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Fabrication of microchannels using polycarbonates as sacrificial materials

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Abstract
The use of polycarbonates as thermally decomposable, sacrificial materials for the formation of microchannels is presented. Polycarbonates decompose in the temperature range of 200–300 °C. Two polycarbonates, polyethylene carbonate and polypropylene carbonate, have been used to fabricate microchannels in three different types of encapsulants: an inorganic glass (silicon dioxide), a thermoplastic polymer (Avatrel dielectric polymer) and a thermoset polymer (bisbenzoycyclobutene Cyclotene 3022-57). This paper presents the details of the fabrication process, a thermogravimetric analysis of the sacrificial materials, and the kinetic parameters for the decomposition process. The presence of oxygen or water was found to impact on the decomposition of the sacrificial material. This paper demonstrates the feasibility of forming buried air-cavities in a variety of encapsulants at a modest temperature, thus enabling the use of a wide range of dielectric materials with different thermal stabilities and properties.

1. Introduction

Buried air-cavities are of interest in electrical interconnects (low dielectric constant), microfluidic devices, and for other applications including microelectromechanical systems (MEMS) [1–7]. The incorporation of air into a dielectric material may be used to lower the effective dielectric constant or vary the index of refraction. In microfluidics, gases or liquids can pass through microchannels to create micro-total-analysis systems (μTAS), miniature heating and cooling systems, reactors and displays. This technology is also applicable in the fabrication of MEMS or other devices where the material acts as a sacrificial mold or a release mechanism.

One approach to air-cavity formation is through the use of a sacrificial material, or 'place-holder', which is patterned into the desired shape, encapsulated with a second material, then removed in subsequent processing. This approach has been previously demonstrated through the use of a thermally decomposable polynorbornene sacrificial polymer, Unity400 (Goodrich), which decomposes at approximately 400 °C [2, 3, 7]. The process sequence for this air-cavity fabrication using microelectronic processing techniques is shown in figure 1. First, the sacrificial polymer is spin-coated onto the substrate (figure 1(*b*)). The thickness of the sacrificial polymer film (ultimately the height of the air-cavity) is controlled by the viscosity of the polymer solution and the spin speed. Next, a hard mask is deposited for subsequent patterning of the sacrificial polymer (figure 1(*c*)). The hard mask is patterned by standard photolithography and the underlying exposed polymer areas are removed by reactive ion etching (RIE) (figures 1(*d*) and 1(*e*)). The hard mask and the remaining photoresist are then removed, leaving only the patterned, sacrificial polymer on the substrate (figure 1(*f*)). This is followed by encapsulation of the sacrificial polymer with the dielectric material (figure 1(*g*)). The sacrificial polymer decomposes into volatile products upon heating to ~400 °C (figure 1(*h*)). The decomposition products diffuse through the encapsulating material and leave behind a hollow cavity with minimal solid residue.

The ability to form air-cavities via a thermally decomposable polymer requires specific properties for both the sacrificial and the encapsulating materials. The sacrificial material must have adequate adhesion to substrates such as Si, SiO_2, polymers and metals. Chemical processing and the use of solvents (following the application of the sacrificial polymer) should not swell or degrade the material. The complete decomposition of the sacrificial material should occur in a narrow temperature range with little or no solid

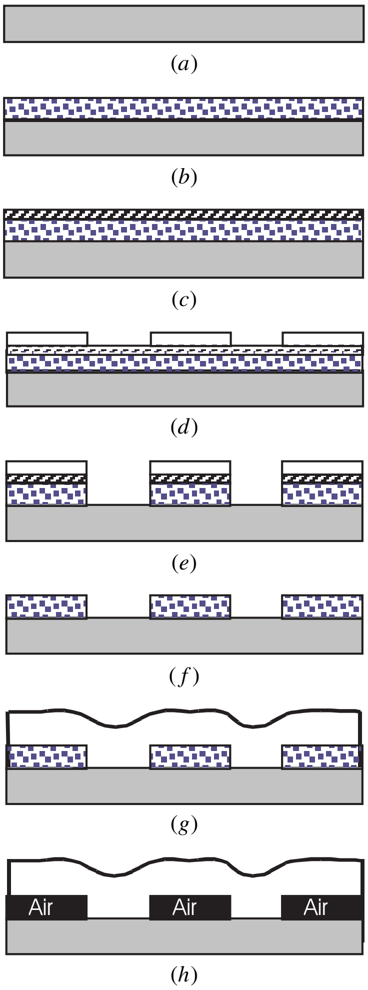


Figure 1. Buried air-cavity fabrication process: (*a*) substrate; (*b*) spin-coating of sacrificial polymer; (*c*) deposition of hard mask; (*d*) spin-coating and patterning of photoresist; (*e*) etch of hard mask and RIE etch of sacrificial polymer; (*f*) removal of photoresist and hard mask; (*g*) spin-coating or deposition of encapsulating material; (*h*) thermal decomposition of sacrificial material.

