

# Study of the Formulations and Process Conditions in the Crosslinking of Polyethylene Foams at Atmospheric Pressure

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**ABSTRACT:** The aim of this work is the study of the foaming process of a commercial polyethylene in the presence of a crosslinking agent. Foams have been produced under nearly atmospheric pressure conditions, which commonly occur during polymer rotomolding. Different processing temperatures and different combinations of blowing agent/kicker (azodicarbonamide/zinc oxide) and crosslinking agent (dicumyl peroxide) concentrations have been employed. Thus, the melt viscosity, crosslinking degree, and temperature of the gas evolution and its rate have been changed to a certain degree. The obtained results have revealed that all these factors are critical to obtaining uniform and low-density foams. Under certain processing tem-

peratures and with an appropriate formulation, foam densities have been reduced up to 70% with respect to non-foamed polymer. The interactions among the different components of the formulation have also been observed, and the results have led to the conclusion that in this kind of process, when a low pressure is applied, the foam density can be controlled by an adequate synchronization of the melt-crosslinking, foaming, and gas-expansion processes. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2028–2037, 2008

**Key words:** crosslinking; curing of polymers; differential scanning calorimetry (DSC); polyethylene (PE); processing

## INTRODUCTION

Foaming has become of great importance in the polymer processing industry because cellular materials offer advantages over traditional materials and noncellular polymers. Foams have unique insulating properties, impact-resistant characteristics, buoyancy, and outstanding strength-to-weight ratios.<sup>1</sup> Their closed-cell structure leads to a low level of water absorption, low water transmission, no dust absorption, and good impact insulation.<sup>2</sup>

Most commercial polyolefin foams are manufactured by the expansion of a gaseous phase dispersed throughout the polymer melt. The gaseous phase can be generated by the separation of a dissolved gas, the vaporization of a volatile liquid, or the release of a gas by a chemical reaction of a chemical blowing agent (CBA). Azodicarbonamide (ADC) is the most employed and effective CBA for plastic

and rubber applications because of its low toxicity and flame self-extinguishing and its relatively high decomposition temperature.<sup>3</sup> An expansion process involves three fundamental steps: bubble initiation (nucleation), bubble growth, and stabilization. Nucleation begins at an initiation site within a polymer melt that has been supersaturated with a blowing agent. If a CBA is used as a blowing agent, when the polymer temperature reaches the CBA decomposition temperature, gas evolves at the surface of each particle of CBA. When sufficient molecules have clustered in a given area, an interface between the gas and the polymer is formed, thus creating a microvoid that eventually becomes part of a bubble. Gas molecules rapidly diffuse into the growing bubble interface, and the plastic is stretched away from the nucleation site. Once a bubble reaches a critical size, it continues growing as the blowing agent gas rapidly diffuses into it. Then, bubble growth continues until the bubble stabilizes or the thin and highly stretched cell walls of molten thermoplastic break down.

Controlled bubble nucleation and growth are essential to produce uniform and low-density foams. The gas must be fully dissolved in the polymer before the initiation of the bubble nucleation and growth processes.<sup>4</sup> Furthermore, the polymer must resist the internal gas pressure of the growing bubbles. This can be accomplished by regulation of the

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pressure process (injection or compression molding). Nevertheless, for a pressure-free process (e.g., rotational molding), only atmospheric pressure is applied to the polymer. This results in immediate bubble formation as soon as the gas is generated by the decomposition of the CBA within the melt polymer matrix. Accordingly, the cell structure in the final foamed part will be coarse. This problem is aggravated in a process in which a CBA (e.g., ADC) decomposition process is exothermic. It is well known that the presence of certain oxides such as zinc oxide (ZnO; typical kicker) and other compounds accelerates the decomposition of certain blowing agents.<sup>5</sup>

Because crosslinking causes a sharp increase in melt strength, it could control bubble expansion and hence bubble coalescence. Chemical crosslinking of polyethylene (PE) can be performed via dicumyl peroxide (DCP), which is the most common peroxide in the industry.<sup>6</sup> Furthermore, DCP is a solid peroxide, thus diminishing the evaporation problems that lower boiling point liquid peroxides entail in a pressure-free process. Consequently, the control of the different variables involved in the process to obtain foam of a certain quality may be a difficult task.

Thus, the aim of this work is to obtain better insight into the behavior of a classical foaming system under atmospheric pressure and to study the effects of processing conditions and formulations on the quality and uniformity of PE foams obtained under atmospheric pressure conditions. For this purpose, selected samples have been processed at different oven temperatures and characterized by differential scanning calorimetry (DSC), gel content, and density.

## EXPERIMENTAL

### Materials

Elite 5610 powder PE (Dow Plastics, Tarragona, Spain) with a melt flow index at 190°C of 15 g/10 min and a density of 935 kg/m<sup>3</sup> was used.

DCP, provided by Merck (Barcelona, Spain), was used as a crosslinking agent. The half-life data for the decomposition of DCP were 1 h at 130°C and 10 h at 177°C. The maximum DCP concentration used was 2 phr because it has been shown that the gel content levels off for DCP concentrations higher than this value.<sup>7</sup>

ADC (grade Unicell D200A, TRAMACO GmbH Pinneberg, Germany) was used as an exothermic CBA. The ADC concentration was kept constant to isolate the effect of the peroxide concentration on the density of the foam. According to Crawford and James,<sup>8</sup> 1 phr ADC is a concentration that yields a density reduction higher than 50%, a typical value for rotomolded foams.

ZnO, supplied by Panreac S.A. (Barcelona, Spain), was used to accelerate the decomposition of the blowing agent. It was added in excess (1 part of ZnO per part of ADC) to guarantee the maximum decrease of the decomposition temperature of ADC. Hereafter, a mixture of ADC and ZnO is called a foaming system.

