Fabrication de mousses syntactiques en thermoplastique élastomère vulcanisé par le procédé d'extrusion.

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Résumé :

L'utilisation de Microcapsules Thermo-Expansibles (MTEs) pour l'allègement de matériaux devient une alternative particulièrement intéressante pour l'industrie automobile. Les systèmes d'étanchéité automobiles sont actuellement majoritairement fabriqués en caoutchouc synthétiques. Néanmoins, les thermoplastiques élastomères sont de plus en plus utilisés car ils combinent une facilité de mise en œuvre via l'extrusion et une meilleure recyclabilité par leur nature. L'association de Thermoplastique Elastomère Vulcanisés (TPE-V) et de MTEs permet d'obtenir une mousse syntactique conservant les propriétés nécessaires pour assurer la fonction d'étanchéité. Ces MTEs consistent en l'encapsulation d'un mélange d'hydrocarbures par une coquille en polymère hermétique. Exposées à des températures élevées, la pression interne gouverne l'expansion de la coquille, produisant ainsi une porosité en présence de matrice élastomère en TPE-V. Les méthodes historiques de moussage, à savoir la voie chimique par libération d'un gaz et la voie physique par incorporation d'un gaz simple ou à l'état supercritique, sont des procédés complexes à contrôler. Les MTEs conduisent quant à elles à un procédé relativement stable avec des microstructures à pores fermées répétables, tout en utilisant une unité d'extrusion standard. L'objectif de ces recherches a été de comprendre où le phénomène de moussage intervient et quels sont les paramètres influençant ce moussage pendant le procédé d'extrusion. Des mesures sous hautes pressions et hautes températures ont été effectuées pour déterminer la position du moussage durant l'extrusion. Ces mesures ont mis en évidence que l'expansion intervient majoritairement dans la filière. C'est pourquoi différentes filières ont été conçues afin de faire varier la perte de charge, la vitesse de perte de charge et le temps de résidence dans la filière. L'impact d'un changement de vis d'extrusion a également été étudié. Sous ces diverses conditions de fabrication, la densité, la microstructure poreuse et la viscosité ont été investiguées. Les domaines balayés par l'étude, qui représentent fidèlement la gamme des conditions industrielles utilisée pour la conception de système d'étanchéité, n'ont pas permis de montrer une influence des paramètres du procédé sur le moussage. Une simulation du phénomène d'expansion dans les conditions d'extrusion vient consolider notre compréhension de cette technologie de moussage appliquée aux matériaux élastomères TPE-V souples. Les connaissances acquises nous permettent aujourd'hui d'envisager une production industrielle de systèmes d'étanchéité basée sur cette technologie.

Abstract:

Thermo-Expandable Microcapsules (TEMs) become to be an attractive alternative to lightweight materials for automotive industry. Currently, weather-strip sealing systems are mainly produced with synthetic rubber. Nevertheless, thermoplastic elastomers are increasingly used because they combine a good processability and they are recyclable by their nature. Combining Vulcanized Thermoplastic Elastomer (TPE-V) and TEMs results to a syntactic foam which keeps necessary sealing features. TEMs consist in encapsulated hydrocarbons with a polymeric shell. Exposed to elevated temperature, internal pressure governs shell expansion, which creates porosity inside the TPE-V matrix. Historical foaming method such as: chemical foaming by gas releasing and physical foaming by adding a simple gas or in supercritical state, are complicated process to control. Conversely to the previous technologies, TEMs expansion lead to a stable process with classic standard extrusion device and produce repeatable close cells microstructure. Research work aim was to understand where the foaming phenomenon occurs, and which process parameters influence the foaming performance during extrusion. Measurements under high pressure and elevated temperature were carried out. They showed that foaming occurs inside the die. As a result, we carefully designed various dies to apply different pressure drop, pressure drop rate and time residence to TPE-V / TEMs mixture, to sweep the range of sealing system production. Under those process conditions, density, porosity microstructure and viscosity were studied. Study scope sweep the range of classic conditions used for sealing system production, it did not show an influence of process parameters on foaming. A simulation of expansion phenomena on faithfully process conditions strengthen our understanding of this foaming technology applied to soft TPE-V. Today, our learnings allow us to consider an industrial production of sealing systems based on this technology.

Mots clefs: Extrusion - Polymer - Foam - Thermoplastic Elastomer - Microcapsules

1   Introduction

Since the middle of the twentieth century, researchers have developed several processes to lightweight and improve foam characteristics. Polymer foams have received attention from industries due to their good mechanical performance versus weight. Lightweight material is also an effective way to reduce the product cost. Foaming innovation is also driven by regulation evolutions. In fact, the understanding of the global warming and chemical effects on human health or the environment, led and may lead in the future to blowing agents restrictions such as: Chlorofluorocarbon (CFC) and more recently Azodicarbonamide (ADCA). ADCA was appointed as a Substance of Very High Concern by the European CHemicals Agency (ECHA) in 2012. However, ADCA is a high effective gas releasing chemical blowing agent. It still be widely used especially in automotive weather-strip industry [1]. An eco-friendlier alternative of ADCA must be found.

Historically, Ethylene-Propylene-Diene-Monomer (EPDM) rubber compounds remain the most used material to produce automotive door seals system. For fifteen years, ThermoPlastic Elastomer (TPE) has gained interest to substitute rubber material in glass run channel sealing systems due to its recyclability and processability [2]. Two kinds of TPE are found on weather-strip on current vehicles: Styrenic block copolymers TPE (TPE-S) and Vulcanized TPE (TPE-V). TPE-Vs usually selected for making weather-strip are a blend of polypropylene and small rubber particles. Rubber nodules are dynamically vulcanized during the compounding, as firstly mentioned by Gessler [3].