residue. The decomposition products should be able to permeate through the overcoat layer. The decomposition temperature must be compatible with subsequent processing and other materials in the structure. The target decomposition temperature is one at which the encapsulating material is already fully cured and resistant to degradation, flow, or deformation. The encapsulating material requires adequate mechanical strength to span the air-cavity without sagging or expanding during decomposition of the sacrificial material. Sufficient permeability to the decomposition products is required for formation of the air-cavity without distortion or rupture during the decomposition process. The encapsulating material also needs to provide adequate step coverage over the patterned sacrificial film.

The formation of microchannels using Unity400 sacrificial polymer has been performed using silicon dioxide, silicon nitride and polyimide encapsulating materials [2, 3, 7]. These encapsulating materials are stable for short periods of time at 400 °C so that complete decomposition of the sacrificial material can be achieved. It is desirable to perform this same process sequence using a sacrificial material at a lower temperature for use with other encapsulating materials and applications which cannot withstand 400 °C. The target temperature range is 250–300 °C in order that encapsulating materials (e.g. epoxy-based materials and some polyimides) with less thermal stability can be used. The purpose of this paper is to present data on the use of polycarbonates as lower temperature sacrificial materials, including decomposition characteristics, fabrication and processing, and compatible lower temperature encapsulating materials. The formation of microchannels with these polycarbonate materials has been demonstrated in a variety of encapsulating materials including an inorganic glass, a thermoset polymer, and a thermoplastic polymer.

2. Experimental details

Polycarbonates are known to decompose in the range of 200–300 °C [8]. Groups in the polycarbonate backbone may be tailored to achieve desired properties such as decomposition temperature, glass transition temperature (T_g), or adhesion. The polycarbonates used in this research include polyethylene carbonate (PEC) and polypropylene carbonate (PPC). The PEC was produced by PAC Polymers Inc., and the structure was verified using infrared spectroscopy and nuclear magnetic resonance spectroscopy. The PPC was obtained from Aldrich Chemical. Solutions used for fabrication and processing consisted of 18 wt% PEC in n-methyl-2-pyrollidinone (NMP) and 12 wt% PPC in gamma-butyrolactone.

