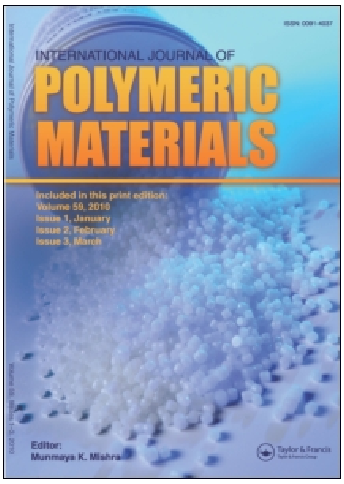

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Effect of the addition of chemical blowing agents on the processability of a rigid PVC compound

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EFFECT OF THE ADDITION OF CHEMICAL BLOWING AGENTS ON THE PROCESSABILITY OF A RIGID PVC COMPOUND

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This work deals with the effect of the addition of a combination of two chemical blowing agents (BA), azobisformamide (ABFA) and/or sodium bicarbonate (SBC), on the processability of rigid polyvinylchloride (PVC) using a Brabender torque rheometer. This technique was previously used under conditions bearing no relation to real polymer processing. Our contribution is to overcome this problem and to provide a complementary understanding. It was found that the addition of BA separately leads to the appearance of a new peak following the melting peak on the Brabender torque rheometer process curve. On the other hand, two distinct peaks were shown when both BAs are added together. These peaks correspond to the decomposition of the BA and the expansion of the resulting cells. From this study, the Brabender torque rheometer has proven to be a valuable new tool to follow the stages of decomposition of the BA and the cell expansion within an environmental polymeric resin under real processing conditions.

Keywords: Poly(vinylchloride), azobisformamide, sodium bicarbonate, decomposition expansion and torque rheometer

INTRODUCTION

With the continuous improvement in PVC compound and the requirement for improved performance, the need for better laboratory

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techniques for evaluating PVC compounds is necessary [1]. In practice, the processability of PVC compounds is generally evaluated on a Brabender torque rheometer, since this apparatus simulates the conditions of temperature and shear that occur during processing. For that reason, this tool was chosen in our study, which deals with the behavior of two chemical blowing agents in a rigid PVC compound under processing conditions.

THEORY

Many techniques have been reported as satisfactory for the evaluation of solid chemical blowing agent systems [2–5], but they mainly refer to decomposition temperature and gas volume in the pure state. Work on the effect of formulated compound ingredients refers mainly to plastisol technology [6], and little information is available on decomposition under pressure [7,8]. Many studies have been reported using Brabender torque rheometer on cellular PVC; for instance the evaluation of the hot melt properties of cellular plastisol [9], the dynamic heat stability of expanded semi–rigid PVC [10], and the decomposition behavior of ABFA in a rigid PVC compound [11].

Before discussing the data of the effect of BA on the processability of a rigid PVC compound, a review of the Brabender torque rheometer process curve for an unfoamed rigid PVC compound with critical points is necessary [1] (see Figure 1). Point 0 is the starting point, where the mixer is empty, i.e. a free rotating rotor, resulting in zero torque. When a quick (sudden) loading chute was applied to compress the sample in powder state against the rotors, a high torque value was temporarily recorded (point 1). Then the torque was reduced rapidly due to the free flowing of dry-blend particles, to reach a minimum torque value (point 2). Beyond this point, particles start to fuse, resulting in a fused layer of the compound, limiting sample and metallic surfaces, where high shear stresses were applied, allowing the torque to increase until point 3. At this point, the compound is in a molten state (complete fusion) and still absorbing heat, resulting in the reduction of viscosity of the system, hence the torque is reduced till point 6. Point 6 is the portion of the curve referred to as equilibrium. At this period, the melt is homogenous. Point 7 is defined as the onset of cross-linking or degradation: it determines the ultimate stability of the compound. This point is defined by the intersection of the slope of the upturning torque and the equilibrium torque. Stability time is the difference between degradation time (point 7) and the fusion time (point 3) [1].

