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Reaction and Morphology Development Influenced by Diffusion in a Thermoplastic/Thermoset Blend

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Summary: Diglycidyl ether of bisphenol A (DGEBA) and 4,4′-methylenebis [2,6-diethylaniline] (MDEA) are miscible in polystyrene at 177 °C. We have studied how their diffusion rate in a molten polystyrene matrix influences their polymerization rate and the morphology of the thermoset particles formed at the end of the reaction. The global composition of the blend was 60 wt% of PS and 40 wt% of epoxy-amine. The diffusional control of the reaction was evidenced by comparing the time of reaction of an initially homogeneous mixture with that of different bi-layer samples. The reaction was controled by the diffusion for relatively thick layers ($>$0.3. mm). A gradient of morphology was obtained due to the diffusionnal control of the reaction. The asymetricity of this gradient may be explained by three factors: differences in diffusion coefficients, in thermodynamic interactions and in viscosity.

Keywords: blend; diffusion; reaction; thermosets

Introduction

Chemical reactions in molten polymers and blends many often involve the introduction of low molar mass organic molecules. The examples are numerous: the chain extension of polycondenstates as polyamide and polyester, the grafting reactions on polyolefines, the polymerization of monomers and copolymers in the molten state, the crosslinking of thermoplastic vulcanizates. Depending on the application, the low molar mass organic molecules may be a chain extender, monomers, an initiator, a catalyst.

The keywords that describe reactive mixing process involving small molecules are: miscibility, mixing, diffusion, reaction. Most often, the miscibility of the components of the reactive system is not characterized in detail since it is not an easy task at high temperature, it is sometimes approached by comparing the solubility parameters of the components. The molecular diffusion is more studied and numerous authors aim to calculate the coefficient of diffusion with the help of diffusion theories such as the free-volume theory.[1] On the other hand, the diffusion of low molar mass molecules in molten polymers is studied experimentally in the scope of the diffusion of solvent and the plastification of rubbers, but more rarely for the purpose of achieving a chemical reaction.[2–5] The mechanisms of mixing in molten polymers have focused the attention of the researchers for a long time, in both experimental and theoretical aspects but it is still difficult to predict the evolution of the heterogeneity of a molten mixture.[6–10]

The justification of such studies is that when a low molar mass molecule is involved in a reactive process with molten polymers, the miscibility of the low viscosity reactant, its rate of mixing, diffusion and reaction can play a determinant role for the production of the desired macromolecular structure, especially when the chemical reaction

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involved is sensitive to the stoichiometry or to heterogeneities of concentration. [11]

The context of the present work is what is generally called reactive processing. The objective is to investigate the complex relations between diffusion and reaction in experimental conditions where no mechanical mixing is imposed. We examine the effect of diffusion on the reaction of small organic molecules miscible in a molten polymer matrix. The polymer is a polystyrene, the reactants are a diepoxy and a diamine. It is a system that we have studied in detail previously in the context of the elaboration of thermoplastic/thermoset blends and that is used here for a different objective. [12,13]

Experimental Section

Materials and Blends

A polystyrene (PS) Lacqrene 1450 N was supplied by Atofina. The epoxy was a diglycidyl ether of bisphenol A (DGEBA) with a degree of polyaddition of $n = 0.15$, supplied by Bakelite. The diamine was 4,4′-methylenebis [2,6-diethylaniline] (MDEA) supplied by Lonza. The global composition of the blend studied was 60 wt % of PS and 40 wt % of epoxy/amine thermoset precursors. Two non reactive mixtures were prepared by extrusion, PS/DGEBA 50/50 wt% and PS/MDEA 73/27 wt%. A PS/DGEBA-MDEA 60/40 blend was also prepared in a batch mixer at low temperature ($T = 80\,°C$) in order to limit the reaction.