### Sample processing

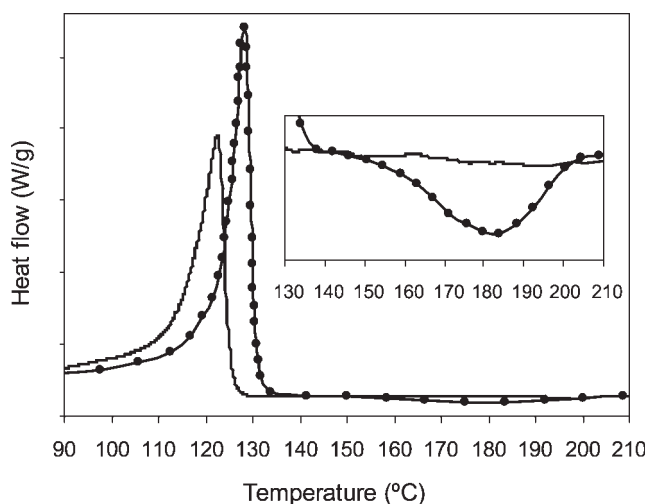
A multicavity mold was designed. Each cylindrical cavity (30 mm in diameter and 20 mm deep) had a thermocouple to monitor the polymer temperature. It allowed the simultaneous processing of eight samples.

Tested blends were classified according to additives present in the formulation: only peroxide (D), peroxide and a blowing agent (DA), and a blowing agent and ZnO (DAZ). The blend compositions are shown in Table I.

Thus, 63 different samples (grouped in nine sets) were obtained by the combination of different peroxide concentrations (0, 0.1, 0.25, 0.5, 0.75, 1, and 2 phr) and curing temperatures (160, 200, and 250°C) and samples containing only peroxide (series D), peroxide plus ADC (series DA), and peroxide plus ADZ and ZnO (series DAZ). Because polymer crosslinking is mainly controlled by the peroxide decomposition, its rate can be taken as the curing rate.<sup>3</sup> Furthermore, for complete polymer crosslinking, a processing time of the order of 5 times the half-lives (96.9% decomposition) is required.<sup>9</sup> According to this rule and DCP kinetic data, required processing times were calculated under the assumption of a

TABLE I  
Formulations of the Processed

Set	DCP (phr)	ADC (phr)	ZnO (phr)
PE + crosslinking agent (D)	0	—	—
	0.1	—	—
	0.25	—	—
	0.5	—	—
	0.75	—	—
	1	—	—
	2	—	—
PE + crosslinking agent + blowing agent (DA)	0	1	—
	0.1	1	—
	0.25	1	—
	0.5	1	—
	0.75	1	—
PE + crosslinking agent + blowing system (DAZ)	1	1	—
	2	1	—
	0	1	1
	0.1	1	1
	0.25	1	1
	0.5	1	1
	0.75	1	1
1	1	1	
2	1	1	



**Figure 1** DSC curves for the binary mixture PE + DCP (1 phr): (●) first heating scan (128.1°C, 147 J/g; 184.5°C, -6.7 J/g) and (—) second heating scan (122.4°C, 130 J/g).

first-order decomposition rate: 40 min at 160°C, 10 min at 200°C, and 5 min at 250°C.

### Calorimetric analysis

Samples of approximately 10 mg were heated from 30 to 250°C at a heating rate of 10°C/min under a nitrogen flow of 20 mL/min (STP) in a PerkinElmer DSC-6 Pyris differential scanning calorimeter (Madrid, Spain). After that, they were cooled to 30°C at 10°C/min and then heated again at 10°C/min to 200°C. Melting and recrystallization temperatures were recorded. The crystallinity was calculated as the ratio of the heat of fusion of the analyzed specimen to the heat of fusion of an ideal PE crystal (288 J/g).<sup>10</sup>

### Gel content

About 0.8 g of each sample was weighed and placed in a cellulose bag to determine the gel content by Soxhlet extraction for 24 h with *p*-xylene as a solvent. After the extraction, the bags were dried in an oven at 80°C until a constant weight. The gel content of the polymer was determined as follows:

$$\text{Gel content (\%)} = \frac{\text{weight sample after extraction}}{\text{initial weight sample}} \times 100$$

A blank sample of PE was added to every extraction to ensure that the extraction process was accomplished.

### Density

Density measurements were performed with a density determination kit for the Ohaus Adventurer

ARRV70 balance (Madrid, Spain). The standard deviation of these measurements was less than 1%.

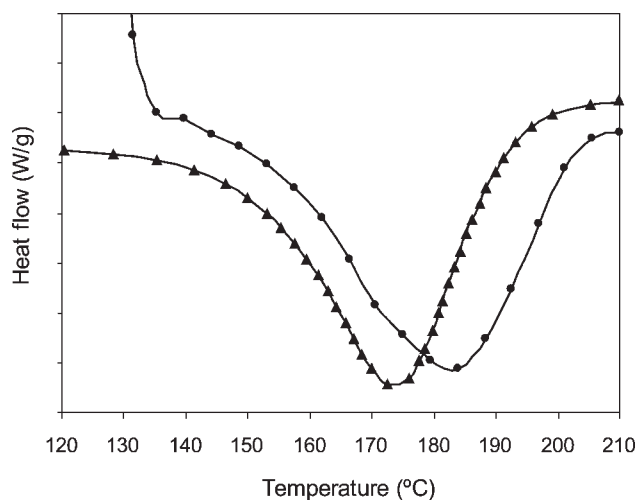
## RESULTS AND DISCUSSION

### Calorimetric analysis of the mixtures

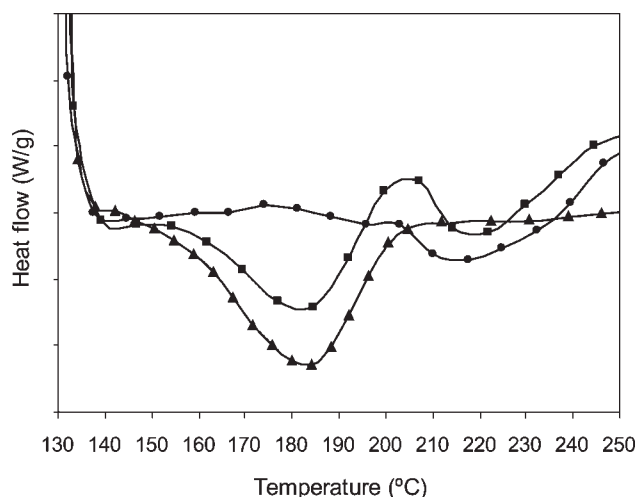
Figure 1 shows the DSC curves for the heating and reheating runs of PE with DCP (1 phr). The first heating run shows a single sharp endothermic peak (128.1°C) attributable to PE melting and an exothermic peak (184.5°C) corresponding to the peroxide decomposition. A consecutive second melting process yields a single broad endothermic peak at 122.4°C, which involves a 4.5% temperature decrease with respect to the first run. The melting enthalpy also decreases approximately 12%, which corresponds to the crystallinity degree reduction due to crosslinking, according to the literature.<sup>9-11</sup>