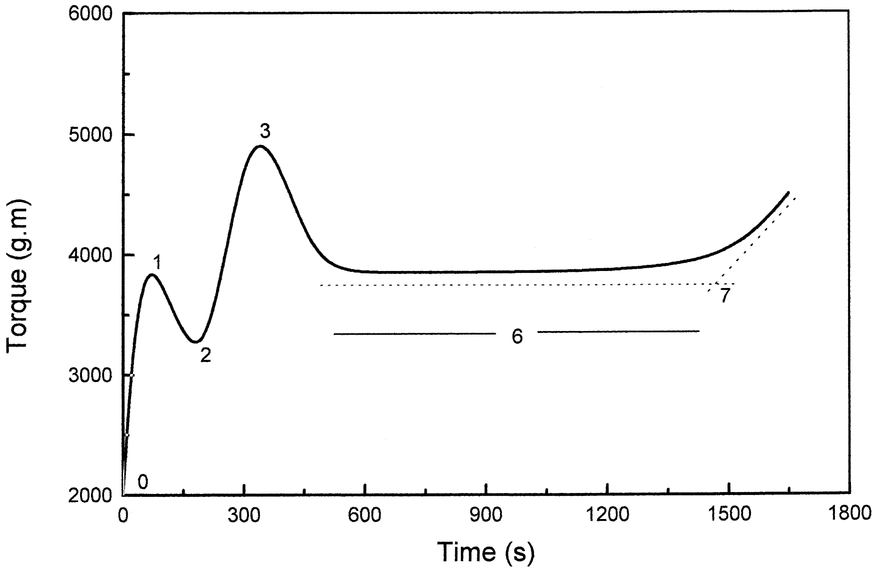

FIGURE 1 The Brabender torque rheometer process curve for an unfoamed rigid PVC compound [1].

NB: The transition from point 3 directly to point 6 is justified by the fact that expanded formulations will present two critical points (point 4 and point 5) before the equilibrium portion (point 6).

EXPERIMENTAL

The sample preparation consists mainly of blending all the ingredients with PVC in a kitchen mixer at full mixing speed for 10 minutes to give a yellow, dry, free–flowing powder (in the absence of ABFA, a white dry-blend was obtained). Once the temperature and roller speed are adjusted (T = 180°C, V = 30rpm), the desired amount of sample, corresponding to 65 g, was charged into an oil–heated Brabender type W 50 roller mixer. Then torque as function of time is recorded.

RAW MATERIALS

The materials employed in this work are:

1- Poly(vinylchloride): A suspension grade PVC was used, whose properties are as follows:
  - Trade name: 4000 LL(ENIP Skikda-Algeria).

- K-value: 55-57
- Degree of polymerization: 570-620
- Apparent density: 0.52-0.57

2- Thermal stabilizers: A combination of dibasic-lead-phosphite and dibasic-lead-stearate were used.

3- Lubricants: dicarbonic-acid-ester was used as an internal lubricant and non-polar hydrocarbon wax as an external one.

4- Blowing agents: azobisformamide (VINSTAB AZ3-HEBRON) was used as an organic BA (exothermic decomposition reaction). Sodium bicarbonate (NORMAPUR) was used as an inorganic BA (endothermic decomposition reaction).

DISCUSSION

In the Brabender torque rheometer test method for the evaluation of chemical blowing agent [11], the BA was added when the resin melted. Whereas, during processing at an industrial scale, it should be dry-blended with all the ingredients constituting the formulation before being fed to the hopper machine, C. Beaning et al. [11] specified that if this done, there will be a gas loss due to decomposition of BA on hot walls of mixer.

Our contribution was to overcome this problem and to get closer to real processing conditions, i.e. adding the BA with the resin at the same time. This was carried out by melting the compound before decomposing the BA. The former operation was adjusted by varying the concentration of external lubricant and the latter was done by varying that of the thermal stabilizer, which acts as ABFA kicker. In order to check if melting really occurs first, samples were taken from the Brabender mixer, while a run was underway, and their colors were examined: at the melting point (see Figure 2), the sample was still yellow (initial color). This is due to the non-decomposition of the ABFA, which is an orange powder, and when blended with PVC, it will result in yellow dry-blend. The latter will turn white after decomposition of the BA. Furthermore, it was noticed that the addition of the BA would result in a sharp drop of the torque, occurring just after the melting point (see Figure 2). This is directly related to the exothermic decomposition of the BA, resulting in a rise of stock temperature, leading to a decrease in viscosity, and thus a rapid reduction in torque.

