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Tuning morphologies of thermoset / thermoplastic blends Part 2: Phase separation of poly(vinyl methyl ether), PVME, using amine mixtures as thermoset hardeners

Nadir Lahlali,[1] *Jérôme Dupuy,*[1] *Michel Dumon* [1, 2*]

[1] *Université de Lyon, Lyon, F-69003, France ; INSA de Lyon, IMP/LMM, Laboratoire des Matériaux Macromoléculaires, Villeurbanne, F-69621, France; CNRS, UMR5627, Ingénierie des Matériaux Polymères, Villeurbanne, F-69621, France.*

[2] *present address : Laboratoire Génie Mécanique et Matériaux, Université Bordeaux 1, IUT département Science et Génie des Matériaux, domaine universitaire, 33 405 Talence, France. fax number (+33)(0) 5 56 84 79 63, e-@mail : michel.dumon@u-bordeaux1.fr*

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Abstract : Part 2 of the study investigates morphologies of epoxy thermoset / thermoplastic blends obtained with formulations of the thermoset hardeners. The thermosetting matrices are composed of one epoxy resin crosslinked by a mixture of two aromatic diamine hardeners, namely MCDEA+DDS or MDEA+DDS (DDS is 4,4'-diaminodiphenylsulfone, MCDEA is 4,4'-methylenebis-(3-chloro-2,6-diethylaniline), MDEA is 4,4'-methylenebis-(2,6-diethylaniline). The blends are made at a fixed concentration of thermoplastic (poly(vinyl methyl ether), PVME, 10wt%) whereas three different cure temperatures are chosen and the matrix composition is varied by the ratio of DDS. DDS is a PVME-insoluble diamine whereas MDEA or MCDEA are PVME-soluble diamines.

The domain size of the PVME nodules is tuned from a few micrometers down to sub micron sizes, typically between 50 and 80 nm. We attempt to explain this evolution thanks to the difference in the reactivity of the amines with the epoxy oligomer coupled to the difference in miscibility of each amine towards PVME. The kinetic study developed in Part 1 of this work is used to calculate the concentrations of each amine along the reaction time and their rate of incorporation in the polymer network. The latter parameter is shown to be the limiting factor for obtaining a nano phase separation.

Introduction

Thermoset/Thermoplastic (TS/TP) blends, especially those dealing with epoxy themosets, classically use *a single hardener* matrix. Studies are currently describing the reaction kinetics and phase separation phenomena [1 and references therein]. Indeed literature does not reveal any real study in the sense of tuning morphologies in epoxy-based matrices by hardener formulations (mixtures of di amines).

One point is to investigate how the evolution of the ratio of each hardener is likely to affect the blend morphologies. For this, a mechanistic kinetic model was developed [1] to calculate the real concentration of each amine along the reaction time whatever the initial amine ratio. Two sets of thermosetting "mixed" matrices are chosen to prepare 10wt% poly(vinyl methylether), PVME / epoxy blends: i) MCDEA- DDS-epoxy i.e. matrices with a PVME-miscible and slow reactive amine; ii) MDEA- DDS-epoxy i.e. matrices with a PVME-miscible and fast reactive amine. The MDEA or MCDEA to DDS ratio is varied in each set. DDS is a PVME-insoluble diamine, MDEA or MCDEA are PVME-soluble diamines.

The aim of this part is to determine the size range of the separated phase which is accessible by such a reaction-induced phase separation process, in particular whether meso or nanoscale phases can be generated. Moreover, PVME is a degradable polymer that can leave pores after a thermal treatment [2, 3].

Results and discussion

Fig.1 reminds the order of reactivity of the hardeners to a single diamine: MDEA>DDS>MCDEA. These reactivities are quite consistent with those observed by Girard Reydet et al. [4]. The kinetic model described in part 1 of our work is used to simulate both the reaction kinetics of mixed matrices based on diamine mixtures and to calculate the extent of reaction versus time for 10wt% PVME blends as it was found that the model applies to the low concentration blends until the cloud point [1]. Thus it is possible to evaluate the reaction kinetics of all 10wt% PVME blends (based on mixed matrices whatever their DDS ratio) and to calculate the cloud point conversions (and gel conversions) from measurements of cloud point times (and gelation times).

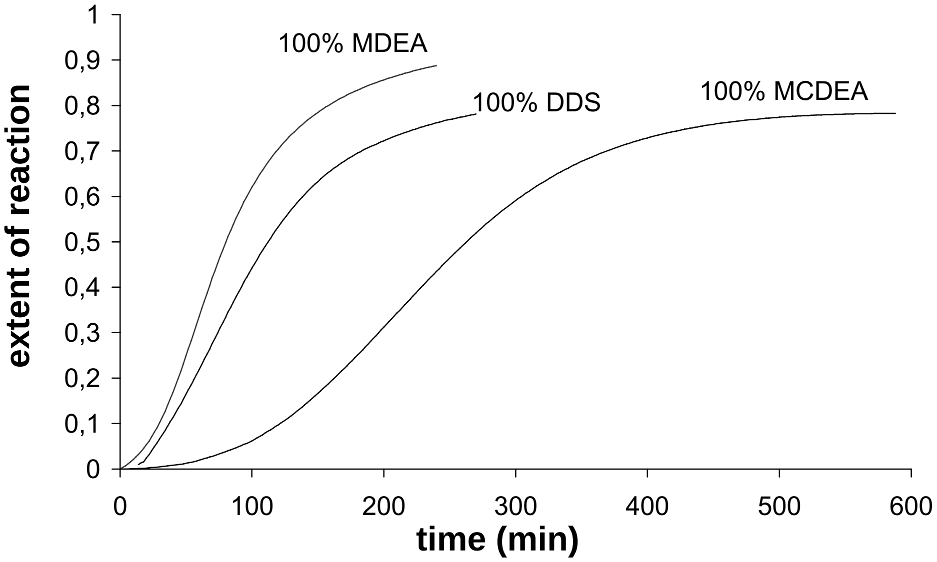


Fig. 1. Extent of reaction of MDEA, DDS, MCDEA crosslinked with DGEBA at 135°C.