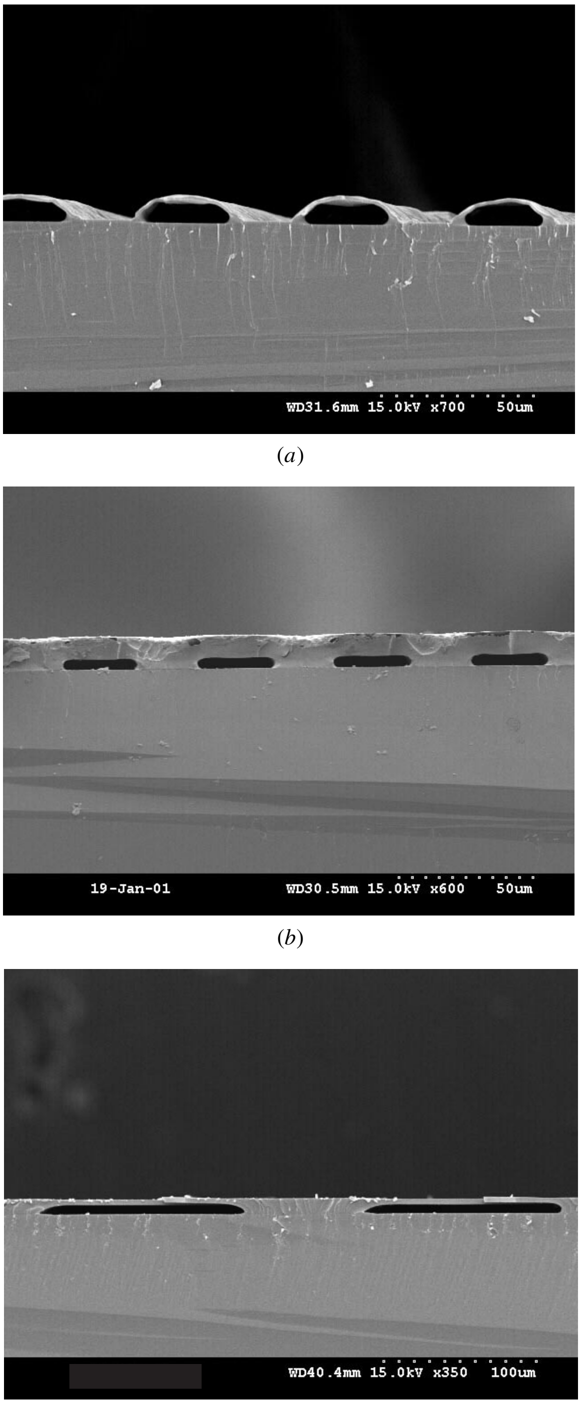
Thermogravimetric analyses (TGA) were performed on PEC and PPC in air and nitrogen atmospheres using a Seiko TG/DTA 320. The dynamic TGA experiments consisted of a constant heating-rate ramp to a final temperature. The dynamic runs were performed at heating rates of 0.5, 1, 2, 5 and 10 °C min^{-1} from 30 to 400 °C. Experiments performed in air were open to the atmosphere under no gas flow. Dynamic experiments in nitrogen were run under a constant nitrogen flow rate of 150 sccm. These runs were preceded by a 1 h nitrogen purge at the same flow rate to achieve an environment <50 ppm O_2. Isothermal experiments consisted of a 20 °C min^{-1} ramp to 110 °C, a 10 min hold to remove moisture, then a 100 °C min^{-1} ramp to the desired hold temperature. An oil bubbler was attached to the exit stream to prevent the backflow of air.

The decomposition of full-surface films of the sacrificial materials on silicon wafers was performed in a Lindberg horizontal quartz tube furnace with nitrogen or dry air flowing at a rate of 1.5 l min^{-1}. Backstreaming of air was prevented by an oil bubbler on the exit stream. The temperature was ramped 5 °C min^{-1} to 230 °C or 250 °C followed by a 1 °C min^{-1} ramp to the final temperature and a 3 h hold. Contact angle measurements were obtained immediately after film decomposition through use of a video contact angle 2500XE system (AST products). A 1 μl drop of distilled water was dispensed onto the sample surface. Both the right and left angles between the sample surface and the tangent line to the droplet were measured.

3. Results

Microchannels have been fabricated via the process flow in figure 1, using PEC and PPC polycarbonates as the sacrificial materials. Three types of encapsulating materials were used: an inorganic glass, plasma enhanced chemically vapor deposited (PECVD) deposited silicon dioxide; a thermoplastic polymer, Avatrel dielectric polymer (Goodrich); and a thermoset polymer, Cyclotene (Dow Chemical) bisbenzocyclobutene 3022-57 resin (BCB). The same process sequence was used to pattern the polycarbonate on all samples. First, the polycarbonate was spin-coated onto silicon substrates at a thickness of 1–5 μm. After spin coating, the polycarbonate film was softbaked at 100 °C for 3 min and 160 °C for 30 min to remove the solvent. Next, metal (Ti, Al or Ti–Au) was sputter deposited onto the polycarbonate. The metal was used as a hard mask for subsequent patterning of the polycarbonate. The hard mask was patterned by photolithography using Shipley Microposit 1813 photoresist and MF319 developer. Wet etching was used to etch the Ti (6:1 HF/H_2O) or Au (40:4:1 H_2O/KI/I_2), and RIE etching was used to pattern the Al (40 sccm BCl_3, 10 sccm Cl_2, 3 sccm $CHCl_3$, power = 125 W, pressure = 30 mTorr, $T = 35$ °C). The exposed polycarbonate areas were then etched by RIE, followed by removal of the remaining hard mask with the same etchants used for patterning. The RIE polymer etch conditions were 15 sccm Ar, 40 sccm O_2, power = 400 W, pressure = 250 mTorr, $T = 35$ °C. The encapsulating material was then deposited (as described later for each material). After encapsulation of the patterned polycarbonates, decomposition was carried out in a horizontal tube furnace in either air or nitrogen. The polycarbonate was patterned into many shapes including meander lines forming parallel microchannels with widths of 140 μm with 60 μm spaces, 70 μm with 30 μm spaces, and 35 μm with 15 μm spaces.

