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STUDY THE INFLUENCE OF FILLING ON FOAMING PROCESS OF RIGID PVC COMPOSITES

**Tahseen A. Saki[1,2], post-graduate student, A.V. Markov[1,@], professor,
E.V. Tokareva[1], student, E.Yu. Vatskova[1], student**

*[1] Department of Chemistry and Technology for Processing of Plastics and Polymeric Composites,
M.V. Lomonosov Moscow State University of Fine Chemical Technologies,
Moscow 119571 Russia
[2] Department of Chemistry, College of Science,
University of Basrah, Basrah, Iraq
[@] Corresponding author e-mail: markovan@bk.ru*

Foaming of rigid PVC composites filled with chalk by azodicarbonamide was studied. Cross-linking PVC and increase in PVC viscosity during filling were found to have the greatest impact on foaming.

Keywords: *polyvinyl chloride, rigid composites, thermal stability, azodicarbonamide, foaming ratio, filling, chalk.*

ИССЛЕДОВАНИЕ ВЛИЯНИЯ НАПОЛНЕНИЯ НА ПРОЦЕСС ВСПЕНИВАНИЯ ЖЕСТКИХ ПОЛИВИНИЛХЛОРИДНЫХ КОМПОЗИЦИЙ

**Тахсин А. Саки[1,2], аспирант, А.В. Марков[1,@], профессор,
Е.В. Токарева[1], студент, Е.Ю. Вацкова[1], студент**

*[1] Кафедра химии и технологии переработки пластмасс и полимерных композитов,
МИТХТ им. М.В. Ломоносова, Москва 119571 Россия
[2] Кафедра химии, Басра университет, Басра, Ирак
[@] Автор для переписки, e-mail: markovan@bk.ru*

Исследован процесс вспенивания жестких наполненных мелом ПВХ-композиций с использованием азодикарбонамида. Установлен приоритет влияния на процесс вспенивания образцов увеличения вязкости ПВХ при наполнении и структурировании поливинилхлорида.

Ключевые слова: *поливинилхлорид, жесткие композиции, термостабильность, азодикарбонамид, вспенивание, наполнение, мел.*

Introduction

Fillers are the special-purpose additives since they serve not only for the modification of properties of polymer materials (for example, rheological and physical-mechanical characteristics, inflammability, electric resistance, and so on), but also for the decline in value of the end product due to decrease in consumption of polymers. This factor plays a significant part in the development of rigid PVC composites [1]. The change in rheological and physical-mechanical properties of filled materials based on PVC is governed, to a large extent, by the interaction of a polymer with a filler and by the decrease in mobility of macromolecules at the boundary layer of a polymer [2, 3]. The most widely used filler in PVC composites is chalk. In addition to low price and availability, chalk is characterized (as a filler) by the following advantages: nontoxicity, absence of odor, white color, low abrasiveness, low water absorption ability, ability to absorb hydrogen chloride and to exert a secondary stabilizing effect on PVC [1]. The filler content usually amounts 30–50 parts by weight per 100 parts by weight of PVC.

Foaming (including that of filled polymers) is another important way to decrease the value of plastic products [4, 5]. Although combination of these methods can greatly improve economic efficiency of manufacture of rigid PVC products, introduction of fillers may lead to increase in structure imperfection for cellular materials [5, 6]. Increase in the filler content can bring about processing difficulties due to considerable rise in melt viscosity. Characteristics of a cellular material in such foamed composites are not necessarily deteriorated when introducing chalk [7].

In turn, azodicarbonamide is the most widely used chemical pore-former (i.e. foaming agent) for PVC [8]. It was stated that the products of PVC thermal decomposition might affect the activity of azodicarbonamide [9, 10].

The goal of this work is to reveal the features of foaming (using azodicarbonamide) for rigid PVC composites filled with chalk.