Influence of amines and pre cure temperature on phase composition

The blends formed from neat matrices (single hardener) are first considered. In the two blends with a PVME-miscible hardener (MCDEA-DGEBA / 10% PVME or MDEA-DGEBA / 10% PVME), the thermoplastic does not separate at any temperature up to complete polymerization. The samples are quite transparent (no cloud point) and no TEM contrast was revealed. On the contrary, the DDS-DGEBA matrix induces a very early phase separation at a conversion of x_{CP}~0.05 whatever the cure temperature.

In the blends formed from "mixed matrices", the occurence of phase separation (i.e. x_{CP}) depends on both the DDS content (X_{DDS}) and on the first cure step temperature (Table 1). Phase separation may be characterized by T_g of the TS-rich phase measured on the post cured samples (Fig. 2 for DDS-MCDEA/DGEBA matrices and Fig. 3 for DDS-MDEA/DGEBA matrices). In fact, Fig 2 and 3 represent the variation of several T_g's as a function of X_{DDS}: i) T_g of neat "mixed matrices" without PVME, ii) T_g of blends with different precure temperatures, iii) T_g calculated by Fox law considering fully miscible blends of 10wt% PVME ($T_{g\ PVME}$= -25°C, the T_g values for the neat mixed matrices are those measured by DSC). One can observe that none of T_g's obeys the Fox law, thus proving that PVME is never fully miscible and should be phase separated at some scale, even if some samples are transparent and TEM did not reveal any morphology (e.g. in Table 1, $0<X_{DDS}<0.20$).

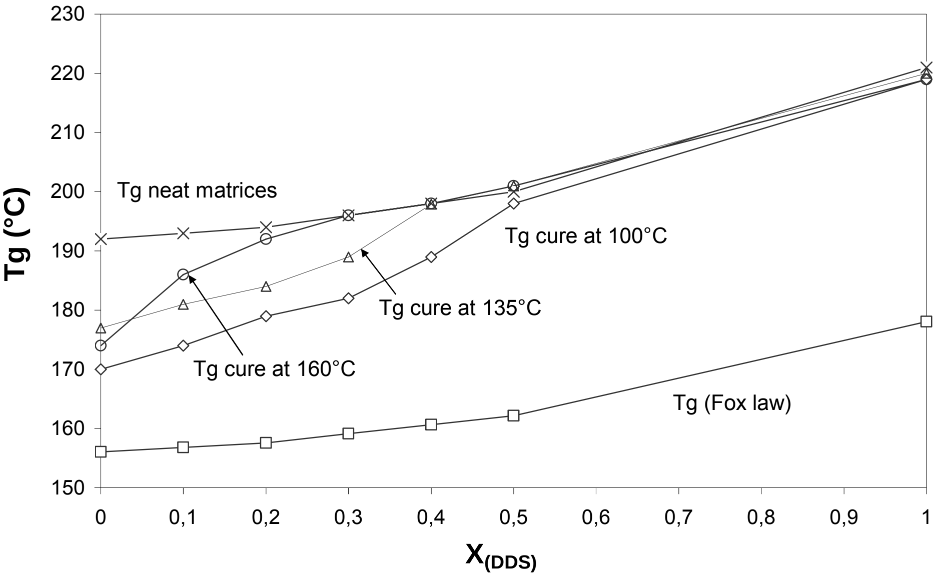


Fig. 2. Evolution of T_g's as a function of DDS content, X_{DDS} in DGEBA- DDS- MCDEA / 10wt% PVME blends. ×: T_g of the neat matrices (without PVME);
T_g of 10%wt PVME blends: ○ first cure step at 160°C, ∆ first cure step at 135°C, ◊ first cure step at 100°C (T_g are measured after postcuring); □: T_g calculated with Fox law considering 10wt% PVME fully miscible.

Consequently, the quantity of PVME dissolved in the mixed matrices depends on the DDS content as indicated in Fig. 4 and 5 for MCDEA (respectively MDEA) - DDS/DGEBA blends. The % of miscible PVME was calculated by Fox law [4]:

$$\frac{1}{Tg_{measured}} = \frac{\varphi_{PVME}}{Tg_{PVME}} + \frac{1-\varphi_{PVME}}{Tg_{neat\ epoxy\ resin}} \quad \textbf{(1)}$$

As Tg of PVME and T_g's of neat systems are known, φ_{PVME} can be easily calculated.