The first overcoat material presented is the PECVD silicon dioxide glass. The silicon dioxide was deposited at a rate of 20 nm min^{-1} using a mixture of 400 sccm SiH_4 and 900 sccm N_2O gases at a pressure of 600 mTorr and a power of 35 W at 200 °C. The PEC polymer was used as the sacrificial material, and a titanium–gold (250 Å/1000 Å) hard mask was used for polymer patterning. The decomposition process consisted of a 5 °C min^{-1} ramp to 230 °C and holding for 2 h. Figure 2(*a*) shows a cross-section scanning electron micrograph (SEM) image of microchannels encapsulated by 1 μm thick silicon dioxide. The microchannels are 5 μm in height and approximately 25 μm in width. Over-etching of the polycarbonate results in a narrowing of the microchannels from the original mask line-width. Cross sections of the PEC lines made before overcoating with silicon dioxide show that they were rectangular in shape. The irregular, dome shape and wrinkling of the oxide seen in figure 2(*a*) is due to the intrinsic stress in the glass from the coefficient of thermal expansion (CTE) mismatch between the oxide and polymer upon cooling from the glass deposition temperature of 200 °C. Deposition of the oxide occurs above the glass transition temperature of the polymer, which also results in some deformation during the oxide deposition. The microchannels appear to be clean with no visible residue, indicating that the decomposition products are able to permeate the overcoat material.



(*a*)

(*b*)

(*c*)

Figure 2. Microchannels fabricated using: (*a*) polyethylene carbonate encapsulated in PECVD deposited silicon dioxide; (*b*) polyethylene carbonate encapsulated in Avatrel dielectric polymer; (*c*) polypropylene carbonate encapsulated in Cyclotene 3022-57.

Microchannels were also fabricated with the PEC encapsulated by a thermoplastic polymer, Avatrel dielectric polymer. A similar titanium–gold hard mask was used to pattern the PEC. The Avatrel dielectric polymer was spin-coated, and softbaked on a hotplate at 100 °C for 10 min. An exposure of this polymer to 250 mJ cm^{-2}, measured at 365 nm, is required to cross-link the polymer. The final overcoat polymer thickness was 11.6 μm. The Avatrel polymer cure and sacrificial material decomposition were performed in a single process step that included a 3 °C min^{-1} ramp to 200 °C and a 1 h hold followed by a 1 °C min^{-1} ramp to 230 °C and a

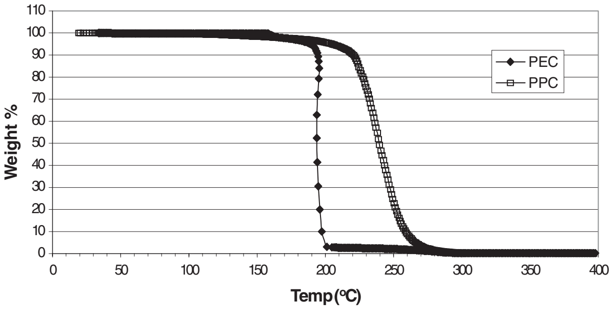


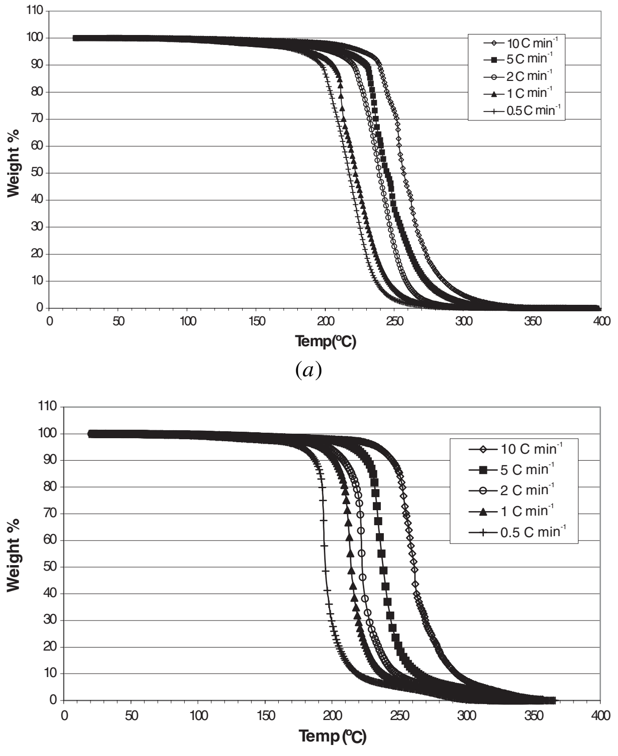
Figure 3. Dynamic TGA weight percentage versus temperature curve for PEC and PPC at 2 °C min^{-1}.