Determination of the Epoxy Conversion

The conversion of the epoxy groups of the DGEBA-MDEA mixture, x_e, was measured in-situ in the near infra-red spectrometer (equinox 55 from Brucker) thermoregulated cell. The area of the absoption bands at 4530 cm^{-1} (epoxy) and 4623 cm^{-1} (phenyl) were used to calculate the conversion with the following relation:

$$x_e = 1 - (A_{4530}/A_{4623})_t/(A_{4530}/A_{4623})_{t=0} \quad (1)$$

Observation of the Morphology

Scanning electron microscopy (SEM) was performed with a Philips XL 20 microscope in order to visualize the morphology. The samples were prepared by cryogenic fracture and gold plated.

Diffusion/Reaction Experiments

In order to study the influence of the diffusion of epoxy and amine monomers on the morphology development and rheological behavior of the reactive blend with PS, two different preparations of the sample test were experienced. The principle of these experiments is shown in Figure 1.

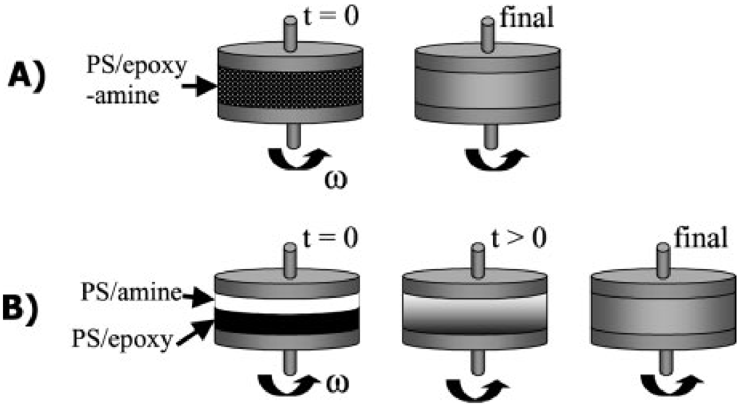

Figure 1.
Scheme of the experimental set up. A) Homogeneous reactive medium B) Non homogeneous reactive medium.

A) The first one is a unique layer of homogeneous PS/DGEBA-MDEA blend. In the present case we assume a homogeneous initial blend of epoxy and amine monomers in PS, at least we suppose that the concentration in reactants at a micro-scale is at the stoichiometry. The case A is actually the reference corresponding to an homogenous concentration of reactants in molten PS matrix.
B) The second one is a two layers sample constituted of PS/DGEBA layer and PS/MDEA. Each layer is not reactive unless it is mixed or put in contact with the other one. The thickness of the polymer discs were adjusted in order to respect the epoxy-amine stoichiometry and the global composition of the blend. Only the total thickness varied in order to emphasize the diffusion control of the reaction.

From an experimental point of view, the measurements were performed on a Rheometrics Mechanical Spectrometer (RMS 800) at a constant temperature of 177 °C and a constant frequency of 1 rad s^{-1}. The geometry used was parallel plates with a diameter of 25 mm. The strain was adjusted all along the experiment from 400% at the beginning of the experiment to 1% at the end in order to remain in the linear domain of the viscoelasticity while having a good sensitivity of the torque.

Ressults and Discussion

Rheological Behavior

Initially, before the reaction of the epoxy groups with amino groups, the phase diagram of PS with the monomers is Upper Critical Solution Temperature (UCST). The reactants are soluble in the PS at the experimental temperature of 177 °C. However, the polymerization induces a phase separation of the epoxy amine oligomers. At the end of the reaction the blend is composed of a pure PS matrix containing crosslinked epoxy-amine particles.

Considering now the viscosity of the system, the miscibility of the two low molar mass molecules with PS leads to a low viscosity, low glass transition temperature blend before the polymerization ($T_g = -20\,°C$). Upon their reaction, the monomers phase separate, diffuse out of the PS-rich matrix and form gelled particles so that the progress of the reaction is accompanied by an increase of the glass transition temperature of the individual phases, and thus an important increase of the viscosity.[12,13] Therefore, the evolution of the viscosity permits to follow the global epoxy conversion rate. On other hand, the biphasic structure formed may bring us information about the progress of the reaction at a local scale.