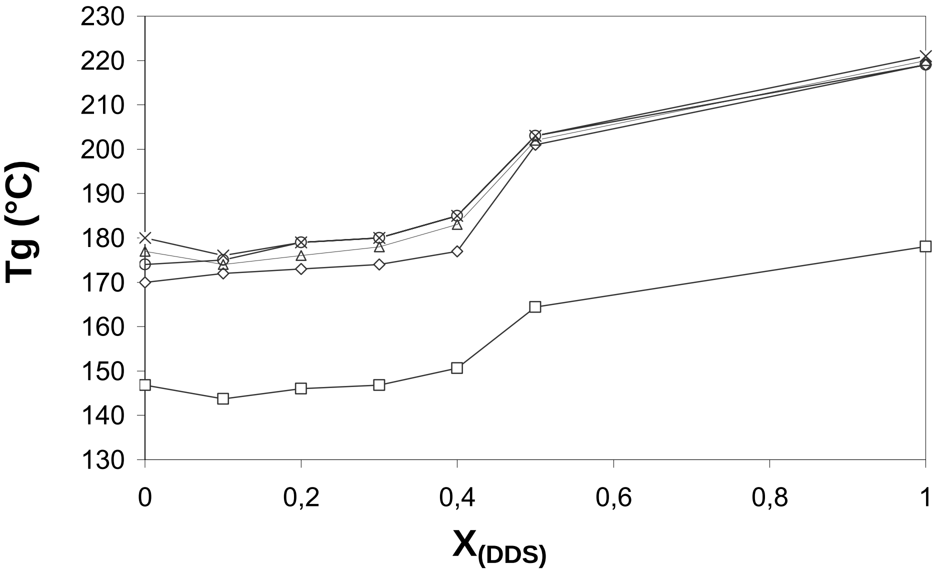


Fig. 3. Evolution of T_g's as a function of DDS content, X_{DDS} in DGEBA- DDS- MDEA / 10wt% PVME blends. ×: T_g of the neat matrices (without PVME); T_g of 10%wt PVME blends: ○ first cure step at 160°C, Δ first cure step at 135°C, ◊: first cure step at 100°C (T_g are measured after postcuring); □: T_g calculated with Fox law considering 10wt% PVME fully miscible.

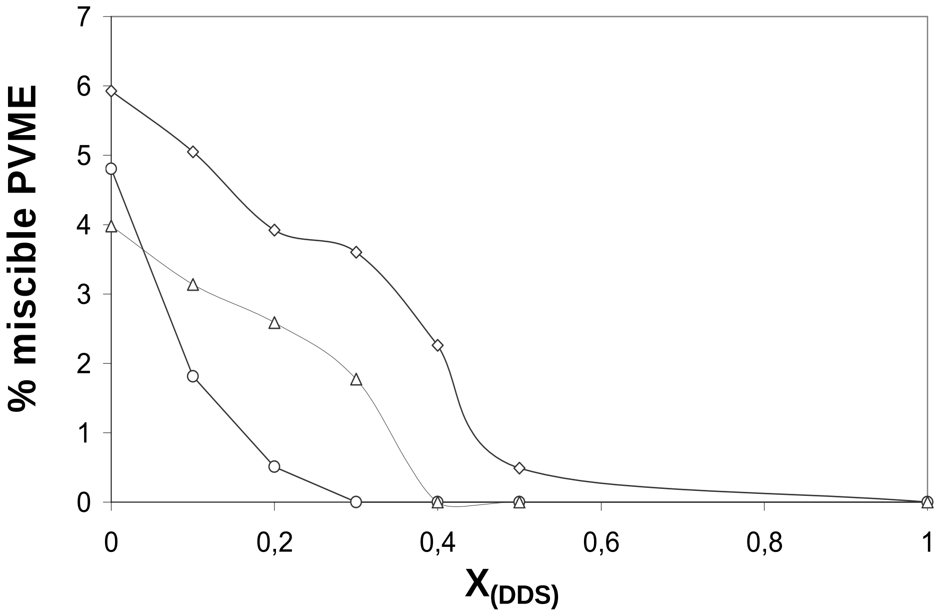


Fig. 4. Evolution of % miscible PVME as a function of DDS content in blends containing initially 10wt% PVME and MCDEA-based matrix. ○: first cure step at 160°C, Δ first cure step at 135°C, ◊ : first step cure at 100°C.

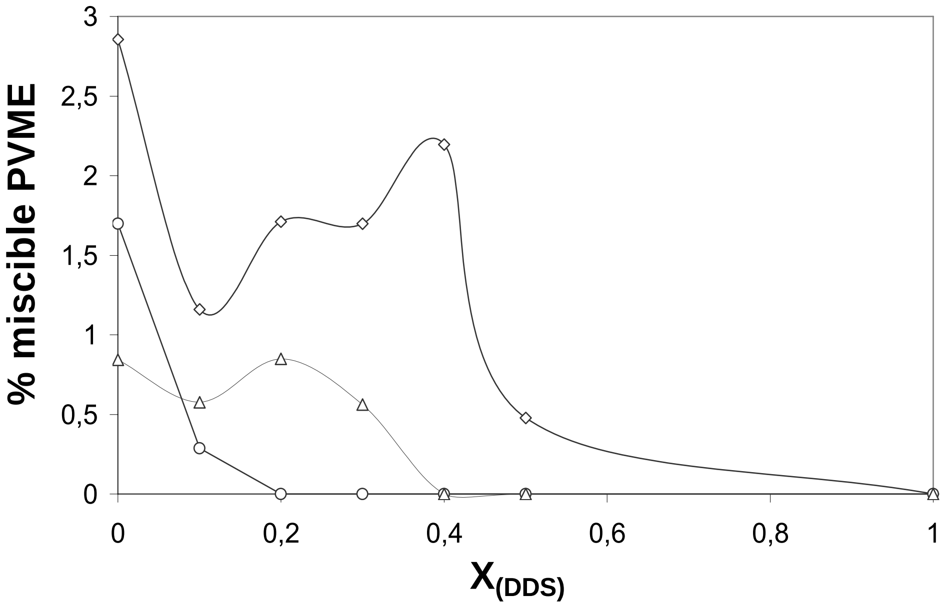


Fig. 5. Evolution of % miscible PVME as a function of DDS content in blends containing initially 10wt% PVME and MDEA-based matrix. ○: first cure step at 160°C, . Δ first cure step at 135°C, ◊ : first cure step at 100°C.