On the other hand, the increase in torque reported by C. Benning et al. [11] was attributed to crosslinking, which is due to free radicals generated during decomposition of ABFA, while the decrease in torque

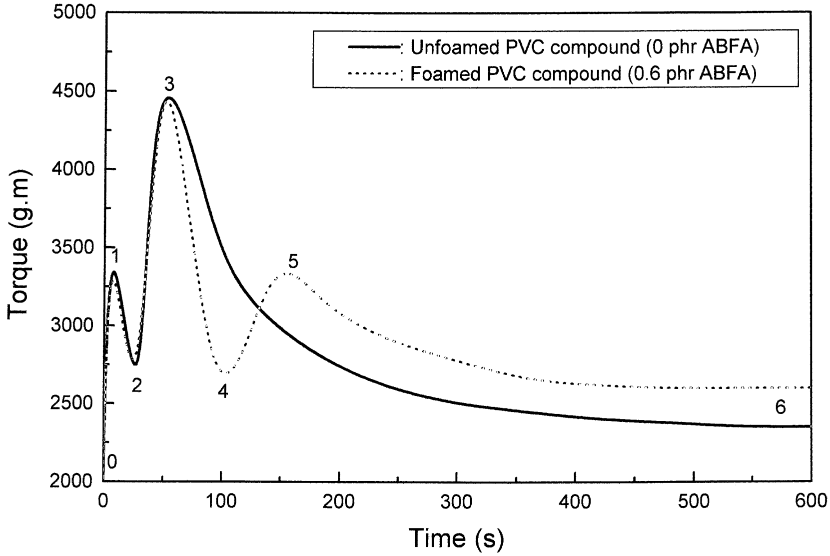

FIGURE 2 Torque evolution as a function of time.

indicated degradation or slippage, which is due to lubricants being present (see Figure 3).

Our explanation of the increase in torque is due to the fact that gas bubbles, which were dissolved in molten polymer matrix, start expanding (point 4) (see Figure 4). Therefore, high pressure on the rotors was exerted, exhibiting a torque increase to an optimum value (point 5).

This assumption is in good agreement with a substantial decrease in sample density (see Figure 4) (samples were also taken from the mixer while a run was underway and evaluated in term of density). Beyond this point, the torque decreased. This is due to a part of gas that escaped to the atmosphere during the course of the run, which was the consequence of cell interpenetration under high shear deformation, since we are dealing with an almost open mixer. This phenomenon was still taking place until most of the gas was removed from the molten matrix. For that reason, the torque was reduced. This assumption was also supported by the increase in sample density.

On the other hand, the substitution of ABFA (which exhibits an exothermic decomposition reaction) by SBC (which decomposes endothermically) (see Figure 5) has proven that there is no crosslinking related to the increase in torque reported by C. Benning et al. [11].