The peak of DCP decomposition in the binary mixture is shifted up 10°C to higher temperatures (Figure 2). This is probably due to the fact that heat transfer is different in both cases (when analyzed pure and dispersed in a polymer matrix) or due to a cage-effect retardation of the DCP decomposition<sup>12</sup> caused by the high polymer melt viscosity.

The calorimetric analysis of the ternary mixture of PE, DCP (1 phr), and ADC (1 phr) does not reveal any interaction between DCP and ADC. This fact is highlighted when the DSC curves of the binary mixtures are compared with the DSC curve of the ternary mixture in the temperature range above the melting point of the PE (Fig. 3). As can be observed, peaks of DCP (184.5°C) and ADC (220.4°C) in their



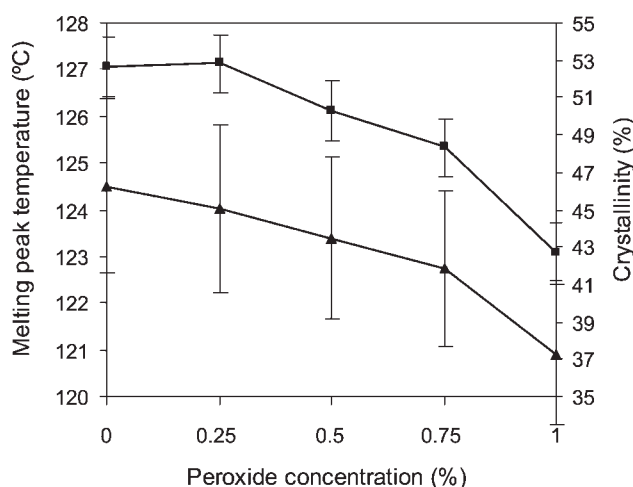
**Figure 2** DSC curves for pure DCP and for the binary mixture over the temperature range corresponding to peroxide decomposition (for a better comparison, the peak of the PE + DCP curve has been enlarged): (●) PE + DCP (1 phr; first heating scan, 184.5°C, -6.7 J/g) and (▲) DCP (174.4°C, -626 J/g).



**Figure 3** DSC curves for the binary and ternary mixtures (first heating scans): (▲) PE + DCP (1 phr; 184.5°C, -6.7 J/g), (●) PE + ADC (1 phr; 220.4°C, -6 J/g), and (■) PE + DCP (1 phr) + ADC (1 phr; 182.0°C, -5 J/g; 218.8°C, -3.0 J/g).

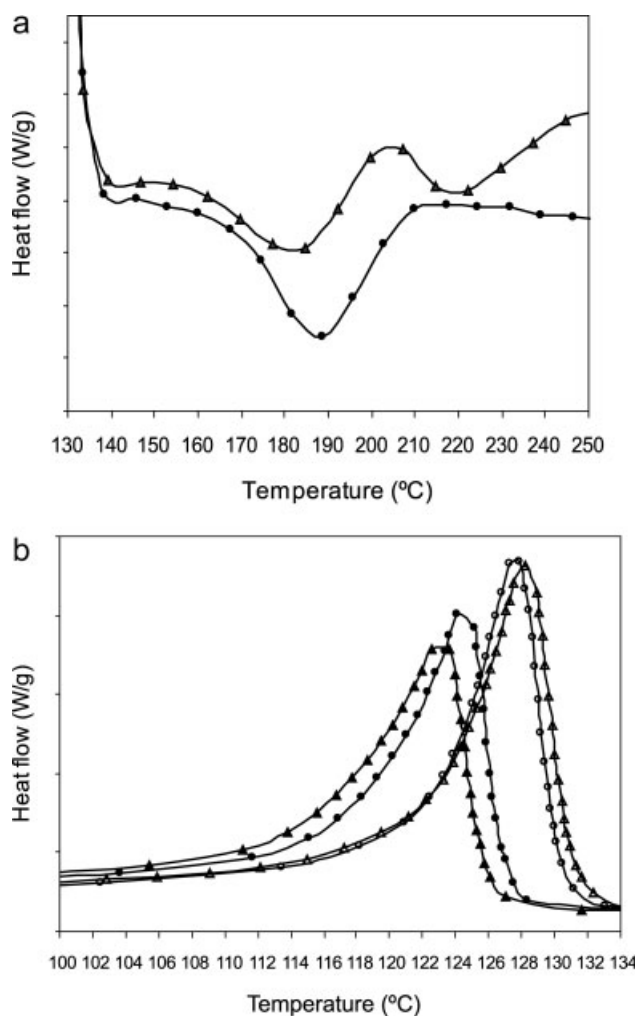
respective binary mixtures with PE coincide with the corresponding peaks of the pure chemicals (182.0°C for DCP and 218.8°C for ADC) in the ternary mixture.

