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Fractal characterization of the fissures occuring during polymerization of low-profile unsaturated polyester resins

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ABSTRACT
Blends of unsaturated polyester resin and polyvinylacetate (PVAc) were cured between two glass slides. In this case, the low-profile effect arises by fissuring with a fractal geometry. This paper shows how the fractal dimension of the fissures depends on the PVAc amount and on the cure temperature. These results are discussed with the present knowledge about the polyester network morphology in two phases more or less co-continuous.

INTRODUCTION

Unsaturated polyester (UP) resin is still the most important resin for SMC (Sheet Molding Compound) and BMC (Bulk Molding Compound) applications. It has been known for twenty years that the addition of a thermoplastic in polyester based systems suppresses most of the molding problems such as poor surface appearance, inability to mold close tolerances and warpage of molded parts. The cause of these problems has been partially attributed to the high polymerization shrinkage during cure [1]. But the mechanisms by which the thermoplastic (PVAc, PMMA, PS,...) compensates for the shrinkage are not well understood. Since 1975, many researchers have tried to complete the Pattison's explanation [2-8] and the knowledge of the polyester network morphology has greatly increased for a few years [9-16]. When PVAc is used as low-profile additive with a correct content, the mixture is initially miscible and the morphology of the cured system is a two-phase structure more or less co-continuous : a particulate type polyester network and the PVAc phase. It is now believed that the shrinkage compensation occurs by formation of microvoids within the thermoplastic phase, the role of PVAc being to subdivide the macrocracks into microvoids. In a previous paper, we have already reported how the molding conditions (temperature and pressure) and the PVAc content influence the shrinkage behavior of a low profile unsaturated polyester system [17]. It was shown that the polymerization shrinkage and thus the morphology of the final product are greatly affected by temperature and pressure.
In order to understand better the low profile mechanism it is interesting to study the microvoids morphology and furthermore to quantify the divided nature of the microvoids. There are two possible approaches to answer the problem : the in-situ study between two slides of an optical microscope and the SEM (Scanning Electron Microscopy) observation of the fracture surface of an actual sample. Several researchers have demonstrated the applicability of the hot stage microscopy in observing the morphology of a low profile resin during cure [2,4,5,6]. They all observed three clearly defined stages on the curing sequence of a single phase low profile resin :
1) The liquid resin is initially homogeneous and transparent.
2) After an induction time a phase separation takes place and a structure of beads on the order of a micron appears. The formation of the first polyester particles is associated to the gelation.
3) After an other induction time, a rapid dendritic growth of fissures is observed throughout the entire sample. This phenomenon occurs suddenly and it is assumed to be linked to the

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macrogelation and to the glass transition temperature of the network with regard to the reaction temperature.
This type of fissures is the manifestation of the low profile effect for a cure made in such a condition of sample thickness. Ross observed some differences in the fissure appearance as a function of the cure temperature [5]. At high temperatures (150°C), the fissures seem to be evenly distributed with extensive branching. At low temperatures (120°C), the fissures appear to have much less branching with larger fissure track.
The fractal theory is believed to allow a qualification of this type of morphology and it is the aim of our work to investigate how the fractal dimension of the fissures is related to the low profile behavior described elsewhere.

FRACTALS DESCRIBING SHAPE

The application of fractals as a mathematical tool for the analysis of rough surfaces or curves has received increasing interest in the recent years [18]. In the strict sense, a fractal is an object that display self-similarity over a wide range of scales and the dimension of which is not necessarily an integer. The analysis of the literature shows that many natural phenomena can be described using the fractal theory. An interesting survey discusses the major applications and methods [19] : fractured surfaces [20], particle characterization [21-25] and irregular crystal growth [26] have been demonstrated as relevant to fractal.
The fractal dimension D is usually determined using image analysis techniques. The basic assumption for the image analysis is that the image of a fractal is fractal itself. Several methods have been summed up in the book of J.L.Chermant and M.Coster [27]. In this work, the image is considered as a subset of the plan. If the subset is covered with X_d, a minimum covering by balls of diameter d, the Minkowski dimension can be computed as :