2 h hold. Figure 2(*b*) shows an SEM image of microchannels, 5 μm tall and 25 μm wide, in Avatrel. The channels in figure 2(*b*) appear to be flat on the surface with slightly rounded corners. This is the same shape as the patterned PEC before encapsulation. This indicates that the deformation occurring in the oxide-encapsulated microchannels (figure 2(*a*)) must be taking place during the PECVD deposition process.

Microchannels have also been fabricated in a thermoset polymer, Cyclotene 3022-57. The polymer was spin-coated and cured at 250 °C for 1 h on top of the patterned PPC. PPC was chosen as the sacrificial polymer in this case because its decomposition temperature is slightly higher than that of PEC, as will be shown later. A titanium mask was used to create the pattern in the sacrificial material. The cure was performed at 250 °C for 1 h, followed by a hold for 2 h at 285 °C to decompose the PPC. Figure 2(*c*) shows an SEM image of microchannels, 140 μm wide and 5 μm tall, formed using the PPC sacrificial material encapsulated with BCB resin. These channels differ from those shown in figures 2(*a*) and 2(*b*) because this overcoat planarizes the PPC very well, resulting in a flat-top surface. The shape of the actual channels appears to be the same as the patterned polycarbonate before the overcoat was applied. Odd-shaped corners are seen in the PPC patterned film following the removal of the titanium hard mask, due to anisotropic etching in the RIE polymer etch process.

Microchannel formation in the three overcoat materials used in this study demonstrates that polycarbonates can be used as thermally decomposable sacrificial materials. These encapsulating materials are different in their method of deposition, and their thermal and mechanical properties. However, all three have thermal stability, rigidity to span the microchannels, and sufficient permeability to allow air-cavity formation. A key similarity is that these materials can be deposited or cured at or below 250 °C, allowing cure of the overcoat before polycarbonate decomposition.

The decomposition (i.e. mechanism, temperature, rate and decomposition products) of the sacrificial material is extremely important to the formation of buried air-cavities. TGA was used to study the rate of reaction. A dynamic TGA thermogram of the remaining sample weight percentage as a function of temperature for PEC and PPC at a constant heating rate (2 °C min^{-1}) in ambient air (40% relative humidity) is shown in figure 3. Figure 3 shows that the decomposition of these materials occurs between 200–280 °C. The materials undergo decomposition within a narrow temperature range, indicated by negligible weight loss to 200 °C, followed by a steep decline in weight. Decomposition is complete with less than 0.01% residual material at about 280 °C. From a visual inspection after the decomposition, the aluminum sample pan appeared to be clean. Isothermal TGA data also confirm that complete decomposition of PPC can occur within a reasonable time at temperatures as low as 240 °C.



(*a*)

(*b*)

Figure 4. Dynamic TGA weight percentage versus temperature curves as a function of temperature ramp rate for PPC (*a*) in air and (*b*) in nitrogen.

The effect of the decomposition rate and environment was investigated by performing TGA in nitrogen and ambient air. Figures 4(*a*) and 4(*b*) show the dynamic TGA results for PPC in nitrogen and ambient air, respectively, at ramp rates of 10, 5, 2, 1 and 0.5 °C min^{-1}. The onset of decomposition is at about 200 °C, and the residual weight is less than 0.01% in both air and nitrogen. The TGA curves shift to the right at higher ramp rates because less time is spent at lower temperature. A comparison of the shapes of the curves in figures 4(*a*) and 4(*b*) shows a difference between the decomposition in air and nitrogen atmospheres. A small foot is seen at approximately 5% weight remaining for the curves in nitrogen. Complete decomposition in nitrogen does not occur until about 300 °C. This indicates that the decomposition mechanism may be environment dependent and oxygen is necessary to facilitate compete decomposition at lower temperatures.