Figure 2 represents the increase of viscosity measured for a homogeneous sample (situation A in Figure 1), and bilayer samples with different thicknesses (situation B in Figure 1). For the initially homogeneous blend, the polymerization is finished after about 80 minutes as can be deduced from the stabilization of the viscosity. The corresponding average conversion of the epoxy groups was determined in a previous work and found equal to 95%. [12]

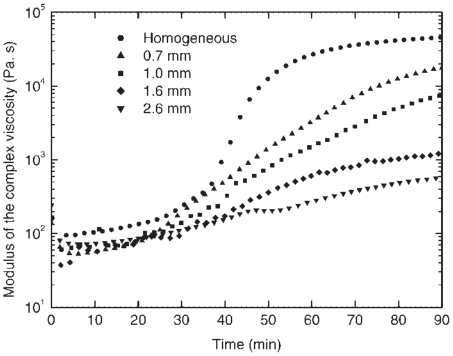

Figure 2.
Evolution of the viscosity with time of a PS/DGEBA-MDEA 60/40 system polymerized at 177 °C. Homogeneous sample (●), two non reactive layers of PS/DGEBA and PS/MDEA with a total thickness of 0.7 mm (▲), 1.0 mm (■), 1.6 mm (◆) and 2.6 mm (▼).

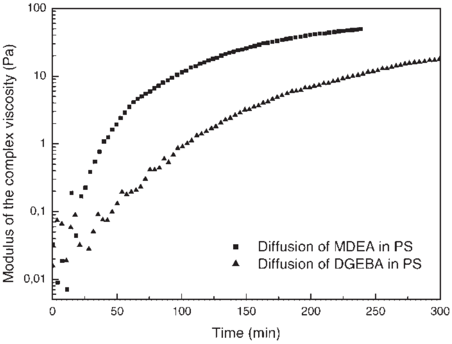

Figure 3.
Evolution of the viscosity with time of a samples constituted of a lower layer of PS and a upper layer of monomer (▲: DGEBA, ■: MDEA). The thickness of each layer is 0.8 mm. Temperature = 177 °C. Frequency = 10 rad s^{-1}.

The reaction is slower for the bi-layer system as one can observe from the slower rise of the viscosity with time. Moreover, the reaction appears to slow down with time. At the beginning, the evolution of the viscosity in both cases is identical but the reaction in the bi-layer situation is slower and slower. This indicates that the diffusion of the monomers and oligomers is limiting the progress of the polymerization and that diffusion is controlling the reaction. As expected in case of a diffusional limitation, the effect is even more marked when the global thickness of the sample increases.

To verify that, we compare the characteristic times of diffusion of the monomers with the characteristic time of reaction of the DGEBA with MDEA at 177°C. The ideal experiment would have been to measure the rate of diffusion of each monomer in a mixture of PS with the other monomer. For instance measure the diffusion of MDEA in a layer of PS/DGEBA seeing that it is more representative of the actual situation. This is obviously not a realistic experiment since DGEBA and MDEA are reactive and the diffusion process will be perturbed by the reaction. This is the reason why we have simply characterized the diffusion of the DGEBA and of MDEA at 177 °C in neat PS. We have measured the changes in viscosity of a sample constituted of a layer of PS and a layer of monomer. The initial viscosity measured before the diffusion starts reflects the properties of the less viscous layer: the liquid monomer. During the diffusion process, the concentration of small molecule into the polymer increases and a concentration gradient establishes which induces an increase of viscosity until the concentration is constant across the sample and the viscosity stabilizes. The technique is described in the paper of Joubert et al.[5] The thickness of the polymer layer was chosen in the same order of magnitude than the one used for the reactive experiments presented in Figure 2 since the distance of diffusion determines the time of diffusion.