$$\lim_{d \to 0}\left[2 - \frac{\log[\mathrm{area}(X_d)]}{\log d}\right]$$

EXPERIMENTAL

Materials

The polyester resin used in this study is a 1:1 copolymer of maleic anhydride and propylene glycol containing 35 wt.% styrene (S), MOO4 from Cray Valley (TOTAL). The number average molecular weight of the unsaturated polyester (UP) is 1500 g/mol and the equivalent molecular weight per mol of double bonds C=C is 156 g/mol with an average of about 10 vinylene groups per molecule. This UP prepolymer is of a typical SMC grade. The investigated low profile additive is LP40A from Union Carbide which is a 40 wt.% styrene solution of PVAc.
All the compositions studied have a styrene molar ratio of 2 with respect to the polyester double bonds (MR), thus the total number of reactive double bonds (N) decreases linearly with the PVAc weight fraction.
The unsaturated polyester resin, styrene and low profile additive were used as received without removal of the inhibitor.
t-butyl perbenzoate (TBPB) is used as a radical initiator for high temperature reactions using a constant ratio of weight versus the total number of double bonds (N), equal to 0.6 g/mol C=C.
Adding hydroquinone (HQ) at a concentration of 0.17 g/mol C=C was necessary to delay the reaction. The compositions studied are listed in Table 1. All the initial mixtures are miscible at 29°C and higher temperatures.

Table 1 : Studied compositions

wt. % PVA	0	3.2	5	7	10	15
wt. % UP	42.4	41.4	40.7	39.9	38.6	36.4
wt. % S	57.6	55.4	54.3	53.1	51.4	48.6
N (10^{-3} mol/g)	8.27	8.14	7.83	7.68	7.42	7.00

Optical microscopy and image analysis

The morphology of the mixture during cure was observed by means of an optical microscope (Zeiss Axioplan) using transmitted light (12V, 100W, halogen filament lamp).

A drop of sample mixture was placed on a microscope slide having carbon fibers as spacer.

The cover slip was pressed slightly to spread the resin out into a uniform film with typical thickness in the range of 10 microns. The sample was then inserted into the microscope hot stage (Mettler FP82) which had been brought up to the temperature at which the experiment has to be run. Photomicrographs and image acquisitions were then taken at appropriate times.

A micrograph can be considered as a continuous distribution of gray levels. The transfer of this image information to the computer supposes that it has been digitized : the image is divided into 512*512 pixels with an associated gray level between 0 and 255. Filtering is used in order to eliminate noise. The same ideal low-pass filter is applied to the Fourier Transforms of all the images (218*201). The filtered image is then reconstructed by an inverse Fourier transform. The intensity histogram of the filtered image shows a bimodal distribution. A binary image is then created using a thresholding technique. The threshold level is chosen at the minimum of the bimodal intensity distribution. The threshold level chosen is found to have negligible influence on the fractal analysis. An example of thresholded image is shown in Figure 1.

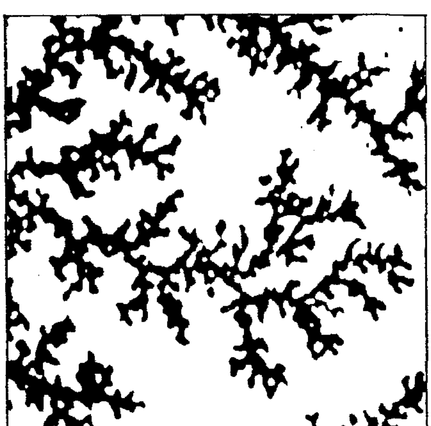

Figure 1 : Binary image of fissures obtained with a 15 wt.-% PVAc composition cured at 130°C.

Some techniques of mathematical morphology are then used to obtain the contour. The thresholded image is eroded with a structuring element C8 $\left(\begin{smallmatrix}***\\***\\***\end{smallmatrix}\right)$. The contour is the result of the subtraction of these two images. The fractal dimension is then determined by means of a program developed especially for this application.

The set X being the contour, the pixel number of the initial contour is called N_i. X_d is computed by means of the dilation of the set X and the area of X_d is the pixel number. The contour is thus thickened λ times with the same increment and the pixel number N_λ is computed for each increment λ. The experimental plots of $\log(\frac{N\lambda}{N_i*\lambda})$ as a function of $\log \lambda$ are actually linear and the slopes are calculated using a least-squares fit. The negative slope can be interpreted as the quantity (1-D). The linearity of the relation between $\log\lambda$ and $\log N_\lambda$ allows to compute a value that represents actually the Minkowski dimension.

Converting a real image in a discrete space (digitization) biases the results and an angle correction must be applied . The correction C_λ is calculated as the average of the deviation introduced by a line having a various angle to the horizontal line (step of 5°). Another aliasing effect exists at high resolutions, for the first points of the curve because of the low-pass filtering.