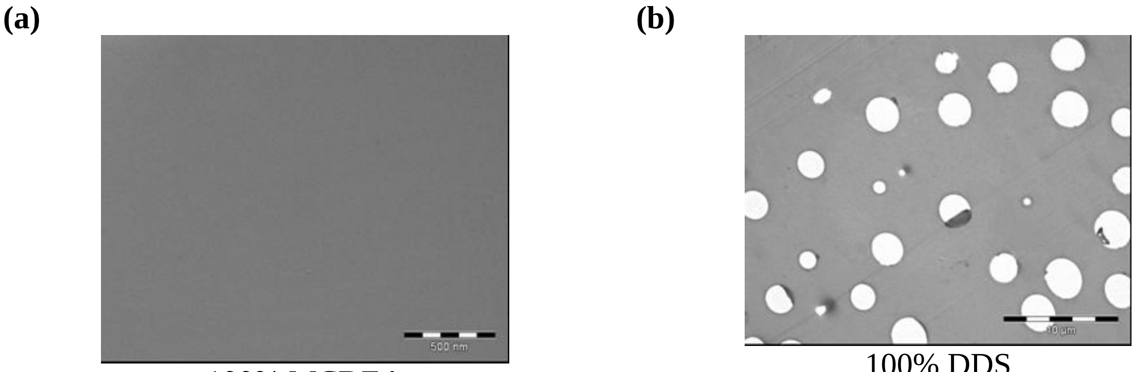
From Figures 2 to 5, several remarks can be drawn: the T_g of TS-rich phase reaches the Tg of neat matrix on increasing DDS content. DDS which is the hardener with the poorest solvent capacity allows a complete phase separation of PVME in MCDEA-based mixed matrices above 50mol% DDS. On the other hand, when $X_{DDS} < 0.50$, PVME is not completely separated due to the very good solvent capacity of MCDEA. The situation is somewhat different for the MDEA-based blends (Fig. 3 and 5). MDEA is still a rather good solvent but appears to be poorer than MCDEA, which is reflected on the whole DDS-composition range by the T_g's being closer to those of neat matrices.

Morphology and phase separation

TEM micrographs of single-amine blends are shown in Fig. 6. As already mentioned, MCDEA do not induce any visible separated phase (Fig.6a) while DDS induces separated nodules in the micrometer range, as displayed in Fig. 6b. The average diameter is $\bar{d} = 2\mu m$ and the surface percentage of separated phase is equal to the initial PVME concentration.

The question is now to know whether a further decrease in the mean size of TP domains is possible in such tunable systems.

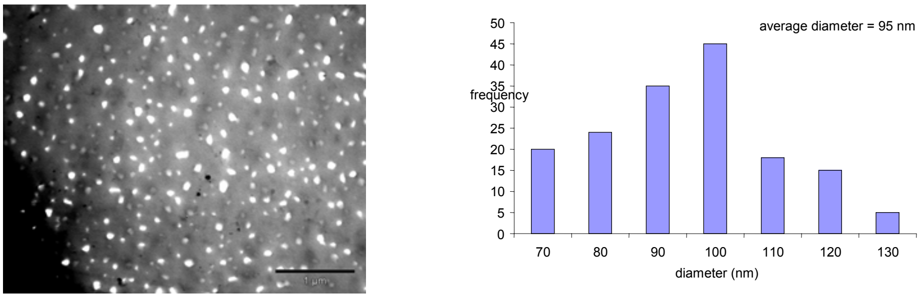
In spite of DDS content, a parameter likely to decrease the domain size is the cure temperature. In our case the observed dependence is classical [5], i.e. an increase in the mean diameter upon increase in cure temperature. As an example, Fig. 7 shows the 70% MDEA-30% DDS/DGEBA 10%wt PVME blends cured at 135 or 160 or 175°C.