Actually, we are aware that the rate of diffusion of the monomers is overestimated since the PS is pure, nevertheless it gives orders of magnitude and it allows to compare the behavior of the two monomers. Also, one important feature is that during the reactive diffusion experiment the monomer are not only diffusing, they are also reacting and their molar mass is increasing. Actually, if we want to account for the overall transport processes, we should consider the diffusion of all the chemical species, monomers and oligomers. We can imagine that a monomer molecule that is diffusing in the reactive medium is progressively slown down when its molar mass rise at each reaction step of its epoxy and/or amino groups so that the diffusion rate of all the reactive species is much lower than that of the unreacted monomer.

The characteristic time of reaction is determined more easily than the diffusion time, by following the disapearance of the epoxy groups of a mixture of DGEBA with MDEA where the stoichiometry in epoxy and amino groups is respected (Figure 4). The polymerization is complete after about 50 minutes.

The conclusion is that for our blend and for the dimensions of our reactive samples the reaction process is faster than the diffusion process and then is controlled by the diffusion.

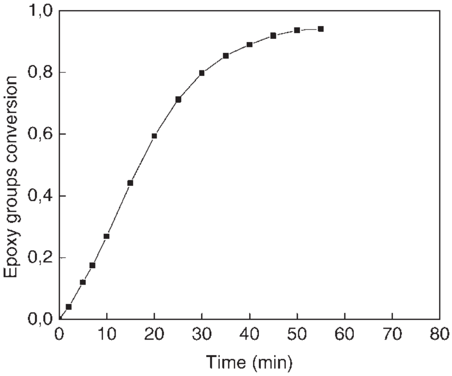

Figure 4.
Evolution of the conversion of the epoxy groups of a stoichiometric mixture of DGEBA with MDEA polymerized at 177 °C.

Morphology Development

A picture of the morphology formed after the polymerization of the epoxy in sample A (homogeneous) is shown in Figure 5. The final structure is a dispersion of spherical crosslinked epoxy particles with an average diameter around 3 μm.

Before analyzing the morphology more in details, we have checked that the measurement in oscillatory mode was not influencing the structure of the blend. In other words, the dynamic deformation should not perturb the mechanisms of relaxation. We have compared the morphology obtained after the rheological experiment to that obtained in a oven in the absence of any shear and they were identical, with epoxy-amine particles of 3 microns average diameter (compare picture a and b in Figure 5). Therefore, no break up or coalescence was produced under linear deformation in dynamic shear test. Actually, this result was expected in the domain of linear viscoelasticity.

The pictures taken across the sample of 1.6 mm thickness are grouped in Figure 6. We observe a gradient of morphology across the sample. The larger diameter particles are present in the middle of the PS/DGEBA layer (picture d). At the interface between the two layers (picture c), where the concentration of monomers is rapidly established, it is not surprising that the morphology is similar to that obtained for the homogeneous sample. Besides, on the amine-rich side, near the rheometer upper plate, a low amount of very small particles is formed (picture a). On the epoxy-rich side, near the rheometer lower plate, the particles are bigger (2 to 5 μm) with a stronger interface, the particles were not pulled out the PS matrix (picture e). This was observed previously and is representative of a sample with an intermediate epoxy conversion around 50–60%. [12]

The morphology observed near the plates (Figure 6a and e) is typical of a regions where the conversion in monomer is low. These two regions are far from the interface and the monomers and oligomers did not have sufficient time to diffuse. Thus,

