

# ANALYSIS OF CELLULAR MICROSTRUCTURE INFLATION IN SOLID POLYAMIC ACID PARTICLES CONTAINING CARBON NANOTUBES

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**SUMMARY:** Solid particle inflation of polyamic acid nanocomposites containing carbon nanotubes has been studied. Solid polyamic acid nanocomposites have been produced through an *in situ* polymerization process. The inflation of polyamic acid powder precursors has been studied for samples containing different carbon nanotube volume fractions. An analysis of the influence of carbon nanotubes on polyamic acid bubble growth has been carried out to determine optimum process conditions for production of polyimide foams from powder precursors. Three different features relating to the inflation process have been analyzed: proportion of single cell structures, multiple cell structures and non-inflated particles, number of cells contained in a multiple cell structure and initial inflation temperature. The increase in volume fraction of well dispersed carbon nanotubes is shown to enhance the production of single cell structures and non-inflated particles and reduces the number of cells contained in multiple cell structures. The influence of carbon nanotubes on the diffusivity, viscosity and glass transition temperature of the polymer justifies the modifications caused by nanotube addition.

**KEYWORDS:** particle inflation, powder precursors, carbon nanotube, nanocomposite, cellular microstructure, polyimide

## INTRODUCTION

High performance polyimide foams have applications in cryogenic, acoustic and structural insulation [1, 2]. The mechanical, thermal and electrical properties of polyimide foams can be modified by the addition of carbon nanotubes (CNTs) [3-8]. Polyimide-CNT foam nanocomposites can be produced from powder precursors [9-12]. The first stage of the polyimide foam nanocomposite production process is the *in-situ* synthesis of the polyamic acid (PAA)-CNT precursor. In this step, a diester and a diamine react to produce PAA in a media containing the future blowing agents as solvents, CNT and surfactants to help the dispersion of the CNTs. Once the PAA-CNT composite is synthesized, a thermal treatment allows the production of PAA cellular microstructures. The polyimide foam is finally obtained after thermal imidization at higher temperatures.

## EXPERIMENTAL SYNTHESIS OF PAA-CNT POWDER PRECURSORS

The production of PAA-CNT composites was based in the diacid-diester route, as proposed by Weiser et al. for synthesis of PAA [1]. The as received multi-walled carbon nanotubes with carboxylic functionalities (MWCNT-COOH) were ground in tetrahydrofuran (THF) to separate macroscopic agglomerates. The CNTs were bath sonicated and horn sonicated in THF. Sodiumdodecylbenzene sulfonate and 4,4'-oxydianiline were added to the CNTs. 3,3',4,4'-benzophenonetetracarboxylic dianhydride was added to a THF/Methanol mixture and reacted to produce diester. The diester was added to the CNT-diamine solution to produce PAA under bath sonication. The PAA thereby synthesized was then partially devolatilized and the solid PAA produced was ground and sieved.

## INFLATION OF POLYAMIC ACID - CARBON NANOTUBE POWDER PRECURSORS

### Description of the Inflation Process

The inflation of PAA-CNT powder precursors is a process driven by the presence and diffusion of blowing agents (THF and methanol) contained in powder precursors [9-11]. At and above the glass transition temperature, the polymer suffers a transition from a glassy to a rubbery state and its viscosity is sharply reduced. This viscosity reduction allows the blowing agent to diffuse easily through the material and accumulate in nucleation sites. The accumulation of blowing agent in the nucleation sites produces an increase in the pressure inside the nuclei that drives the initial stages of the inflation process. As temperature increases, the amidation of the polymer increases its viscosity and the diffusion of blowing agent through the polymer matrix becomes the controlling step for cellular growth. Particle inflation ceases when the increase in the polymer molecular weight and corresponding viscosity is sufficient to maintain constant the cellular wall thickness. The initial and final frames obtained from microscopic evaluation of particle inflation are shown in Fig 1.