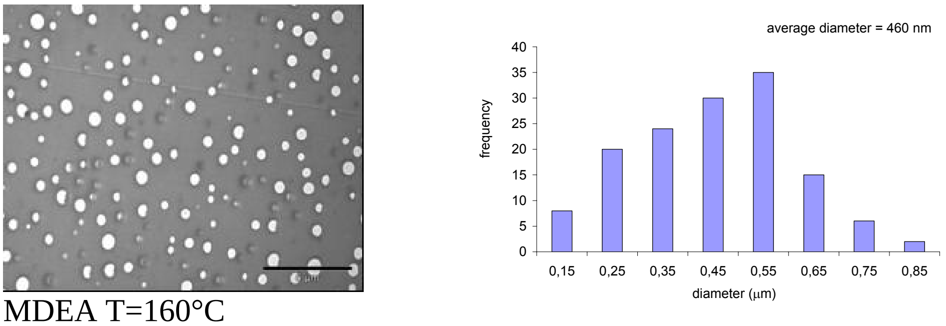
100% MCDEA

100% DDS

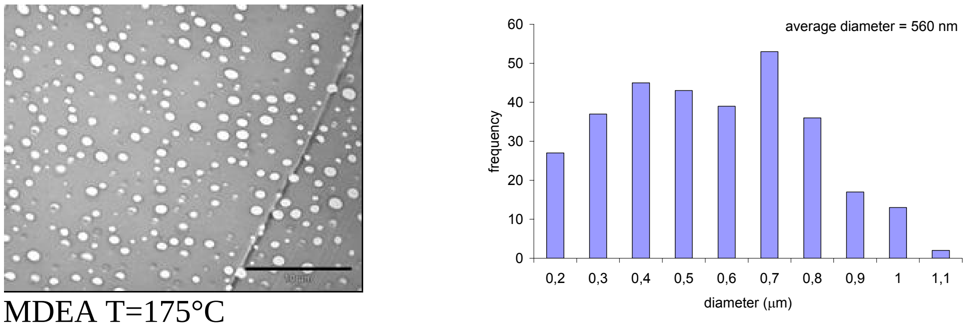
Fig. 6. Morphologies (TEM) of 10% PVME blends (reaction at 135°C) from (a) 100% MCDEA or (b) 100% DDS matrices.



70% MDEA T=135°C



70% MDEA T=160°C



70% MDEA T=175°C

Fig. 7. Influence of the first cure temperature on the morphology : TEM micrographs of a 70%MDEA-30%DDS / DGEBA-10% PVME blend cured at 135 or 160 or 175 °C.

Secondly, one should check how the location of the cloud point (x_{CP}) modifies the average nodule diameter. The proximity of cloud and gel points may be expected to freeze nascent morphologies. The cloud point conversions of the two sets of blends are compared in Table 1. It appears that, whatever the DDS content or the cure temperature, x_{CP} of any MDEA-based blend is observed at a nearly constant value, x_{CP}~0.55; whereas x_{CP} of MCDEA-based blends are also located around an almost invariable value of x_{CP}~0.25. Thus, the ratio of DDS is not a straight forward means to allow a variation of the location of x_{CP}.

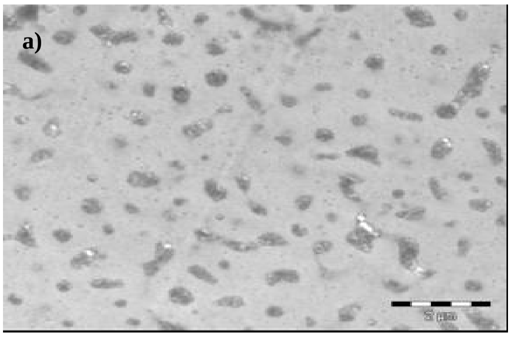
Furthermore, when x_{CP} is located very close to the gel point conversion (this is the case of MDEA-based blends where x_{gel}=0.57, x_{CP}~0.55), the final domain size is not effectively reduced compared to the systems where x_{CP} is located far from gel conversion (MCDEA-based blends). It seems that the position of the cloud point compared to the gel point, x_{gel} - x_{CP}, has very little influence on final morphologies.

Tab. 1. Phase separation behaviour and nodules size of 10wt% PVME blends

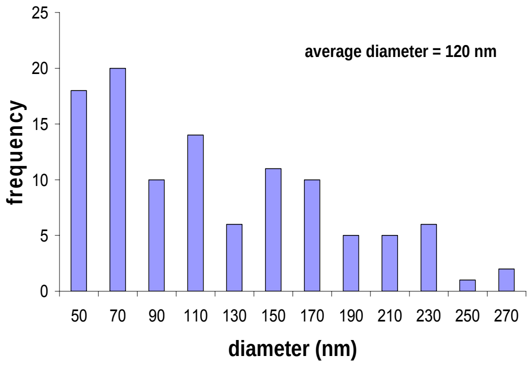
Formulations		MCDEA				MDEA			
		T=135°C		T=160°C		T=135°C		T=160°C	
		x_{cp}	**D (nm)**	x_{cp}	**D (nm)**	x_{cp}	**D (nm)**	x_{cp}	**D (nm)**
Single-amine matrix	100% DDS	*0.04*	**3200**	*0.05*	**3200**	*0.04*	**3200**	*0.05*	**3200**
	100% (A_2 or A'_2)	No CP transparent							
Two-amine matrices	50% DDS + (A_2 or A'_2)	*0.15*	**950**	*0.19*	**1400**	*0.52*	/	*0.53*	/
	40% DDS + (A_2 or A'_2)	*0.17*	**690**	*0.22*	**1150**	*0.55*	**400**	*0.54*	/
	35% DDS + A_2	*0.21*	**120**	/	/	/	/	/	/
	30% DDS + (A_2 or A'_2)	No CP transparent		*0.25*	**350**	*0.57*	**100**	*0.56*	**460**
	25% DDS + (A_2 or A'_2)			*0.30*	***75, 150**	No CP transparent		/	/
	20% DDS+ (A_2 or A'_2)			No CP transparent				*0.58*	**160**
	15% DDS+ (A_2 or A'_2)							No CP transparent	
	10% DDS + (A_2 or A'_2)								

x_{cp} : cloud point conversion,
D (nm): PVME-nodule mean diameter,
(/: existence of CP but the value has not been determined; * : bimodal population)

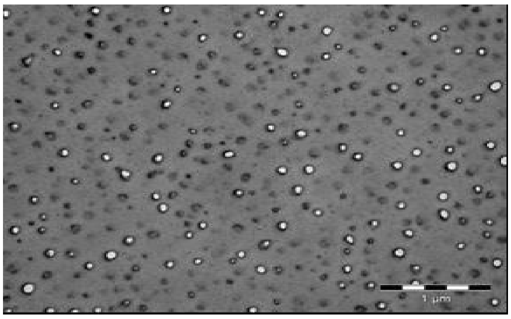
Figure 8 presents examples of TEM and SEM micrographs showing the effect of the amine type and amine concentration on morphologies. They prove that nodule diametres down to 50-65 nm are accessible by a reaction induced phase separation processs. The mean size of all blends is reported in Table 1.