The effect of the DCP concentration on the cross-linking degree was investigated by the determination of the melting peak temperature for the second heating run and the degree of crystallinity versus the peroxide concentration (Fig. 4). The maximum reduction in the melting peak is around 4%, and the sharpest drop in crystallinity with respect to the pure polymer is about 18%. The decomposition heat of the peroxide in these ternary blends has also been measured; it increases with the DCP concentration, in good agreement with the literature.<sup>13</sup>



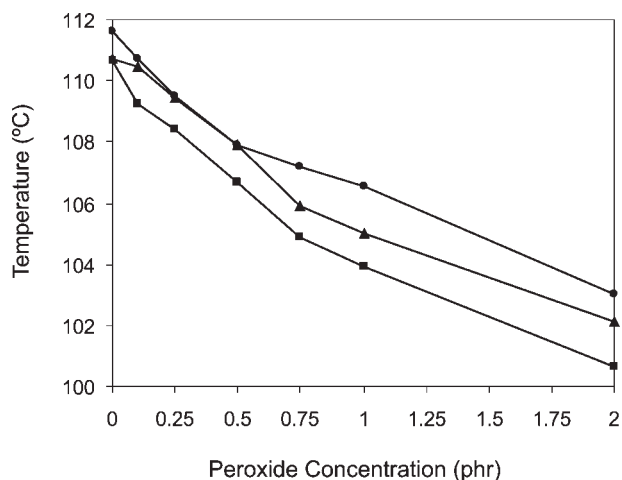
**Figure 4** (■) Melting peak temperature (second heating) and (▲) crystallinity versus the peroxide concentration for the ternary sample PE + DCP + ADC (1 phr).

ZnO was added to the former formulation to study the effect of the blowing agent decomposition temperature in the foaming process. In this case, the ADC peak is shifted to lower temperatures until it overlaps with the peroxide decomposition peak [Fig. 5(a)]. The decomposition enthalpy of the quaternary blend (-7.3 J/g) is close to the addition of the enthalpies of the DCP (-4.7 J/g) and ADC peaks (-3.0 J/g) in the ternary mixture. Figure 5(b) shows that the decrease in the peak temperature and melting enthalpy between the first and second heating runs for the quaternary blend is not as marked as in



**Figure 5** (a) DSC curves for the ternary and quaternary mixtures over the temperature range corresponding to DCP and ADC decomposition (first heating scans): (▲) PE + DCP (1 phr) + ADC (1 phr; 182.0°C, -4.7 J/g; 218.8°C, -3.0 J/g) and (●) PE + DCP (1 phr) + ADC (1 phr) + ZnO (1 phr; 186.5°C, -7.3 J/g). (b) DSC curves for the ternary and quaternary mixtures: (△) PE + DCP (1 phr) + ADC (1 phr; first heating scan, 128.2°C, 139 J/g), (▲) PE + DCP (1 phr) + ADC (1 phr; second heating scan, 123.1°C, 107 J/g), (○) PE + DCP (1 phr) + ADC (1 phr) + ZnO (1 phr; first heating scan, 127.6°C, 128 J/g), and (●) PE + DCP (1 phr) + ADC (1 phr) + ZnO (1 phr; second heating scan, 124.6°C, 115 J/g).





**Figure 6** Crystallization peak temperatures for the three sets of samples processed at 250°C versus the peroxide concentration: (■) D250 (PE + DCP), (▲) DA250 [PE + DCP + ADC (1 phr)], and (●) DAZ250 [PE + DCP + ADC (1 phr) + ZnO (1 phr)].

the case of the ternary blend. This fact involves a reduction in the degree of crosslinking for the quaternary blend, although it contains the same peroxide concentration (1 phr), showing a certain interaction between DCP and ZnO.

#### Calorimetric analysis of the processed samples

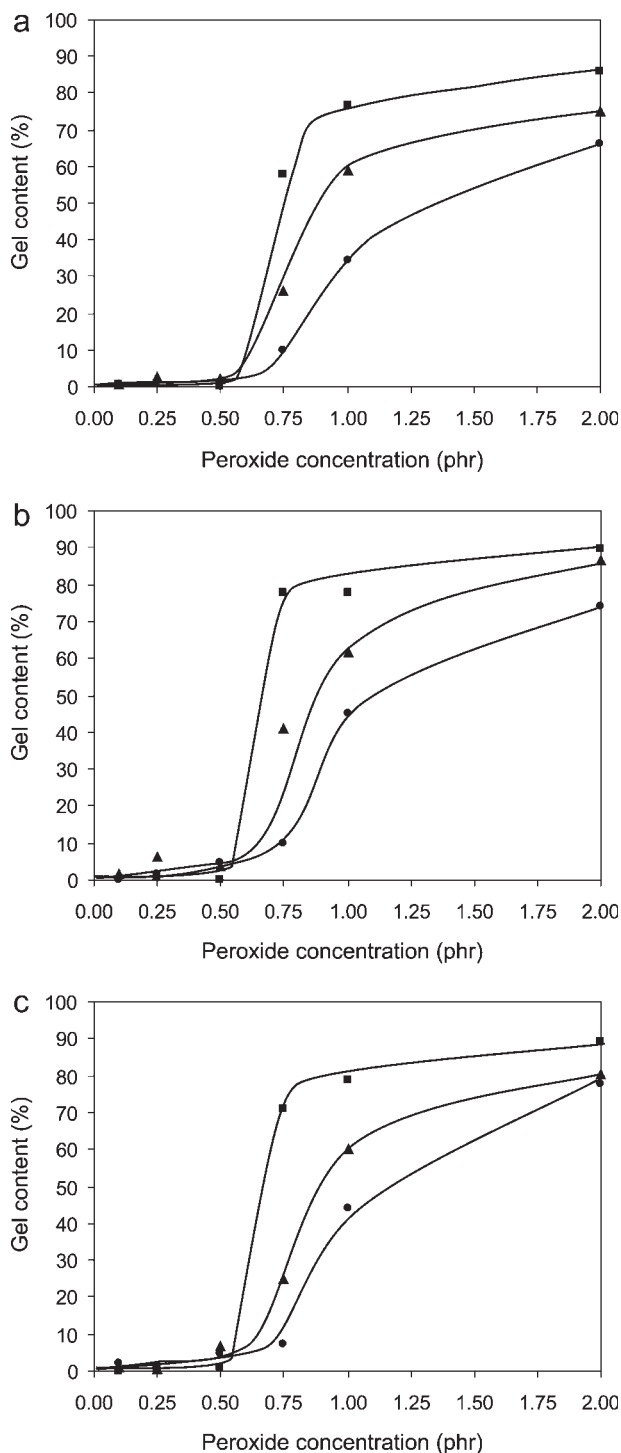
Figure 6 shows the crystallization peak temperature versus the peroxide concentration for the three sets of samples processed at 250°C. The crosslinking degree has been monitored by the study of the crystallization peak temperature during the remelting step. In good agreement with the literature,<sup>14</sup> the obtained results show that the crystallization temperature decreases with increasing peroxide concentration; this involves a decrease in the crystallinity degree. The crystallization peak temperatures for the samples containing ZnO (DAZ250) are the highest, and this also reveals that ZnO has a negative effect on the crosslinking degree, as observed previously.

