspectives

The presence of this new phase can have a notable influence on the mechanical characteristics of the cured composite The micro-structural observations have made it possible to precisely pinpoint the organization of the constituents in the material versus the formulation (Fig. 8).

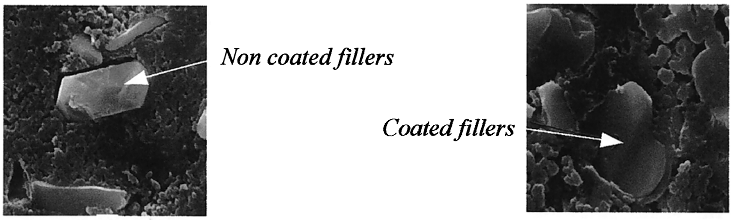


Fig. 8 : Polished surfaces - Filler : Alumine particles - Scale : 5 microns

The perspectives in this domain are very interesting. It is possible to coat the mineral charges of a rubber polyester phase in order to improve a composite's shock resistance, or to create a flexibilized polyester network.

By playing with the respective quantities of each basic constituent, the microstructure of this kind of material can be controlled, and consequently, so can its mechanical characteristics.

References

1. F. Jaffiol, F. Cote, C. Gauthier, Composites, n° 3, (1989)
2. Y. S. Yang, L. J. Lee, Polymer Vol. 29, (1988)
3. C. P. Hsu, L. J. Lee, Polymer Vol. 32, 2263, (1991)
4. K. E. Atkins, Polymer Blends Vol. 2, 391-414 (1978)
5. E. J. Bartkus, C. H. Kroekel, Appl. Poly. Symp. N°15, 113, (1970)
6. L. R. Ross, S. P. Hardebeck, 43th Ann. Conf. Soc. Plas. Ind., 1-5 (1988)
7. V. A. Pattison, R. R. Hindersinn, J. Appl. Pol. Sci. Vol 18, (1978)
8. C. B. Bucknall, P. Davies, Polymer, Vol 29, (1985)
9. L. Suspene, D. Fourquier, Polymer, Vol. 32, (1991)
10. P. Arlaud, P. Blondeaux, Composites, 5, (1985)