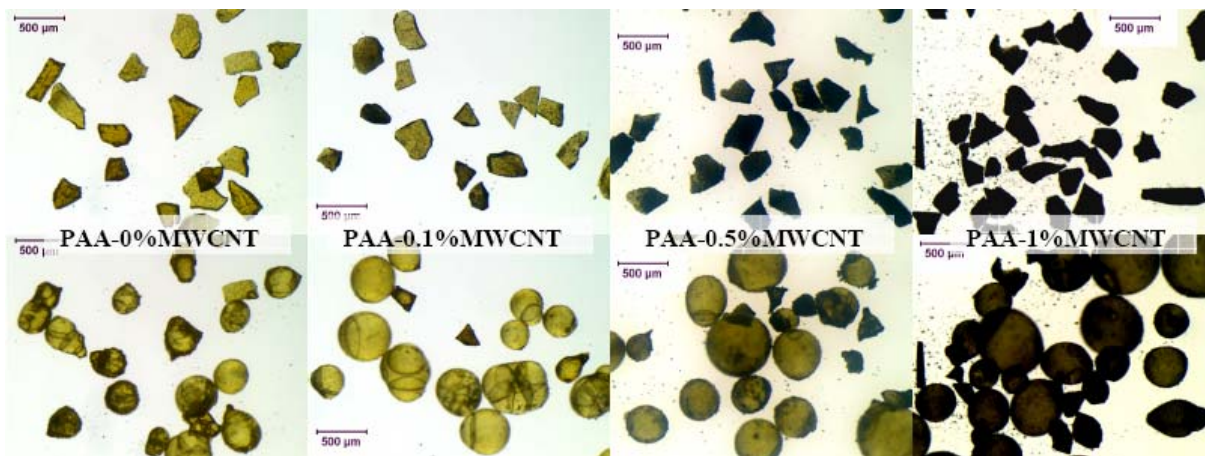


Fig. 1 Micrographs of PAA-CNT precursors and PAA-CNT cellular microstructures produced with 5°C/min heating rate.

## Influence of Carbon Nanotubes in the Proportion of Single Cell Structures, Multiple Cell Structures and Non-Inflated Particles

As shown in Fig. 2a, the proportion of single cell structures and non-inflated particles increases with increasing nanotube concentration. The variation of these proportions with nanotube volume fraction resembles the effect of two different contributions related to the presence of nanotubes. These competing effects could be related to viscosity and glass transition temperature ( $T_g$ ) and can be explained as follows. When a given material has a greater viscosity, the viscous forces acting against cellular microstructure growth are increased. This increase in viscous forces will raise the proportion of single cell structures and non-inflated particles because the number of nuclei that can reach the critical size and develop a cellular microstructure will be reduced as the viscous forces are increased. The increase in the viscosity of a polymer due to addition of carbon nanotubes will be related to the volume fraction of nanotubes and their aspect ratio [13]. The effective aspect ratio of the nanotubes will also be related to the volume fraction, since increases in nanotube concentration will likely retard the CNT dispersion and thereby the aspect ratio.

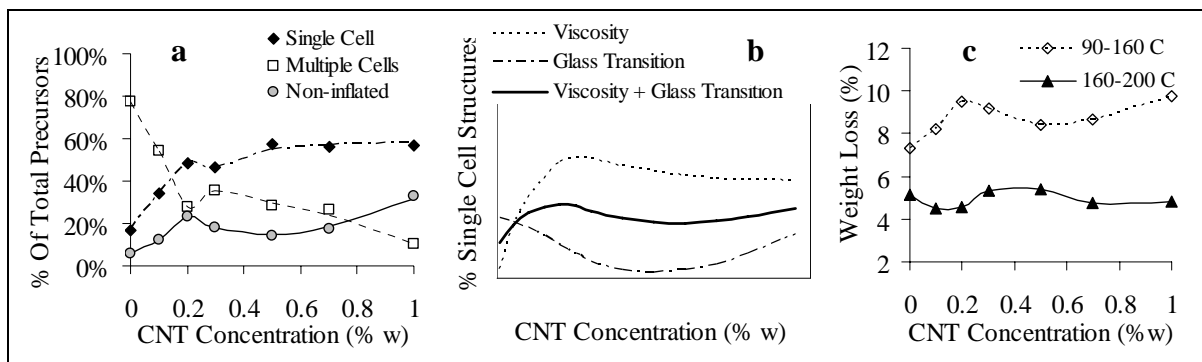


Fig. 2 a) Proportion of single cell structures, multiple cell structures and non-inflated particles versus CNT concentration (5°C/min); b) effect of the combination of viscosity and glass transition temperature in the proportion of single cell structures; and c) weight loss for particle inflation and post-inflation (Thermo-Gravimetric Analysis at 5°C/min).

The second phenomenon that could explain the observed distribution of single cell structures and non-inflated particles is the modification in the  $T_g$ . This temperature can be understood as a switch for the cellular microstructure growth. Below the  $T_g$  the diffusion of blowing agent through the material is significantly constrained. Above the  $T_g$ , the viscosity is considerably reduced and rapid blowing agent diffusion occurs [9]. The consequences of the increase in this “switch” temperature are more rapid diffusion of blowing agent into nucleation sites and reduction of the energy necessary to overcome the nucleus critical size and produce bubble growth. The combination of these two phenomena produces an increase in the number of nuclei that are of the critical size. Therefore, the proportion of multiple cell structures increases and the number of non-inflated particles decreases.

The  $T_g$  of the polymer is related to the concentration and quality of the nanotube dispersion. When the contact surface area of the nanotubes and the polymer chains is increased, the macroscopic movement of the polymer chains is reduced and the  $T_g$  increases. If the CNT concentration is increased and the dispersion quality remains constant, the  $T_g$  increases. When the CNT volume fraction increases, the dispersion becomes more difficult and the effective

aspect ratio decreases. Therefore, the  $T_g$  will initially increase with CNT concentration and will decrease with further addition of CNT when dispersion is less complete.