The validity of our method is checked in different cases. Figure 2 shows the plots for a constructed polygon, a constructed fractal, the image of an actual circle and an experimental contour. The constructed fractal is a Von Koch curve with a theoretical dimension of 1.5. The experimental value calculated from the slope is (1.49 ± 0.01). The polygon and the circle, being Euclidean curves, will have a fractal dimension equal to its topological dimension, i.e. unity. The experimental value for the polygon is actually found to be 1 which indicates that the correction works properly. The plot obtained for the circle shows that the first points are not to be taken into account for the drawing of the straight line in the case of an acquired image. The fourth example shows an experimental result for a 10 wt.-% PVAc cured at 150°C. The fractal nature of the fissuring is displayed by the non integer value of the slope.

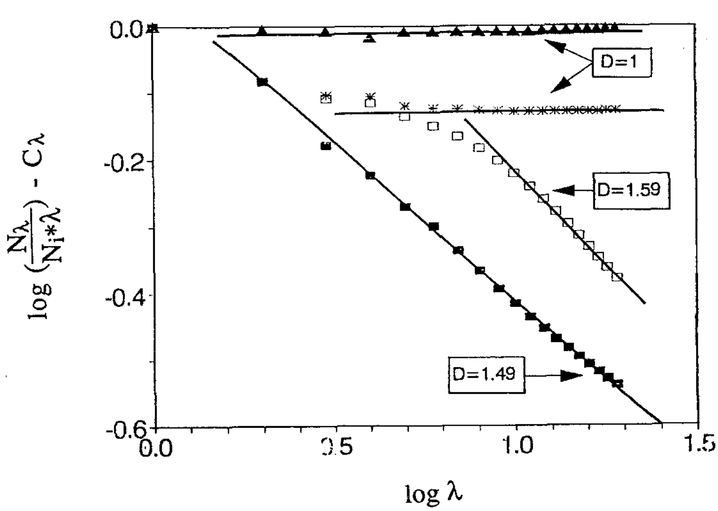

Figure 2 : Fractal plots for (▲) a constructed polygon, (■) a constructed fractal ($D_{theo.}$ = 1.5), (✳) the image of a circle and, (☐) the contour of an experimental image .

KINETICS OF FISSURATION

The fissuring phenomenon has been widely described in the literature [2,4,5]. When the polymerization of a low profile unsaturated polyester resin occurs between two glass slides, a rapid dendritic growth of fissures may be observed progressing across the field of the microscope. The diffraction at the fissure surfaces causes the dark appearance but these same areas appear white when viewed with reflected light. The growth is more or less rapid depending on the mixture composition and on the temperature. The 5 and 7 wt.-% PVAc compositions exhibit a rate of growth much higher than the 10 and 15 wt.-% PVAc mixtures. No fissuring is observed for 0 and 3 wt.-% PVAc. The rate of growth increases obviously as the cure temperature is increased. The acquisition of an image sequence was made at 130°C for the 15 wt.-% PVAc composition and the fractal dimension was computed for each image. The variation of D as a function of time is shown in Figure 3 in which the zero time point is chosen when fissures appear in the field of view. The fractal dimension is found to increase when the fissure front moves across the field of view. The D value is stabilized only after the front has gone past the field. This final dimension is therefore the one to be considered in the following.

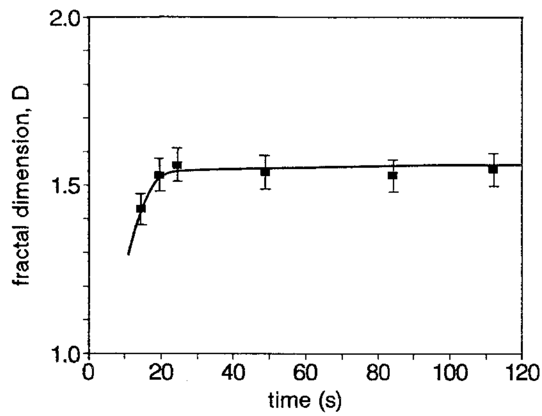

Figure 3 : Kinetics of fissuration for a 15 wt.-% PVAc composition cured at 130°C.