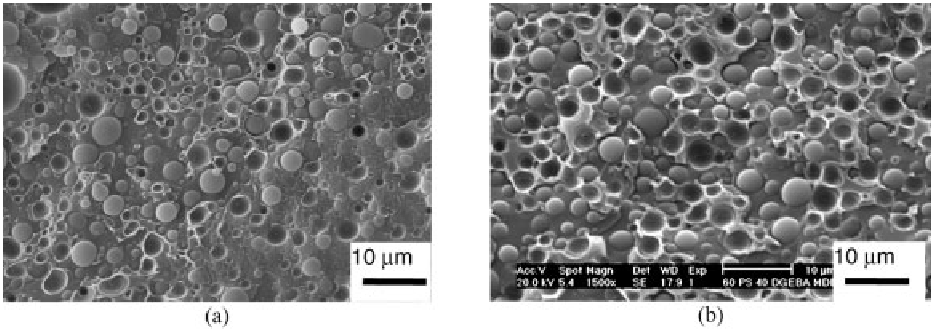

Figure 5.
Morphology obtained after the polymerization of the epoxy in the PS/DGEBA-MDEA 60/40 blend at 177 °. a) homogeneous sample polymerized in the rheometer and submitted to oscillatory shear at 1 rad s^{-1} and a deformation ranging from 400 to 1%, b) homogeneous sample polymerized in a oven.