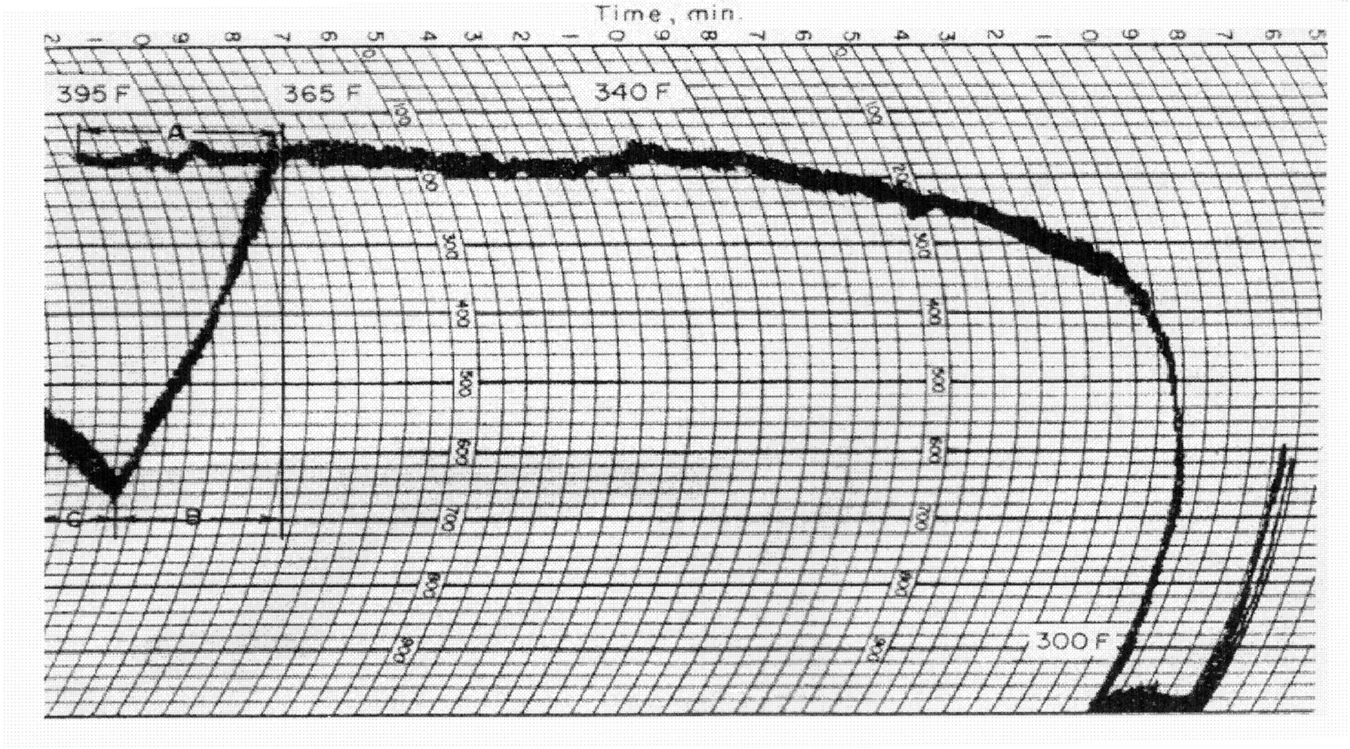

FIGURE 3 Torque evolution as a function of time [11].

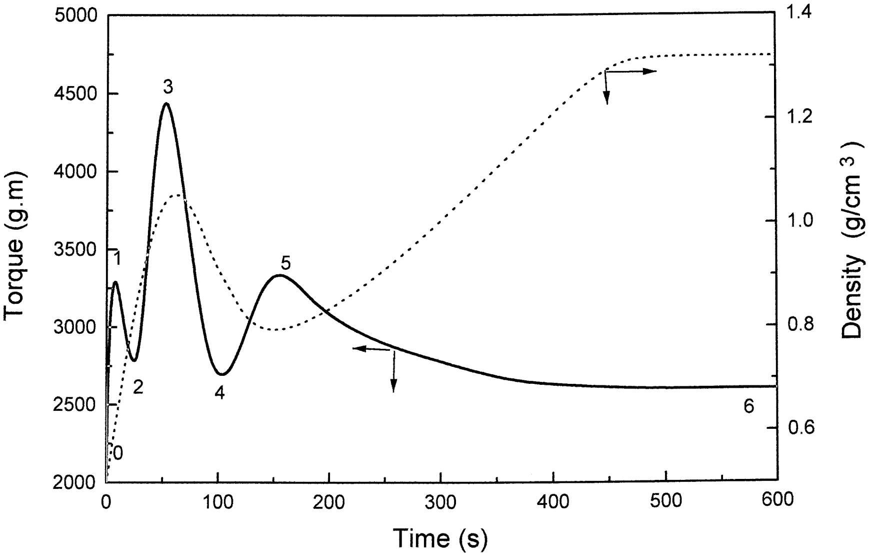

FIGURE 4 Torque and density evolution as a function of time (0.6 phr ABFA).

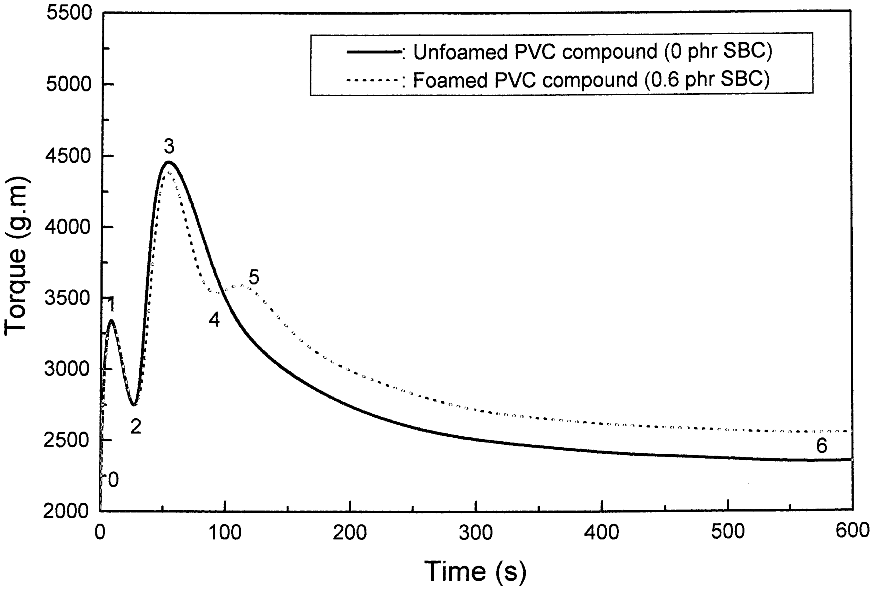

FIGURE 5 Torque evolution as a function of time.