#### Gel content of the processed samples

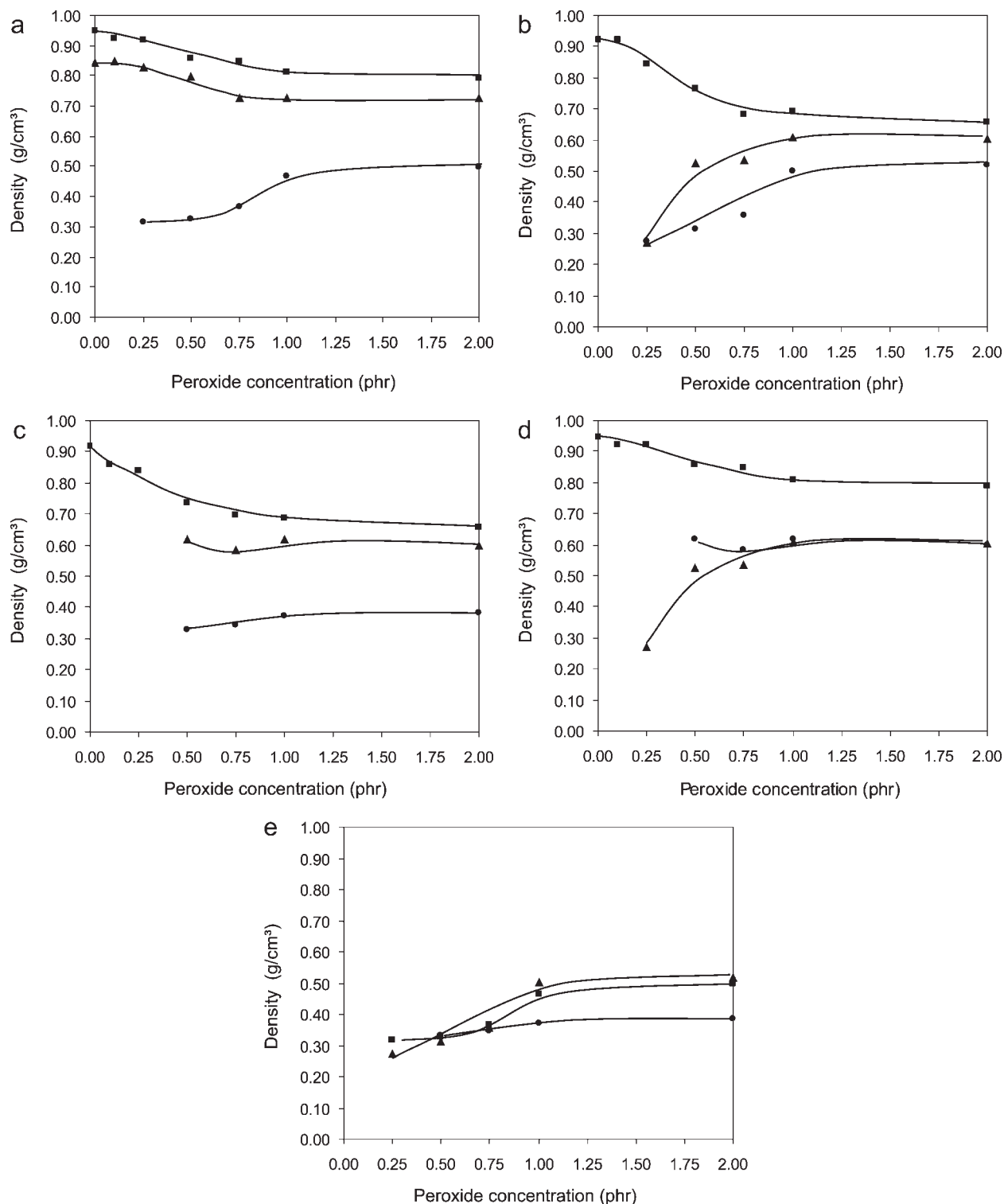
Figure 7 shows the gel content as a function of the peroxide concentration for all the samples. The gel content of the samples containing only peroxide (D160, D200, and D250) is similar to values reported by other authors.<sup>15,16</sup> As stated previously,<sup>17</sup> samples with a DCP concentration lower than 0.5 phr have a very low gel content.

Gel contents determined for samples with ADC are slightly lower than those for samples containing only peroxide, and this indicates that some of the intermediate products of ADC decomposition may

react with peroxide radicals. This effect could not be observed in the DSC experiments. With ZnO, the effect is more marked, and the gel content evolution