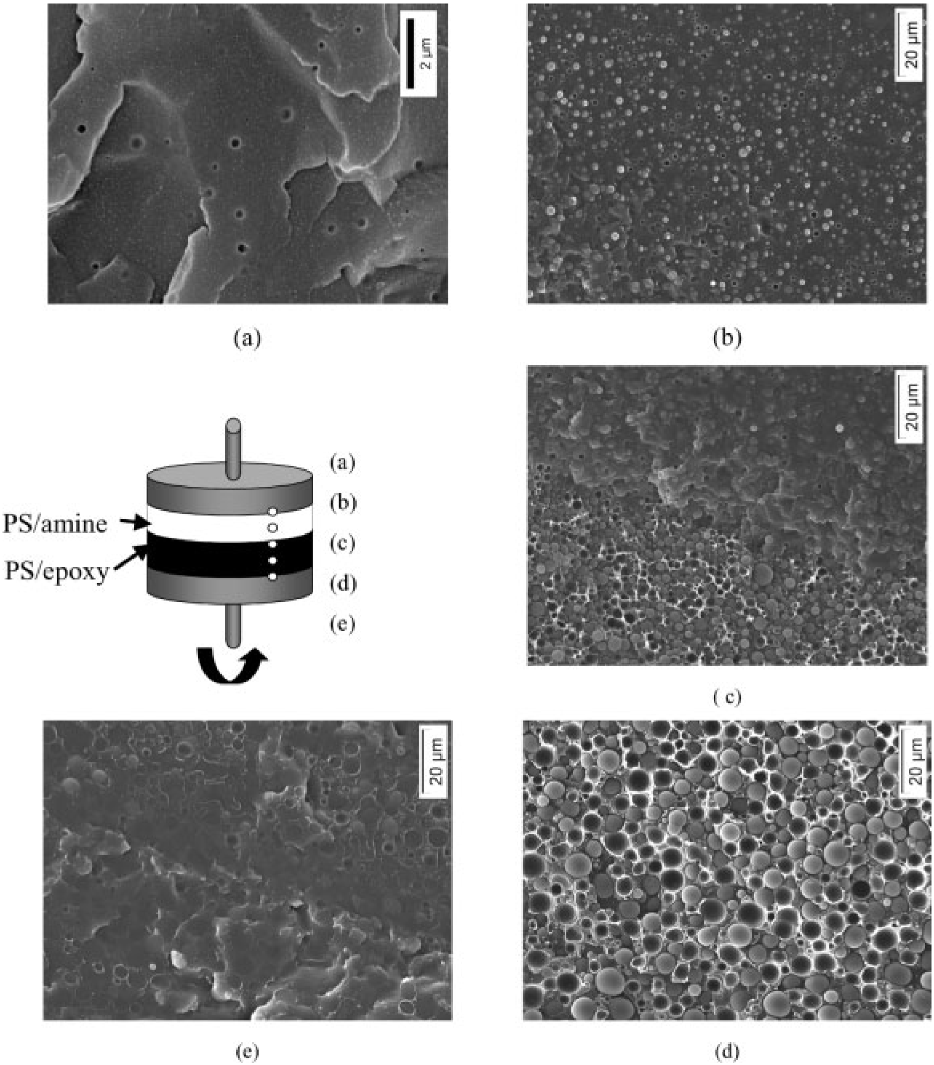

Figure 6.
Morphology of the 1.6 mm bi-layer sample after 90 minutes of polymerization at 177°C. (a) external side of the PS/amine layer, (b) middle of the PS/amine layer, (c) interface between PS/amine and PS/epoxy, (d) middle of the PS/epoxy layer, (e) external side of the PS/epoxy layer.

the existence of a gradient of morphology starting at the interface and going to the external sides of the sample is easily explained by the necessity of the diffusion of the monomers in order to react and consequently phase separate.

A second interesting point is that the micrographs of the middle of the PS/amine and PS/epoxy layers are different from each other: smaller particles (<2 µm) are present in the PS/amine layer, compared to 5–8 µm in the PS/epoxy side (pictures b and d). As a matter of fact, an asymmetric gradient of morphology is observed with larger diameter particles in the PS/epoxy side. The asymmetry of the gradient is not so easily interpreted since several reasons may be proposed to account for this asymmetry. First of all, a faster diffusion of the amine in the PS/epoxy than the diffusion of the epoxy in the PS/amine side would lead to such an asymmetry. The data presented previously in Figure 3 demonstrate that DGEBA is diffusing slower than MDEA in pure PS. However, it is important to remind that in the conditions of diffusion described in Figure 1, the DGEBA is not diffusing in pure PS but in a mixture of PS/MDEA 73/27, and MDEA is diffusing in a mixture of PS/DGEBA 50/50. Thus the MDEA, actually diffuses in a more ''diluted'' mixture than the DGEBA and we may hypothesize that the differences in diffusion rate between DGEBA and MDEA will be even greater for the actual experimental conditions, the epoxy diffusing much slower.

A second explanation for the asymmetric gradient is linked to the miscibility of the monomers. The MDEA is miscible with PS at 177 °C and also at room temperature while DGEBA is only miscible above 120 °C.[13] The more favorable thermodynamic interaction in the amine side may lead to a phase separation at a higher monomer conversion and thus smaller particle.

The third explanation may be the lower viscosity of the PS/DGEBA mixture compared to the PS/MDEA. The modulus of the complex viscosity at 177 °C has been measured. At 1 rad. s^{-1}, it is equal to 30 Pa.s for the PS/DGEBA mixture and 200 Pa.s for the PS/MDEA mixture. The viscosity of the medium where a phase separation develops has a great influence on the size of the particles formed. The lower the viscosity is, the bigger the separated domains are.

It is tricky to establish what factor is responsible for the asymmetric gradient of particle size since the effect of the three reasons presented above would produce the same qualitative effect that is bigger epoxy particles in the epoxy side of the sample.

Conclusion

We have examined how the diffusion process of miscible thermoset precursors in a thermoplastic polymer may influence their apparent polymerization rate and the development of the morphology of the resulting thermoplastic/thermoset blend. The relations between the reaction rate and the diffusion rate of two monomers in polystyrene matrix was emphasized by comparing their characteristic times of reaction and diffusion. Actually, depending on the dimension of the sample studied, the reaction rate may be limited by the diffusion process of the monomers and oligomers. As a consequence of the diffusional limitation, a gradient of morphology is obtained across the by-layer samples. However the asymmetricity of the gradient is difficult to attribute with certainty to one of the three determinant parameters that we have identified: a higher rate of diffusion of the MDEA in the PS/DGEBA side compared to the diffusion of the DGEBA in the PS/MDEA side, a phase separation occuring at lower conversion in the PS/DGEBA due to the less favorable interactions between PS and DGEBA and a lower viscosity of the PS/DGEBA side.

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