Subjects and Methods of Research

This work deals with polymeric composites PVC S-6359 (ZAO “Kaustik”, Russian Federation). Azodicarbonamide (ADCA) Azobul (Arkema, France) was used as the foaming agent in amounts of 1 part by weight per 100 parts by weight of polyvinyl chloride (hereinafter referred to as “phr”). All PVC composites also contained at least 4 phr of tribasic lead sulfate (TBLS) Akstab PB KLSS (Akdeniz, Turkey) as the main heat stabilizer of polyvinyl chloride. Powder of natural enriched chalk MMOP (in accordance with GOST 12085-88) was used as the filler in an amounts of 5–30 phr. The mixture was plastified and then homogenized in a Brabender plastograph at a temperature of 170^{o}C (below its decomposition temperature) for 3 min. Kinetics of foaming was studied using an IIRT-2 instrument (in accordance with GOST 11645-73) equipped with the device for recording the vertical movement of the rod [6]. The sample of a composite was placed in the IIRT-2 working chamber on the plug between two fluoroplastic gaskets to prevent melt leakages. The tablets under study were kept in the chamber of an IIRT-2 instrument at constant temperature (200, 210, and 220°C) under the weight of 2.16 kg. To facilitate correlation of the results obtained at different temperatures (T) and pressures (P), the foaming ratio (F_{ratio}) was calculated using the volume of evolved gases reduced to standard conditions (0.1 MPa, 298 K) [11]:

$$F \qquad = \frac{V \ \ + v}{V} = 1 + \frac{hT \ \ M}{P} \tag{1}$$

where V_0 is initial tablet volume under normal conditions (m^3), v_0 is increment in tablet volume due to gases evolved during decomposition of the foaming agent, reduced to standard conditions(m^3), H is initial tablet height (m), h is measured increment in tablet height due to gases released during decomposition of the foaming agent under experimental conditions (m), S is cross-section of the working cylindrical chamber of IIRT instrument (m), M is load weight (N), P is pressure in the working chamber (P=P0+M/S, N/m^2), P_0 is atmospheric pressure (≈105 N/m^2), T is working temperature (K), T_0 is temperature 298 K.

Foaming potential of a foaming agent can be described in terms of the limit values of the foaming ratio (F_{limit}) for polymeric composites provided that viscous resistance of polymer melt and gas loss are absent. As in [9], such limit values were calculated at any specific time of foaming from the data on kinetics of gas evolution during ADCA decomposition [11] with due account for thermal expansion of a polymer in the rigid cylindrical chamber:

$$F_{\mathrm{limit}} = \rho/\rho_{\mathrm{T}} + Q_\tau \, \varphi\rho \tag{2}$$

where Q_τ is the volume (reduced to standard conditions) of gases (m^3) evolved from 1 kg of the foaming agent (the limit value of Q_τ is the gas number; the gas number of azodicarbonamide amounts to 0.200–0.220 m^3/kg), φ is the mass fraction of ADCA in a composite, ρ is the material density under standard conditions (~1400 kg/m^3 without regard to thermal expansion of a polymer), ρ_T is density of a polymer (kg/m^3) at the foaming temperature (T). To account for the influence of thermal expansion of the polymer, dilatometric measurements were performed for composites free of the foaming agent. It was found that ρ/ρ_T=1.09–1.10 in the studied temperature range. Based upon the equation (2), one can conclude that at 200–220^{o}C the maximum (full decomposition of ADCA, 1 part by weight per 100 parts by weight of PVC) values F_{max} (foaming potential of azodicarbonamide) for rigid PVC composites with out of kickers should not exceed 3.9–4.2.

Melt flow index (MFI) for PVC composites was determined in accordance with GOST 11645-73 at 200–220^{o}C with a standard weight of 21.6 kg using an IIRT instrument within the period of melt thermal stability. Thermal stability of melts for PVC composites was evaluated from the change in MFI. Melt heating period lasted up to the decrease in MFI by 15% from the maximum value was taken as the period of melt thermal stability ($\tau_{t.st.}$). The average period of melt thermal stability was found to be (9.5±0.4) min at a temperature of 200°C, (6.0±0.3) min at a temperature of 210°C, and (4.5±0.3) min at a temperature of 220°C.

