

# IDENTIFICATION OF THE COMBINED RHEOLOGY OF MIXTURES OF EPOXY RESINS WITH DIFFERENT INITIAL CURING STATES

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Received: 13.1.2013, Final version: 22.3.2013

## ABSTRACT:

A commercial epoxy resin system was tested under several different mixing conditions with viscometer and rheometer apparatuses. In each test, two portions of the same resin, prepared at different times, were mixed and their joint behavior was analysed. The differences between the behavior of this blend and the neat (unmixed) resin after the mixing point were, then, critically assessed. Both the preparation time gap and the mixing ratio of the two portions coherently affected the overall blend behavior. However, the commonly accepted linear combination of the contributions of the portions of resin with different degrees of cure, usually employed to describe the joint behavior, was not applicable for the entire time interval after mixture.

## ZUSAMMENFASSUNG:

Ein kommerzielles Epoxidharz-System wurde unter verschiedenen Mischbedingungen mit Viskosimetern und Rheometern getestet. In jedem Test wurden zwei Proben aus dem gleichen Harz, zu unterschiedlichen Zeiten hergestellt, gemischt und anschliessend vermessen. Die Unterschiede zwischen den Mischung und sortenrein Harzen nach der Mischung wurden dann beurteilt. Sowohl die zeitliche Lücke zwischen den Mischungen als auch das Mischungsverhältnis der beiden Proben beeinflussen das Verhalten der gesamten Mischung. Es zeigt sich, dass der allgemein akzeptierte lineare Zusammenhang der Harze mit verschiedenen Graden der Ausheilung nicht auf das gesamte Zeitintervall nach der Mischung anwendbar ist.

## RÉSUMÉ:

Un système commercial de résine époxy a été testé dans plusieurs différentes conditions de mélange avec les appareils viscosimètre et rhéomètre. Dans chaque test, deux portions de la même résine, préparés en moments différentes, ont été mélangés et leur comportement conjoint a été analysée. Les différences entre le comportement de ce mélange et de la pur (non mélangé) de résine après le point de mélange ont, ensuite, été évaluées de façon critique. À la fois, l'intervalle de temps de préparation et la proportion de mélange des deux parties ont affectée de manière cohérente le comportement global de la mélange. Cependant, la combinaison linéaire communément accepté des contributions des portions de résine avec différents degrés de cure, habituellement utilisé pour décrire le comportement conjoint, n'était pas applicable à tout l'intervalle de temps après mélange.

**KEY WORDS:** thermosetting resin, curing, rheology, mixture, complex viscosity

## 1 INTRODUCTION

In thermosetting-based composites manufacturing, the evolution of both the degree of cure and the viscosity of the resin as the cure progresses govern its ability to flow through the porous fibre bed and, thus, the consolidation of the composite laminate. The physical properties of the resin, such as viscosity, are mostly dependent on time, since the irreversible chemical reaction starts after the mixture of its constituents. In a previous study conducted with two different thermosetting epoxy systems in neat (unmixed) conditions

[1], it was shown that other conditions, like the mass of the sample and the surrounding temperature, also affect significantly the kinetic and rheological behavior of these systems.

In order to model the consolidation of composite laminates, the degree of cure and viscosity should be known for each point of the laminate at each moment. For the majority of the manufacturing processes, the assessment of the intrinsic behavior of the neat resin subjected to comparable temperature and mass conditions is a very good approximation to its behavior with-

the analysis of the time needed to achieve such a state may be of interest. If upon mixture the kinetic behavior could be described by linear combination of the two individual behavior, then the additional time required to reach gelation should be of the same order of the cure time gap (for 1:1 mixing ratios). This behavior was not verified. The delay in reaching gelation was neither similar to the time gap of the curing histories of the two portions nor proportional to their mixing ratios.

Looking at the rheometry results, the overall viscosities of the samples at gelation decreased as the mass ratio increased and were nearly unchanged for different cure time gaps. The gel times were calculated using an established criterion [14]. This suggested that, unlike the viscosimetry results, for the time gaps studied, the resin mixtures were able to accommodate (or “correct”) its viscosity on time for the gelation. Within the range of 1:2 to 2:1, particularly, the viscosity at gelation seems to be an intrinsic characteristic of this epoxy resin, not affected by the two parameters altered through the test series. The time needed to reach such characteristic viscosity, however, was consistently affected by the two parameters. The fact that the times needed to achieve gelation did not remain constant nor increased equally to the cure gap times suggested that none of the individual resin portions governed the blend behavior.

It became clear that, despite the rheological behavior of the resins blend (portion 1 mixed with portion 2) should be described through a combination of the individual behavior, such combination must not be solely weighed by their relative volume contents. In other words, the relationship itself should account for an evolution with time. In graphical terms this is better visualized by noting that the viscosity curve of the mixture/blend is not “parallel” to the two individual (idealized) curves of the neat resins, which are “parallel” to each other (Figure 3). This meant that the relation presented in Equation 1, even though setting a reasonable approximation, could not describe accurately the

evolution of the viscosity upon mixture of two portions with different cure histories. In addition, contrary to the viscosimetry data, the direct application of the linear combination mixing rules did not return consistent estimations for the idealized viscosity of the second portion at time of mixture (Table 4). This further weakened the validity of the assumed linear combination relation.

## 5 CONCLUSIONS

After performing a detailed analysis of the viscosimetry and rheometry results, for the tests conducted on SR<sup>®</sup> 1500/SD<sup>®</sup>2505 resin samples constituted by a mixture of two portions with different curing histories at near to room temperature, the following conclusions are drawn:

- Equation 1 was able to reasonably approximate the viscosity of the resin blend at the moment of mixture ( $t \approx$  cure time gap) for cure time gaps lower than 35 % of the neat idealized gel time
- The rheological behavior of the resins blend after their mixture was a time dependent combination of the two individual behavior, thus not fully describable through the proposed equation

The the relation proposed in Equation 1 is, nevertheless, a reasonable approximation for most engineering applications. The actual region between the two individual idealized behavior was relatively small, i.e. the error of such linear combination would be always lower than the one resulting from using one of the two ideal behavior of the contributing resin portions.

## ACKNOWLEDGEMENTS

The authors acknowledge the Portuguese Foundation for Science and Technology for partially supporting the work presented herewith, through the co-funded project ModEFil.

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Test ID	Mixture Mass Ratio	Neat Cure Time Gap [s (min)]	Viscosity at gelification [Pa.s]	$\mu_1$ before mix [Pa.s]	$\mu_{mix}$ [Pa.s]	$\mu_2$ (calculated) [Pa.s]
SRHF1101	3:1	544 (9)	2.091	0.750	0.639	0.306
SRHF1102	2:1	536 (9)	2.639	0.750	0.720	0.661
SRHF1103	1:1	540 (9)	2.472	0.750	0.583	0.416
SRHF1104	1:2	565 (9)	2.858	0.750	0.520	0.404
SRHF1105	1:1	960 (15)	2.761	1.095	0.690	0.285
SRHF1106	1:1	1500 (25)	2.676	2.075	0.982	-0.112
SRHF1107	1:1	245 (4)	3.007	0.505	0.515	0.525

Table 4: Values estimated through linear combination for the initial viscosities of the second resin portions for the rheometry tests of SR<sup>®</sup> 1500/SD<sup>®</sup> 2505 mixed (blended) samples.

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