The influence of the viscosity on the proportion of single cell structures and non-inflated particles is opposite to that of the  $T_g$  (Fig. 2b). The combination of the two phenomena provides a feasible explanation for the relationship of proportion of single cell structures and non-inflated particles with CNT concentration.

The trends observed by microscopic analysis of cellular growth were confirmed by the analysis of the nanocomposite weight loss in the temperature range for cellular microstructure growth (Fig. 2c). The samples with greater weight losses will have a greater number of non-inflated particles, since the blowing agent in these particles is released from the particle rather than being accumulated inside the cellular structure. Therefore, the relationship of weight loss and CNT concentration is the same than the relationship of the proportion of non-inflated precursor particles and CNT concentration. The blowing agent accumulated inside the cellular microstructures during the inflation process is released at higher temperatures. Therefore, the weight losses observed after the inflation process has completed (160-200°C) have the opposite behavior to the weight losses during the inflation process (90-160°C).

### Influence of Carbon Nanotubes in the Number of Cells Contained in Multiple Cell Structures

The evolution of the number of cells contained in a multiple cell structure with CNT volume fraction is shown in Fig 3. This relationship is directly proportional to the number of nuclei that reach the critical nucleus size and produce a cellular microstructure. As discussed above, the number of nuclei that can reach the critical size is related to the viscosity and  $T_g$  of the polymer. The relationship of these two variables with CNT concentration provides an average number of cells in a multiple cell structure that is directly proportional to the number of particles achieving inflation.

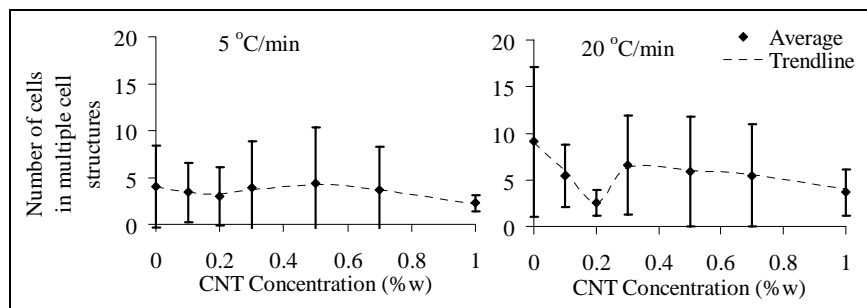


Fig. 3: Number of cells in multiple cell structures versus CNT content in PAA-CNT precursors.

## Influence of Carbon Nanotubes in the Temperature for Initial Cellular Inflation

The temperature for initial inflation of cellular microstructures is strongly influenced by  $T_g$  and diffusivity. When the  $T_g$  is increased, the temperature for initial inflation will increase since  $T_g$  is a necessary condition for the initiation of the cellular growth. The diffusivity of the material is directly proportional to the temperature for initial inflation, because diffusion of blowing agent enhances the cellular growth. The diffusion of blowing agent through the material is inversely proportional to its viscosity. Given the relationship of  $T_g$  and viscosity with CNT concentration explained above, the combination of  $T_g$  and diffusivity provides an explanation for the variation of the temperature of initial inflation with nanotube concentration (Fig. 4).

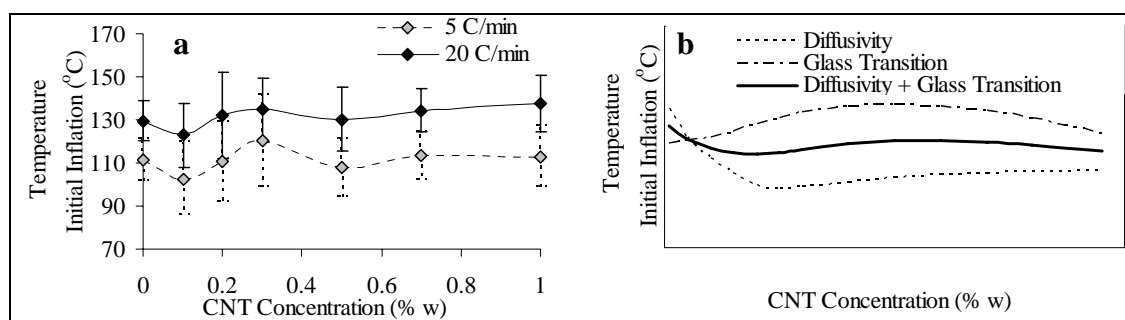


Fig. 4: a) Temperature for initial cellular inflation versus CNT concentration in PAA-CNT nanocomposites; and b) effect of the combination of  $T_g$  and diffusivity in the temperature for initial cellular inflation.

## CONCLUSIONS

The inflation of PAA powder precursors is modified by the addition of CNTs. When the nanotube volume fraction is increased, the diffusivity, viscosity and glass transition temperature of the polymer are modified. When the CNTs are well dispersed, their presence enhances the production of single cell structures and non-inflated particles and reduces the number of cells contained in multiple cell structures.

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