Results and Discussion

Rigid PVC composites are characterized by high viscosity and low thermal stability of melts. Short periods of melt thermal stability limit process parameters for processing of polymer materials to low temperatures and short times. In turn, low temperatures and high values of melt viscosity can slow down foaming (growth of bubbles). The foam-filled PVC compounds [12] are even more problematic. Fig. 1 gives kinetic curves illustrating the influence of filling with chalk on the increase in the foaming ratio of PVC composites at a temperature of 210°C.

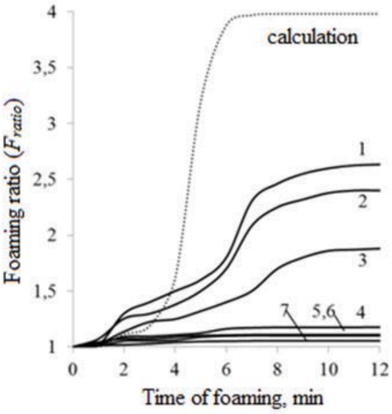

Fig. 1. Kinetics of foaming for rigid PVC composites containing 4.0 phr of TBLS and 1.0 phr of ADCA by weight of PVC with different content of chalk at a temperature of 210°C.
Symbols: 1 – 0; 2 – 5; 3 – 10; 4 – 15; 5 – 20; 6 – 25; 7 – 30 phr of chalk (the dotted curve describes the values calculated according to the equation 2).

Typical diagrams for foaming of PVC composites by azodicarbonamide can be divided into several regions [12]:

− induction period, sample heating, activation of ADCA decomposition;

− the first stage of foaming characterized by low rate;

− the second stage of foaming characterized by high rate;

− completion of foaming, attainment of constant volume “plateau” which corresponds to the maximum foaming ratio (F_{max}).

Foaming at the first stage is related to the beginning of ADCA decomposition, while accelerated foaming at the second stage is dictated by the evolution of hydrogen chloride (HCl) at the initial stage of PVC thermal degradation, which accelerates the decomposition of azodicarbonamide. In this case hydrogen chloride acts as a kicker for azodicarbonamide [12].

The experimental time dependencies of F_{ratio} are located below the calculated (according to the equation № 2) dotted curve due to high melt viscosity of PVC composites. As foaming temperature decreases, the maximum values of foaming ratio (F_{max}) decrease (see Fig. 2). The similar effect is observed for composites filled with chalk: the curves for filled composites are located below the curve for uncompounded PVC composite (see Fig. 1). The average foaming rate values (V_f) also decreases. The average foaming rate can be evaluated by means of the slope of curves (see Fig. 1) using the following equation:

$$V_f = F_{max}/(\tau_{max} - \tau_{ind}), \qquad (3)$$

where F_{max} – the maximum value of F_{ratio}, τ_{ind} – induction period (min), τ_{max} – time to F_{max} (min) including both stages of foaming. Decrease in values of the foaming rate is usually associated with slowdown in the growth of bubbles upon polymer viscosity increase. Growth rate of bubbles depends on melt viscosity (η) as follows [13, 14]:

$$R_\tau = R_\infty(1 - \exp(P\tau/\eta)) \qquad (4)$$

where Rτ and R∞ is the current at τ (s) and the final (equilibrium) values for the radius of a growing bubble (m), η is melt viscosity (Pa*s), P is gas pressure in a bubble (Pa) which increases up to the maximum level and then decreases to the atmospheric pressure in the wake of growth of bubbles. It should be noted that the level of Fratio values is governed not only by the volume of gases evolved during decomposition of azodicarbonamide (see Fig. 1, the dotted curve), but also by the increase in melt viscosity of a foaming composite due to thermal degradation and cross-linking of PVC upon heating [12].