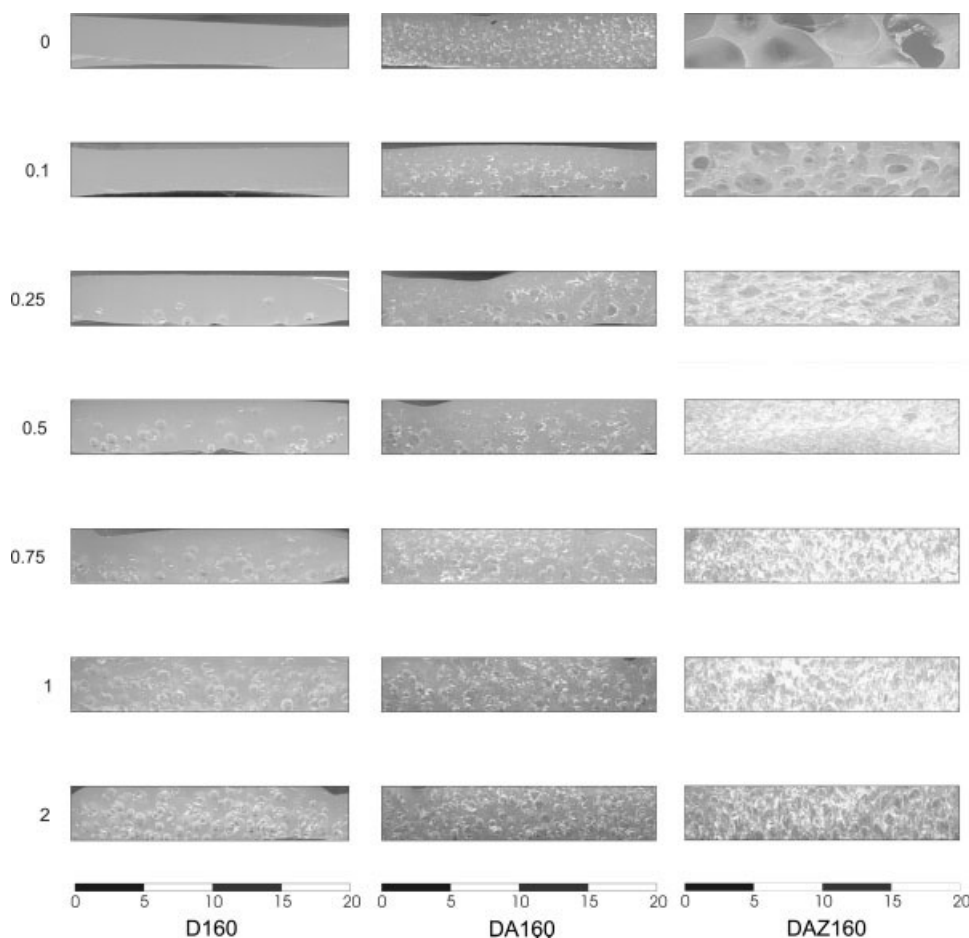
**Figure 7** (a) Gel content versus the peroxide concentration for the sets of samples cured at 160°C: (■) D160, (▲) DA160, and (●) DAZ160. (b) Gel content versus the peroxide concentration for the sets of samples cured at 200°C: (■) D200, (▲) DA200, and (●) DAZ200. (c) Gel content versus the peroxide concentration for the sets of samples cured at 250°C: (■) D250, (▲) DA250, and (●) DAZ250.



**Figure 8** (a) Density versus the peroxide concentration for the sets of samples cured at 160°C: (■) D160, (▲) DA160, and (●) DAZ160. (b) Density versus the peroxide concentration for the sets of samples cured at 200°C: (■) D200, (▲) DA200, and (●) DAZ200. (c) Density versus the peroxide concentration for the sets of samples cured at 250°C: (■) D250, (▲) DA250, and (●) DAZ250. (d) Density versus the peroxide concentration for the sets of samples with DCP and ADC: (■) DA160, (▲) DA200, and (●) DA250. (e) Density versus the peroxide concentration for the sets of samples with DCP, ADC, and ZnO: (■) DAZ160, (▲) DAZ200, and (●) DAZ250.

pattern is shifted to higher peroxide concentrations. For example, at a DCP concentration of 1 phr, the average gel content for the three samples with only

peroxide is 77.7%. At the same level of DCP, the average value is 60.3% (a 22% decrease) for the samples with DCP and ADC and 41.2% for the samples



**Figure 9** Images of the cross sections for the three sets of samples cured at 160°C (scale bar in millimeters).

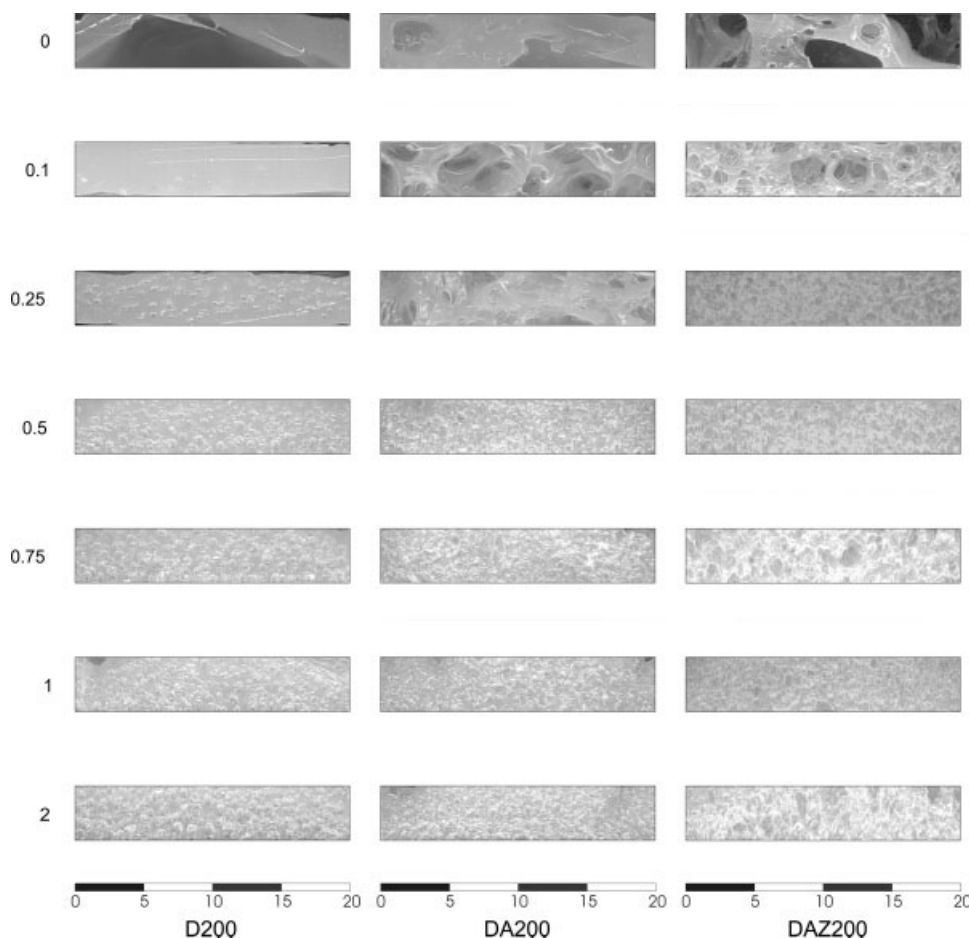
with DCP, ADC, and ZnO (a 47% reduction). This fact is very important for using the appropriate peroxide concentration to obtain the desired crosslinking degree.