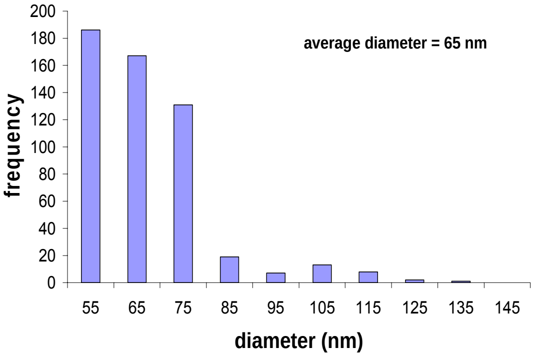
50% MCDEA / 50 % DDS : T_{cure}=100°C
——— Scale bar = 2 µm



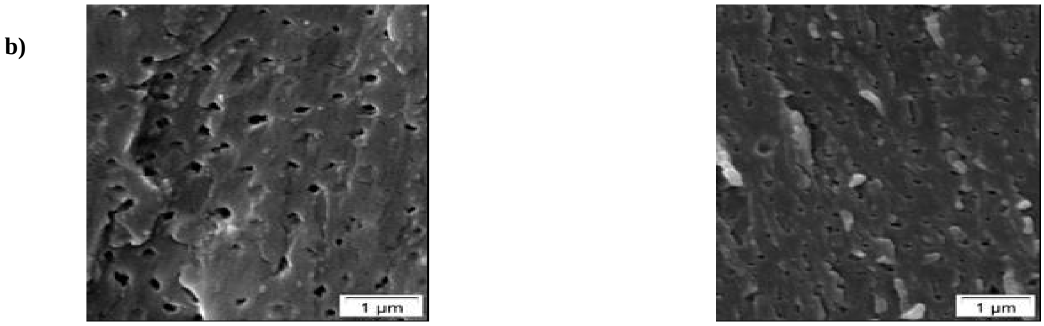
Area % of separated PVME (image analysis) = 2.3 %
% separated PVME (DSC) = 4.5 %



50 % MDEA / 50 % DDS : T_{cure} = 100°C
——— Scale bar = 1 µm



Area % of separated PVME (image analysis) = 5.8 %
% separated PVME (DSC) = 6.3 %



65% MCDEA-35% DDS T= 135°C

50% MCDEA-50% DDS T= 100°C

Fig. 8. a- influence of the amine hardener type on the morphology: TEM micrographs of 50%MDEA or 50%MCDEA -50%DDS / DGEBA- 10% PVME blends. b- influence of the % of the “soluble amine” on the morphology: SEM micrographs of 65%MCDEA or 50%MCDEA – (35 or 50%) DDS / DGEBA- 10% PVME blends.

Such morphological evolutions can be linked to the type and composition of the growing species when the network is built. The previous kinetic model [1] is used to calculate the real conversions in amino groups at cloud point $\alpha_{(DDS)CP}$, $\alpha_{(MCDEA)CP}$ and the concentrations in residual diamine molecules $(C_{MCDEA})_{CP}$, $(C_{DDS})_{CP}$ in the different MCDEA/DDS/PVME formulations. This concentration is calculated according to the following equation :

$$C_a / C_{0a} = (1-\alpha_a)^4 \Rightarrow C_a = C_{0a}(1-\alpha_a)^4 \qquad \textbf{(2)}$$

The results are given in Table 2. A first obvious comparison concerns the ratios initially and at CP of amine concentrations : $(C_{DDS})_{CP}$ / $[(C_{MCDEA})_{CP}$ + $(C_{DDS})_{CP}$ $[DDS]_{CP}]$ << $(C_{DDS})_0$ $[DDS]_0$ / $[(C_{MCDEA})_0$ + $(C_{DDS})_0]$; or in other words $(\%DDS)_{CP}$ << $(\%DDS)_0$ which reflects the enrichment of the reacting media in MCDEA.

Secondly, the ratio of amines at CP appears nearly constant with DDS initial content (Table 2). This indicates that, at CP, the unreacted species (i.e. the amines as monomers) have the same solvent capacity whatever the initial DDS ratio. It is consistent with the observed constancy of x_{CP} within a series of blends (as shown in Table 1).

Tab. 2. Calculated conversions at cloud point $\alpha(\mathrm{MCDEA})_{CP}$, $\alpha(\mathrm{DDS})_{CP}$ and concentrations $(C_{MCDEA})_{CP}$, $(C_{DDS})_{CP}$ of amines or initially $(C_{MCDEA})_0$, $(C_{DDS})_0$ (135°C); for short A_1 refers to DDS, A_2 refers to MCDEA.