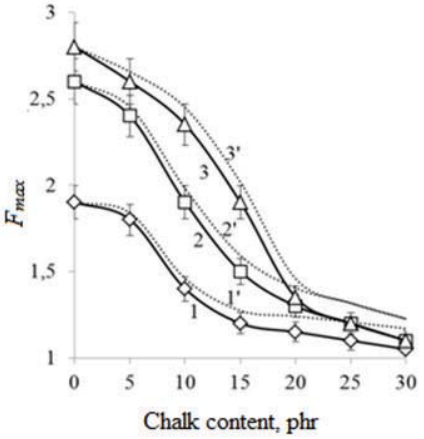

Fig. 2. Dependencies of the maximum values of foaming ratio (F_{max}) for rigid PVC composites on the content of chalk at different temperatures: 1,1’ – 200°C; 2,2’ – 210°C;3,3’ – 220°C (the dotted curves correspond to reduction of the values to the same volumetric content of ADCA in accordance with the equation 4).

Fig. 2 illustrates the influence of filling on the F_{max} values. Even at high temperatures the F_{max} values decrease rapidly with increase in the chalk content over 5–10 parts by weight. It should be noted that the percentage of azodicarbonamide in the bulk of a composite (while the ratio of 1 phr of PVC is kept constant) decreases slightly with increase in the chalk content during preparation of filled PVC composites. To eliminate this inconsistency, the F_{max} values were increased proportionally to the reduction of ADCA volumetric content in composites with increase in the chalk content (see Fig. 2, the dotted curves):

$$\varphi_{ADCA} = 100\rho\varpi_{ADCA}/(\rho_{ADCA}(\varpi_{PVC} + \varpi_{TBLS} + \varpi_{ADCA} + \varpi_{chalk})) \quad (5)$$

where φ_{ADCA} is ADCA content (vol.%); ω_{PVC}, ω_{TBLS}, ω_{ADCA}, ω_{chalk} is the content of the components (PVC, TBLS, ADCA, chalk) in parts by weight per 100 parts by weight of PVC; ρ_{ADCA} is azodicarbonamide density (1660 kg/m^3); ρ is density of a PVC composite (kg/m^3). Density of the filled PVC composites under study varies from 1410 to 1560 kg/m^3. In our case the volume percent of chalk changes from 4.6 to 22.2 (while ADCA content decreases from 0.43 to 0.38 vol.%) with an increase in the chalk content from 5 to 30 parts by weight. As evident from Fig. 2, no considerable change in the behavior of dependencies is observed after such adjustment.

As we might expect (see the equation № 4), decrease in the Fmax values is observed simultaneously with decrease in MFI of filled PVC composites (Fig. 3). It should be noted that MFI values determined within the periods of melt thermal stability (the maximum values of MFI) considerably decrease with increase in the chalk content. However, the periods of melt thermal stability ($\tau_{t.st.}$) are changed only slightly with increase in the chalk content. The similar dependencies were also obtained previously for rigid PVC composites filled with chalk [15].

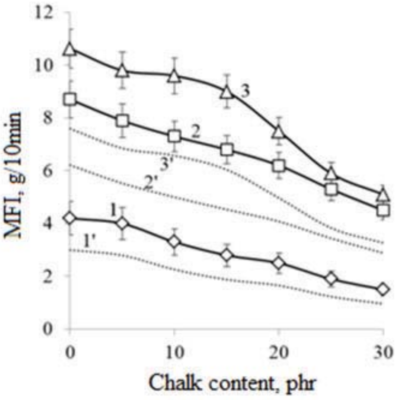

Fig. 3. Dependencies of the maximum MFI values for rigid PVC composites on the chalk content at different temperatures: 1,1' – 200°C; 2,2' – 210°C; 3,3' – 220°C (The dotted curves: MFI recalculated in cm3/10min).