The decomposition mechanism follows *n*th-order reaction kinetics represented by equation (1)

$$-\frac{\mathrm{d}W}{\mathrm{d}t} = A\exp\left(\frac{-E_\mathrm{a}}{RT}\right)W^n \qquad (1)$$

where W is the sample weight, t is the time, A is the pre-exponential factor, E_a is the activation energy, R is the gas constant, T is the temperature, and n is the reaction order. The Ozawa method [9] uses an integrated form of equation (1) to calculate an overall reaction order and an activation energy for the complete decomposition reaction. Both dynamic and isothermal TGA data for PPC have been utilized to calculate the kinetic parameters for decomposition in ambient air and nitrogen atmospheres. The parameters in ambient air were calculated from the dynamic TGA data to be a reaction order of 1.71 ± 0.37 and an activation energy of 152.7 ± 18.4 kJ mol^{-1}, where the error represents a 95% confidence limit. The isothermal data agreed with this dynamic data, yielding a reaction order of 1.61 and an activation energy of 173.2 kJ mol^{-1}. In a nitrogen atmosphere, the dynamic data yielded an overall reaction order of 2.28 ± 0.37 and an activation energy of 92.7 ± 3.4 kJ mol^{-1}. However, the values calculated from the isothermal data have shown that the reaction order changed with temperature. The reaction order decreased from 3.66 at 262 °C to 1.16 at 340 °C. This change in reaction order indicates a change in mechanism, which is being investigated and will be the subject of a future publication. Also, the large differences between the kinetic parameters for the nitrogen and air atmospheres are indicative of the participation of the ambient gas in the reaction.

In order to characterize the surface after decomposition, full surface films of the polycarbonates on silicon wafers were decomposed in dry air, ambient air (74% relative humidity), and nitrogen at 300 °C. Films decomposed in dry and ambient air visually appeared to be cleaner after decomposition than those decomposed in nitrogen. The contact angle of distilled water with the resulting silicon surface was measured immediately after decomposition and cooling to room temperature. A bare silicon control sample with no polymer film exposed only to the furnace temperature program has a contact angle of 25.1° ± 1.8° before heat treatment, 60.0° ± 2.8° after treatment in nitrogen, 35.4° ± 0.8° after treatment in dry air, and 32.8° ± 1.3° after treatment in ambient air. For the PEC film samples, the contact angle of the PEC surface was 62.2° ± 1.7° after complete decomposition in nitrogen, 33.0° ± 1.4° after decomposition in dry air, and 27.1° ± 1.7° after decomposition in ambient air. The PPC contact angle results were 78.5° ± 0.5 ° in nitrogen, 57.6° ± 0.3° in dry air, and 44.2° ± 0.4° in ambient air. These contact angle measurements in dry air, ambient air and nitrogen indicate a difference in the residues remaining on the substrate surface. The substrates become more hydrophobic than the original untreated surface after either polycarbonate decomposition or heat treatment. PPC films are more hydrophobic than PEC films. Also, the decomposition environment does impact on the surface affinity for water. Films decomposed in ambient air are more hydrophilic than in dry air, and both are more hydrophilic than those decomposed in nitrogen. This indicates that different residues may remain on the silicon surface. Further studies using x-ray photoelectron spectroscopy (XPS) and other surface analytical techniques are planned to study these issues in more detail.

4. Conclusion

The use of polycarbonates as thermally decomposable sacrificial materials has been demonstrated using polyethylene and polypropylene carbonates in an inorganic glass, a thermoplastic polymer and a thermoset polymer. The decomposition characteristics of these polycarbonates satisfy the criteria for use in air-cavity formation, including complete decomposition in a narrow and useful temperature range and little or no solid residue. The TGA results, calculated kinetic parameters, and full surface film decomposition results all indicate that the presence of oxygen impacts on the decomposition mechanism. The ability to form air-cavities at lower processing temperatures, as described in this paper, expands the use of this process to include a range of materials with lower thermal stabilities. In addition, the ability to change substituents in the polycarbonate backbone may allow pinpointing of the decomposition temperature to allow full cure of the encapsulating material with negligible decomposition of the sacrificial material.

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