$(\%DDS)_0$	$\alpha(\mathrm{MCDEA})_{CP}$	$\alpha(\mathrm{DDS})_{CP}$	$(C_{MCDEA})_0$ mol.l^{-1}	$(C_{DDS})_0$ mol.l^{-1}	$(C_{MCDEA})_{cp}$ mol.l^{-1}	$(C_{DDS})_{cp}$ mol.l^{-1}	$\frac{C_{cp}^{A_2}}{C_{cp}^{A_1}+C_{cp}^{A_2}}$	$(\%DDS)_{CP}$
50 %	0.08	0.23	0.5725	0.5725	0.41	0.2012	0.671	33%
40 %	0.09	0.23	0.6765	0.451	0.464	0.163	0.74	36%
35 %	0.20	0.29	0.7265	0.39	0.2976	0.1	0.75	25%

Finally, we calculated the rate of dissappearance of each amine at CP, $(v_{MCDEA})_{CP}$, $(v_{DDS})_{CP}$ by (this equation is similar to Eq. 12 in ref. [1])
:

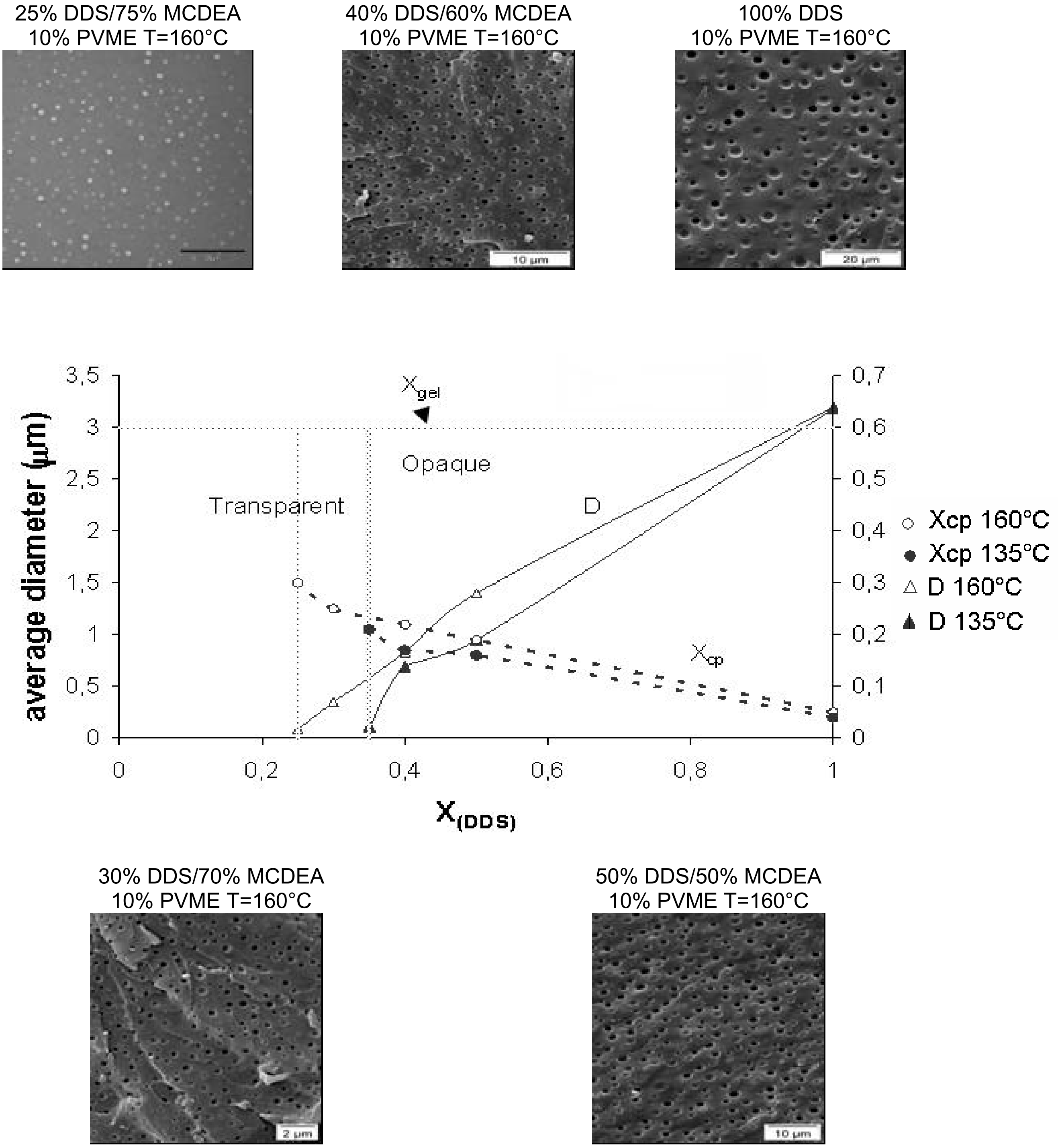
$$v_i(t) = \left(k_1 + k_1^{'}[OH]\right) \times E(t) \times A_i(t) \text{ with } [OH] = x \times E_0 \qquad \textbf{(3)}$$

Tab. 3. Calculated rates of disappearance of amines (135°C), $(v_{MCDEA})_{CP}$, $(v_{DDS})_{CP}$.

Formulation	E_0 (mol.l^{-1})	v_{MCDEA}^{cp} (mol.l^{-1}.s^{-1})	v_{DDS}^{cp} (mol.l^{-1}.s^{-1})	$r_v = \frac{v_{DDS}}{v_{MCDEA}}$
50% DDS	4.58	7.7×10^{-5}	1.5×10^{-4}	1.89
40% DDS	4.51	8.6×10^{-5}	1.1×10^{-4}	1.40
35% DDS	4.47	8.4×10^{-5}	8.3×10^{-5}	0.98

The results are given in Table 3. The interesting feature lies in the evolution of this rate with DDS content; for high DDS-concentration blends (X_{DDS}>50%), the DDS amine incorporates in the TS matrix at least twice as fast as the MCDEA amine.