#### Density of the processed samples

Figure 8 shows the density of PE samples with different DCP concentrations processed at different temperatures.

In Figure 8(a), it is possible to observe densities of different sets processed at 160°C. D samples show a mild density decrease as the peroxide concentration increases because some of the products formed by peroxide decomposition are gaseous at this temperature. According to Gulmine and Akcelrud,<sup>6</sup>  $\alpha$ -methylstyrene, acetophenone, and cumyl alcohol are released (the latter two have a boiling point of 202°C, whereas the former boils at 165.4°C) during peroxide decomposition. Densities of DA samples are slightly lower than those of the D series because some ADC has already been decomposed, although samples have a marked yellowish color. In this case, the density also decreases with the peroxide concen-

tration because most of the gases that have evolved come from peroxide decomposition. The observed trend for DAZ samples is somewhat different; in this case, ZnO causes an advance in the temperature of ADC decomposition, and in accordance with the images in Figure 9, foaming has taken place at a high degree. In this case, when the peroxide concentration is too low (i.e., 0 or 0.1 phr peroxide), samples present huge bubbles in which their coalescence is evident and the quality of the foams obtained is very poor; it may even be hard to consider such products as foams. For this reason, the measured densities lack physical meaning because if coalescence does not occur and the foam collapses, the densities cannot be determined. Consequently, these have not been included in Figure 8(a). Although above 0.1 phr peroxide the gel content is relatively low, this low crosslinking degree causes an increase in the melt strength high enough to avoid bubble coalescence, yielding densities of around 0.30 g/cm<sup>3</sup>. At higher peroxide concentrations, crosslinking readily takes place [the gel content is ca. 10% at 0.75 phr peroxide; Fig. 7(a)], and the consequent increase in the melt viscosity hinders the foaming process



**Figure 10** Images of the cross sections for the three sets of samples cured at 200°C (scale bar in millimeters).

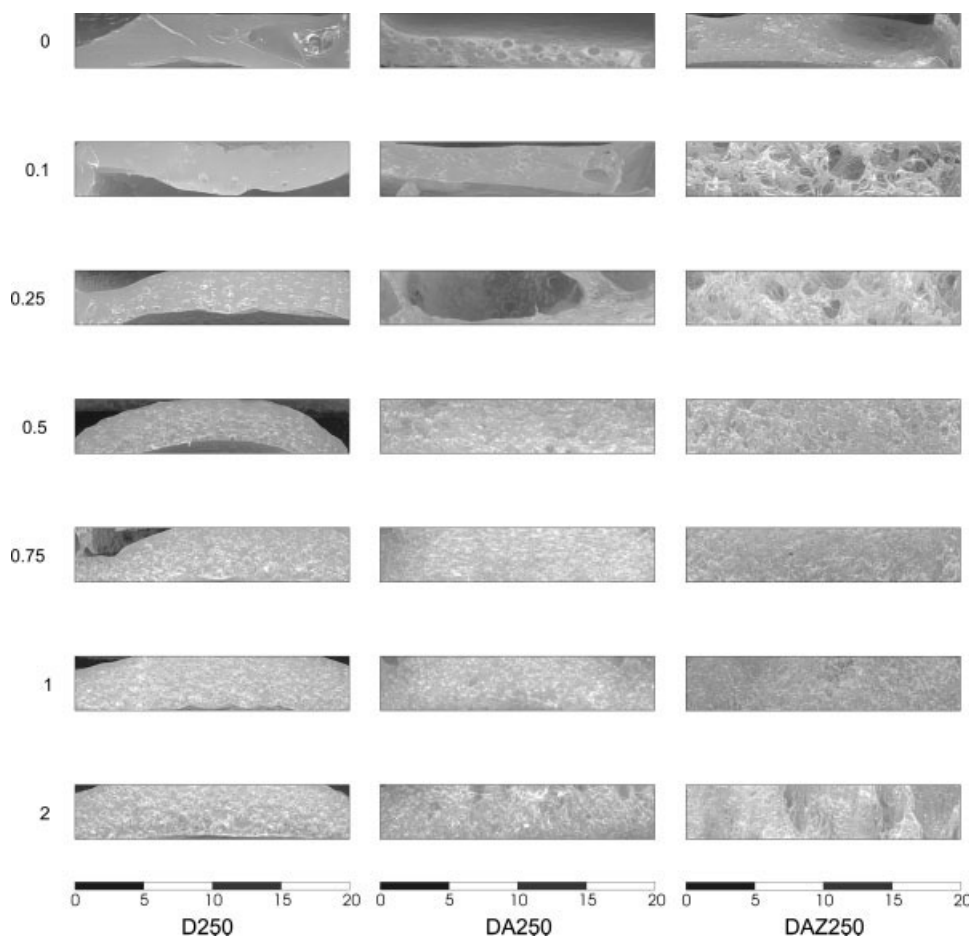
because bubbles have to grow in a polymer whose strength is markedly higher than that at lower peroxide concentrations. Above 0.75 phr peroxide, this causes the density to increase with the peroxide concentration until a point at which the polymer is so crosslinked (1 phr peroxide) that the foam density is independent of the peroxide concentration.