INFLUENCE OF THE PVAc CONTENT ON THE FRACTAL DIMENSION

To investigate the effect of the concentration of the low profile additive, mixtures containing 0, 3, 5, 7, 10 and 15 wt.- % PVAc were cured at 150°C. Figure 4 shows the results of the dimensions for all the mixtures. The integer dimension 1 is attributed to both systems exhibiting no fissure. The mixtures with a PVAc content higher than 5 % present a dimension in the range of 1.5. Several authors [8,11,12,13] and our own work [17] suggested that this spectacular change in behavior can be explained by morphological reasons. Indeed the low profile behavior is enhanced if the thermoplastic phase is well distributed i.e. if the microstructure is actually "co-continuous". In the peculiar case of a reaction between two glass slides, the shrinkage compensation occurs by the extension of fissures through the whole sample. Several researchers have already displayed by SEM that the microvoids are located in the thermoplastic phase [7, 8]. The assumption in the present paper is that the fissures can only develop if the PVAc phase is enough connected to permit the fissures to grow through the entire volume. Bucknall et al. [16] found that a PVAc content higher than 6 wt.-% was necessary to have a "co-continuous", i.e. connected, morphology at 120°C. In a previous paper we reported that an optimal microstructure is obtained for the 7 wt.-% PVAc mixture molded at 135°C and 1.6 MPa [17]. In the present case, the minimal PVAc content seems to be around 5 wt.-%. Furthermore the fractal dimension could have a trend to increase with increasing the PVAc content.

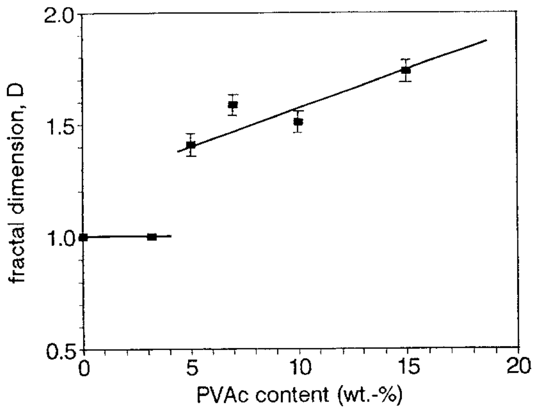

Figure 4 : Influence of the PVAc content on the fractal dimension for curing at 150°C.

INFLUENCE OF THE CURE TEMPERATURE ON THE FRACTAL DIMENSION

From a theoretical point of view, the morphology and then the phase separation are controlled by thermodynamics. The cure temperature is one of the thermodynamics parameter which can be easily modified. The 15 wt.-% PVAc composition has been cured at four temperatures : 130, 140, 150 and 165°C. The fissuring behavior is severely affected by the curing temperature. As already described by Ross [5], the fissures show more branching and they are thinner at high temperatures. This apparent behavior is confirmed by the fractal dimension values. As shown in figure 5, D increases as the cure temperature is increased. The fissure geometry is more divided which reveals the thinness of the PVAc phase. This result is in agreement with another authors' conclusions [11, 15]. The increase in molding temperature induces a morphology of smaller particles. Indeed the acceleration of the reaction kinetics does not allow the growth of polyester particle to be complete. However the system cured at 165°C does not exhibit any fissuring because this temperature is above the glass temperature region of the polyester network.

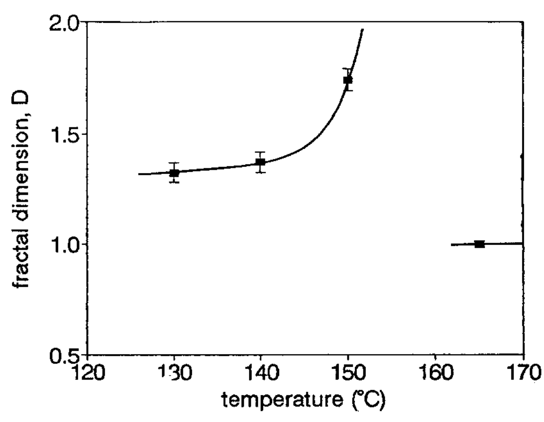

Figure 5 : Influence of the curing temperature on the fractal dimension for a 15 wt.% PVAc composition.

CONCLUSION

In the case of a polymerization between two glass slides, the shrinkage of a low-profile polyester system occurs by the formation of bi-dimensional fissures with a fractal morphology. This work describes how their fractal dimension are calculated and how they depend on the amount of PVAc, on the thermodynamic and on the kinetic parameters. These results are in agreement with those depicted in previous papers in which the formation of a continuous two-phase morphology was found to be the major factor governing the low-profile behavior.

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