But in low DDS-concentration blends (X_{DDS}<30%), MCDEA incorporates at the same rate or even faster. Therefore the high reaction rate constant (k_i) of DDS is counter balanced by dilution of the DDS amine functions; thus inducing an equal incorporation of DDS and MCDEA and preventing phase separation. It is therefore understood why low DDS contents cannot provide phase separated blends at a nanometric scale (typically less than 50 nm) as it was first expected.



25% DDS/75% MCDEA
10% PVME T=160°C

40% DDS/60% MCDEA
10% PVME T=160°C

100% DDS
10% PVME T=160°C

30% DDS/70% MCDEA
10% PVME T=160°C

50% DDS/50% MCDEA
10% PVME T=160°C

Fig. 9. General scheme of morpholgy evolution in 10wt% PVME blends made from a mixed thermoset matrices.

As a result, upon DDS decrease, the materials show an abrupt change from opaque to transparent (Fig. 9). In the transparent region as previously mentioned, no morphology has yet been observed (TEM observations). Neverthless the introduction of two amines can decrease the size of the separated domains to quite an extent (sub micron sizes).

Conclusions

Thermoplastic (PVME, 10wt%) / thermoset blends, in which matrices are composed of a DGEBA epoxy resin crosslinked with a hardener formulation (two aromatic diamines in varying proportions), have been prepared in order to test the possibility of decreasing the size of the thermoplastic domains down to meso or nano scales. The choice of amines was such that one amine is thermoplastic-miscible while the other one is highly thermoplastic-immiscible; besides the amines were selected to have very different reaction rate constants with the aim to incorporate them selectively into the growing thermosetting network. The main parameter which allowed tuning of morphologies is indeed the miscible-amine concentration of the hardener formulation. Sub micron morphologies were thus obtained by adjusting the hardener formulation; nodules with mean diameters of about 50-70 nm (cure at 100 °C) to 150nm (cure at 160°C) were characterized. However separated domains at a lower scale were not revealed. The rate of incorporation of the two amines in the thermosetting network is a limitation to the use of amines formulations to control morphologies of TP/TS blends. TP/TS blends of nanometric size are not accessible via a reaction induced phase separation process. In spite of different reaction rate constants, the real rate of dissappearance at cloud point of each amine also depends on dilution of amine functions so that the role of reactivity can be dubbed non efficient. One prospective for these materials is the preparation of mesoporous thermosets after removal of the thermoplastic phase.

Experimental

Materials and sample preparation

The chemical structures and characteristics of compounds used are given in Table 1 of Part 1 of the work [1]. The epoxy oligomer is crosslinked with the following diamines: A_1=DDS (4,4'-diaminodiphenylsulfone, Aldrich), A_2=MCDEA (4,4'-methylenebis-[3-chloro 2,6-diethylaniline], Lonza, Switzerland) or A'_2=MDEA (4,4'-methylenebis-[2,6-diethylaniline], Lonza, Switzerland). The ratio of total amino hydrogens (NH) to epoxy functions is always kept equal to one but the ratio of A_1 to A_2 or A_1 to A'_2 varies from 0 to 100% expressed as mole % of amino groups from DDS. The molar fraction of A_1 is then defined by $X_{A1}= X_{DDS}=n_{A1}/ (n_{A1}+n_{A2 \text{ or } A'2})$, where n_{Ai} is the number of mole of the amine A_i.

The additive is poly(vinyl methyl ether), PVME, with a number average molar mass M_n= 32 000 g.mol^{-1}. PVME was received as a water solution, from Aldrich, and was carefully dried before use at 100°C under vacuum for 24h. Homogeneous solutions of epoxy, amine and 10wt% PVME were prepared by mechanical stirring at 80°C for 15 to 20 min. Four different cure cycles were applied to the blends: first isothermal cure step at either 100 °C, 135 °C, 160 °C or 175 °C for 24, 12, 6 or 6 hours respectively followed by a post cure at 200 °C for 2 hours for all blends.

Cloud points (CP)

Cloud point times were measured, during isothermal cures, by visible light scattering through a test tube in which polymerization takes place [6]. This technique begins to detect particles when average diameters are in the order of 0.1 μm. The cloud point times, t_{CP} were converted into cloud point conversions (x_{CP}) thanks to the kinetic model used in Part 1 of this paper [1].

Morphology analysis

-SEM

Scanning Electron Microscopy (SEM, Philips XL 20) was used to observe the cryofractured surface of samples. Observations were observed under an accelerating voltage of 5 to 25 kV. All samples were coated with gold.

-TEM

Samples were microtomed at room temperature with a Leica EMFCS instrument equipped with a diamond knife. The resulting thin sections of 80 nm thickness were picked up on copper grids and stained in the vapour of an aqueous solution of RuO_4. Stained samples were imaged in a Philips CM 120 transmission electron microscope (TEM) with an accelerating voltage of 120 kV.

Image Analysis

TEM micrographs with ImageJ (image analysis software) [7]. First, pictures are converted into a grey level image. The picture is then converted into a binary image. The software gives us automatically the area fraction corresponding to the separated phase, and the surface of each nodule. Thus, a mean diameter is calculated. The mean size is chosen where it is less threshold-dependent.

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