The behavior of samples processed at higher temperatures [Fig. 8(b)] can be explained in similar terms. D200 samples, similarly to D160, also decrease with the peroxide concentration because of gaseous species released from peroxide decomposition. The former samples have slightly lower densities, as expected, because at higher temperatures, these gases have a higher volume, and hence foams with lower density are obtained. At 200°C, ADC decomposition readily takes place in all DA samples, and the same coalescence effect appears. At low peroxide concentrations, coalescence is also evident, and in some cases, the foam seems to have been formed and partially (0.1 phr peroxide) or totally (0 phr peroxide) collapsed; these values have also been omitted in Figure 8(b). Above 0.1 phr peroxide, a trend similar to that in DAZ160 samples is observed: the

density increases with the peroxide concentration. Low crosslinking degrees or gel contents [Fig. 7(b)] impart enough strength to the polymer melt that at 0.25 phr peroxide, bubble coalescence seems to have been avoided, but as the melt strength increases with the peroxide concentration, the foam density also increases. In fact, samples with a peroxide concentration above 0.5 phr show foams with tiny bubbles (Fig. 10). DAZ samples present the same trend, although the densities are lower, probably because of two different factors: the volume of gases released in the presence of the catalyst is significantly higher, and according to gel content data [Fig. 7(b)], the crosslinking degree of DAZ samples is lower than that of the DA samples (consequently, they have a lower melt strength).

At higher temperatures [Fig. 8(c)], D250 samples present the same trend as the D200 and D160 series, but with lower densities, because at this temperature, acetophenone and cumyl alcohol are approximately 50°C above their respective boiling points at the same time that the gas expansion is more prominent, and hence bigger bubbles and lower densities are produced.





**Figure 11** Images of the cross sections for the three sets of samples cured at 250°C (scale bar in millimeters).

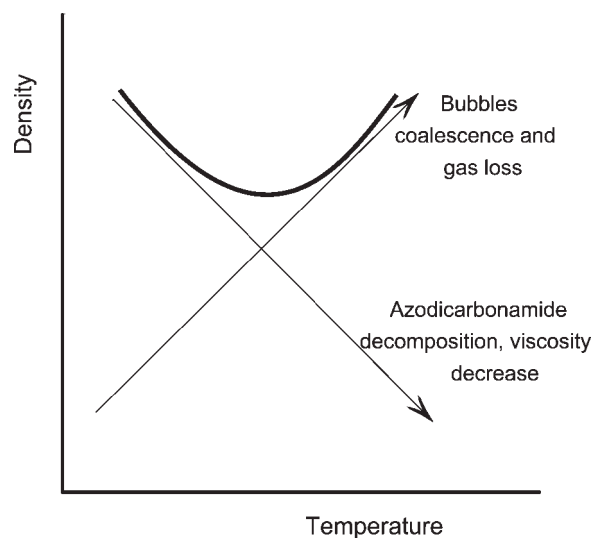
When ADC is present, bubble coalescence at this temperature becomes more prominent, and even a peroxide concentration of 0.5 phr does not cause a viscosity increase high enough to avoid coalescence, as occurs at 200°C. This is the reason that densities of DA250 and DAZ250 samples with a peroxide concentration below 0.50 phr are not reported in Figure 8(c). Above this concentration, the observed density trend is similar to that of the 200°C curves. The DA density curve is located at higher density levels than the DAZ curve for the reasons stated previously: the lower gel content levels of DAZ specimens and the higher volume of gases released when ZnO is present. Furthermore, the nucleating effect of ZnO is clear in the DAZ200 and DAZ250 samples in view of the higher uniformity of foams generated (Figs. 10 and 11). Similarly to the 200°C case, the density of both the DA and DAZ samples increases with the peroxide concentration because crosslinking is progressively taking place, with the restriction that it involves bubble growth.

It is also worth mentioning the behavior of DA samples presented in Figure 8(d). It is possible to observe that 200°C is an optimum temperature from

the point of view of foam density. At 160°C, ADC decomposition has taken place to a very low extent, and densities are consequently relatively similar to those of D samples. At 200°C, ADC decomposition has already occurred, but at 250°C, the gases produced have been released so fast and they occupy such a high volume that some could have been lost during the process, losing part of the foaming effectiveness (Fig. 12).

When the behavior of DAZ samples is analyzed [Fig. 8(e)], the optimum temperature is found to be located at 250°C, instead of 200°C. In this case, the nucleating effect of the catalyst could be responsible for the creation of a higher number of bubbles, in good agreement with images of Figure 11, in which the gas is uniformly distributed, making difficult the creation of huge bubbles and disabling in a certain way the gas loss.

In conclusion, all the obtained results indicate that the synchronization between foaming and crosslinking processes should be ensured to obtain low-density foams with a good cell distribution. Crosslinking can help in controlling bubble growth and coalescence, but when it occurs to a high degree, it



**Figure 12** Effect of temperature on the foam density.

actually contributes to increasing densities. The case of DAZ specimens is a clear example demonstrating that crosslinking can be a useful way of controlling foam densities in processes in which a low pressure is applied, if it is conveniently coupled with the blowing agent decomposition process.

### CONCLUSIONS

Although PE crosslinking via peroxide at atmospheric pressure can prevent bubble formation, it can be used to control PE foaming. Bubble coalescence and gas loss have been controlled by increases in the PE melt strength with the DCP concentrations above 0.5 phr. The use of ZnO has allowed the simultaneous decomposition of DCP and ADC, leading to a controlled foam expansion in which bubble formation occurs at lower temperatures and with an

adequate level of crosslinking, which leads to the processed foams with the lowest densities. The studied systems have allowed a likely explanation to be provided for the abnormal behavior detected at low peroxide concentrations. It has been demonstrated that ZnO reduces the gel content of the processed samples by around 30% (with respect to the sample that contains only DCP and ADC), and therefore it is necessary to increase the concentration of the peroxide to obtain the same level of gel content.

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