To take into account the change in density of composites, MFI values were recalculated from g/10min to cm^3/10min (MFI/ρ) [see Fig. 3, the dotted curves]. Although a little change in the behavior of dependencies is observed after the above-mentioned conversion, MFI values describe melt fluidity of PVC composites in a more correct manner. The values of foaming rate and foaming ratio should depend on melt fluidity provided that the equation № 4 is fulfilled. Fig. 4 shows the dependencies of the F_{max} values on MFI (cm^3/10min). It turned out that even after the above-mentioned conversion the curves coincided only for high contents of chalk (low MFI values) for all temperatures. At 10–15 parts by weight of chalk, the F_{ratio} values increase more slowly than anticipated. Hence, the change in foaming characteristics of filled PVC composites can't be explained only by the change in viscosity, since the composites foamed at different temperatures have different Fmax values at the same values of MFI. This doesn't mean that equation (4) is not applicable to the materials under study. Foaming rates definitely depend on viscosity, but equation (4) disregards the limitation for time of foaming associated with rapid growth in viscosity and loss of fluidity (cross-linking) ($\tau_{cr.}$) for melts at heating times exceeding the periods of melt thermal stability ($\tau_{t.st.}$) of PVC.

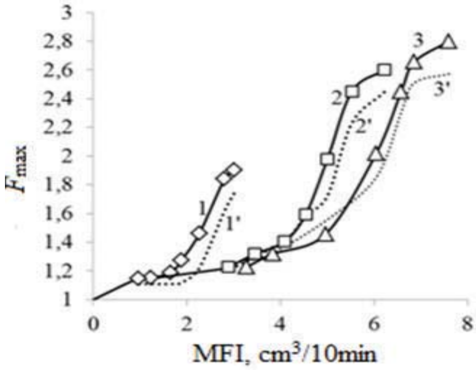

Fig. 4. Dependencies of the F_{max} values for PVC composites with different chalk content on MFI values at different temperatures: 1,1' – 200°C; 2,2' – 210°C; 3,3' – 220°C (The dotted curves correspond to the values calculated in accordance with the equation 6).

As foaming temperature increases, the values of foaming rate increase, but the values of $\tau_{t.st.}$ and $\tau_{cr.}$ decrease. Filling results in the additional decrease in foaming rate, but $\tau_{T.St.}$ values remain practically constant. Based on the known values of the average foaming rate (Vf = f(MFI)) and $\tau_{cr.}$ one can evaluate the dependencies of on MFI:

$$F^{/}_{max} = \rho/\rho_T + V_f(\tau_{cr.} - \tau_{ind}) \quad (6)$$

where ρ/ρ_T is correction factor (ρ/ρ_T = 1.09-1.10) taking into account the thermal expansion of the sample up to the beginning of foaming (see the equation № 2),τ_{ind} is induction period (min), $\tau_{cr.}$. is the loss of fluidity period (min), V_f is the average foaming rate of a PVC composite (min^{-1}) calculated according to equation (3). The dotted curves obtained on the basis of the equation № 6 are similar to the experimental ones, and the calculated maximum values of foaming ratio are close to the experimental ones. This means, among other things, that τ_{max} and $\tau_{cr.}$. values are close to each other (see the equation № 3). Thus, cross-linking of the PVC chains additionally limits the maximum values of foaming ratio (F_{max}) for filled PVC composites.

Conclusion

It was stated that the introduction of a filler (chalk) in rigid PVC composites with azodicarbonamide reduce the rate of foaming. In turn, the maximum ratio of foaming (completeness of the process of foaming) of these composites is determined by the relative rates of foaming and the rate of rise of viscosity its melts due to thermal degradation of PVC and cross-linking.

Melt flow index (MFI) and time of melt thermal degradation and loss of fluidity period for filled rigid PVC composites are the main characteristics which determine the foaming ratio and the acceptable level of filling.

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