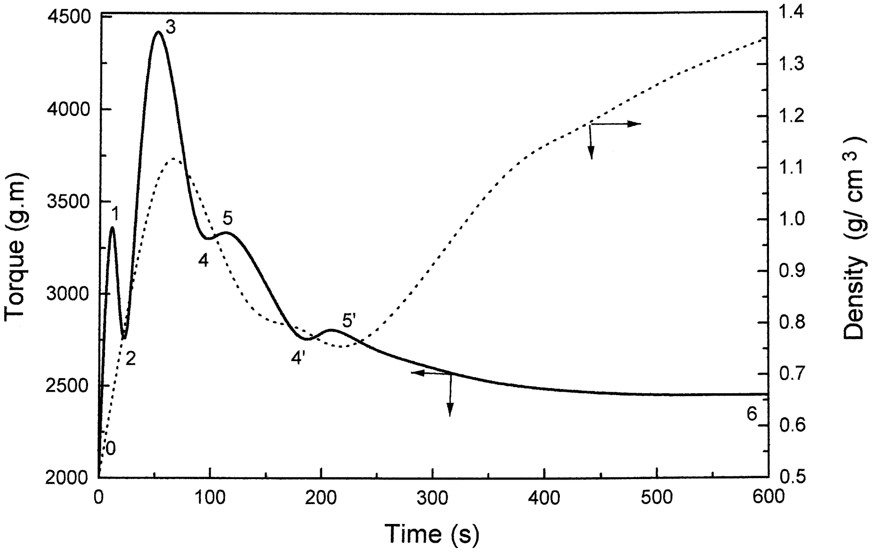

FIGURE 6 Torque and density evolution as a function of time (0.3 phr SBC + 0.3 ABFA).

Finally, when a combined use of two BA was done, two distinct peaks were shown (see Figure 6). In order to identify the origin of each peak, a variation of level of one of the BA was elaborated. By this, the first one was identified to correspond to the SBC, and it was almost within the same range of time as observed when used alone. However, that of the ABFA was delayed to higher time. This shifting can be explained by the fact that when SBC started decomposing endothermically [12], the temperature of the system decreased, leading to the delay of the decomposition of ABFA, which is time and temperature dependent [12].

CONCLUSION

The Branbender torque rheometer was shown, from this work, to be a versatile tool in the vinyl industry. Its use in our investigation has proven how valuable this technique can be in helping to understand the behavior of rigid PVC compound loaded with BA, by following the stages of decomposition and cell expansion.

An addition of BA leads to the appearance of a new peak after melting one on the Brabender torque process curve.

Two distinct peaks were shown when a combined use of two BA was carried out.

REFERENCES

[1] Hawkins, T. (1982). *Journal of Vinyl Technology*, **4**, 110.

[2] Reed, R. A. (1955). *Chemistry of Modern Blowing Agents, Plast. Progress, British Plastics Conf.*

[3] Cram, D. J., Lavendor, C. M., Reed, R. A. and Scholfield, D. (1962). *Brit. Plastics*, Sept.

[4] ASTM D1715, *Method of Test for Gas Evolved from Chemical Blowing Agents for Cellular Plastics.*

[5] Hansen, R. H. (1962). *SPE Journal*, **80**, 181.

[6] Lally, R. E. and Alter, L. M. (1967). *SPE Journal*, Nov.

[7] Collington, K. T. (1973). *Plastics and Polymers*, Feb.

[8] Collington, K. T. (1975). *Journal of Cellular Plastics*, **1**, 213.

[9] Buckley, C. D. (1971). *Journal of Cellular Plastics*, **1**, 23.

[10] Tu, C. F. (1978). *Journal of Cellular Plastics*, **1**, 92.

[11] Benning, C. and Grace, W. R. (1967). *Plastics Technology*, **13**, 56.

[12] Nass, I. L. and Heiberger, C. A. (1975). *Encyclopedia of PVC*, 2nd edition, volume 2, (New York: Marcel Dekker), pp. 618–623.