First TPE-V foaming investigation was done by Dutta and Cakmak in 1992 [4]. Santoprene TPE-V made by mixing PP and EPDM particles was foamed by ADCA blowing agent. They concluded that foaming occurs in PP plastic phase, consequently the maximum expansion ratio was rigorously

dependent of the TPE-V composition. For softer grades, porosity needs to be introduced inside EPDM phase to achieve lower densities. In 1998, Kropp et al. [5] investigated physical foaming of TPEs with carbon dioxide and Hydrocerol® (sodium bicarbonate) as nucleating agent. More recently, others gas molecules have been tested such as water, hydrocarbons and nitrogen. [6, 7]. Solubility and diffusion ability of the gas are directly related to nucleation and cell growth phenomenon, and by the end, its foaming performance. CO_2 has gained in interest because finer cell size and uniform distribution, which enhance mechanical properties, can be obtained [8, 9]. Some studies have been done to investigate the effect of pressure drop rate on expansion ratio [10-13]. They showed that die design can significantly affect foam microstructure. They observed that a higher pressure drop rate is increasing cell nucleation, which is favorable to promote the expansion ratio. Nucleation and diffusion inside the polymer is also related to the polymer nature and temperature. Even if CO_2 can produce good foaming result, it still be complicated to control microstructure for various polymers and product designs at an industrial scale.

That is why, Thermo-Expandable Microcapsules (TEMs) have recently appeared as a new alternative to foam polymer. They consist in a mixture of hydrocarbons encapsulated within a rigid polymer shell. Exposed to elevated temperature, the shell becomes softer and the vapor pressure of hydrocarbons drives the microcapsule expansion. TEMs was firstly introduce by Dow Chemicals [14]. Originally used in wallpaper, paint and textile for textural properties, now TEMs are economically interesting to be used as a blowing agent in shoe soles and automotive industry. TEMs preserve its structure even after foaming, as a result, a closed cell microstructure is created. This kind of foam is called "syntactic foam". Only few literature papers are dealing with TPE syntactic foam produced with TEMs. [15, 16]. They achieved 25 to 40 % weight reduction. More recently, Guo et al. [17] worked on TPU foaming with TEMs during extrusion process. They showed at low shear rate (20 to 110 s-1), that higher pressure drops along a capillary die increase the expansion ratio. They suggested for high pressure in the die, the main part of expansion occurs after die exit, whereas for low pressure in the die, the expansion can occur inside the die.

In this study, we intend to better understand foaming process of TEMs inside a low hardness TPE-V elastomer. In a first approach, we aim to find the location where the microcapsules are foaming during extrusion process. Then, inspired by the study done by Xu et al. in 2008 [12], we have designed a set of 9 dies to apply different pressure drop rate and time residence. The objective was to investigate in the range of thermoplastic elastomer sealing system extrusion, if die design could influence the expansion level of the produced TPE-V syntactic foams.

2   Experimental

2.1   Materials

A low hardness TPE-V. This material was chosen because it can exhibit good elasticity and compressibility properties on sealing geometry. TEMs has been used as blowing agent in this study. TEM grade was chosen because it is consistent with the temperature range used for TPE-V extrusion process. Main characteristics of materials are presented in Tables (1) and (2). A custom-made Masterbatch (MBTEM) was designed with 40% of TEMs and Ethylene-Vinyl-Acetate (EVA), supplied by Repsol. The use of a low melting point polymer is necessary to avoid any expansion during the masterbatch compounding. In this work, the EVA inside MBTEM plays two distinct roles: firstly, as a carrier to dose TEMs during extrusion and secondly as a matrix during expansion pressure measurements. For the last, the idea was to roughly represent external rheology seen by TEMs during extrusion process.

TABLE 1). Polymer Material characteristics

Material	Density (ISO 1183) [kg/m³]	Melting point (Internal) [°C]	Hardness (ISO 868) [Shore A]
TPE-V	925	155	38
EVA	937	85	83

TABLE 2). TEMs characteristics

Material	Initial density (ISO 1183) [kg/m³]	Tstart (Internal) [°C]	Tmax (Internal) [°C]	Initial diameter (Internal) [µm]	Maximal diameter (internal) [µm]
TEMs	1100	170	208	16.8	58.8

To figure out how the expansion occurs during the extrusion process requires to investigate TPE-V and TPE-V foam rheology. For this study we performed rheological measurements with a home-made in-situ rheometric die. The section of the die is a ribbon strip of 2x40 mm. Rheological behaviors of TPE-V and foam TPE-V are presented in Figure 1 (a). Auto-heating during measurements are corrected by Arrhenius law from previous capillary rheology measurements. TPE-V and TPE-V foam are following power law, in agreement with literature [6, 18, 19]. As TPE-V foam does not highly affect rheology, the same Arrhenius law is applied to correct auto-heating. To neglect the influence of the EVA rheology on the overall mixture behavior, a small amount of masterbatch (1,62%) was introduced in the samples. Hence, TEMs effective amount is 0,65%. Due to the small amount of TEMs, TPE-V foam shows a slightly lower viscosity. This result was also expected following microcellular influence on foam [17, 20].

We measured EVA rheology with a plate and plate geometry rheometer and with a capillary rheometer at 120°C and 190°C. Cox-merz rule [21] and thermodependency, using Arrhenius law, were done to determine EVA mastercurve at 200°C (Figure 1 (a)). 4 parameters Carreau-Yasuda model (Figure 1 (b)) was used to fit experimental data and rheological parameter are presented in Table 3. As explained above, Figure 1 shows the viscosity at 200°C of EVA at low shear rate (η_{EVA} = 10 Pa.s) which is not so far from the viscosity of TPE-V (η_{TPV} = 30 Pa.s) when it flows into the slit die with a shear rate in the range of 10^3 s^{-1}.
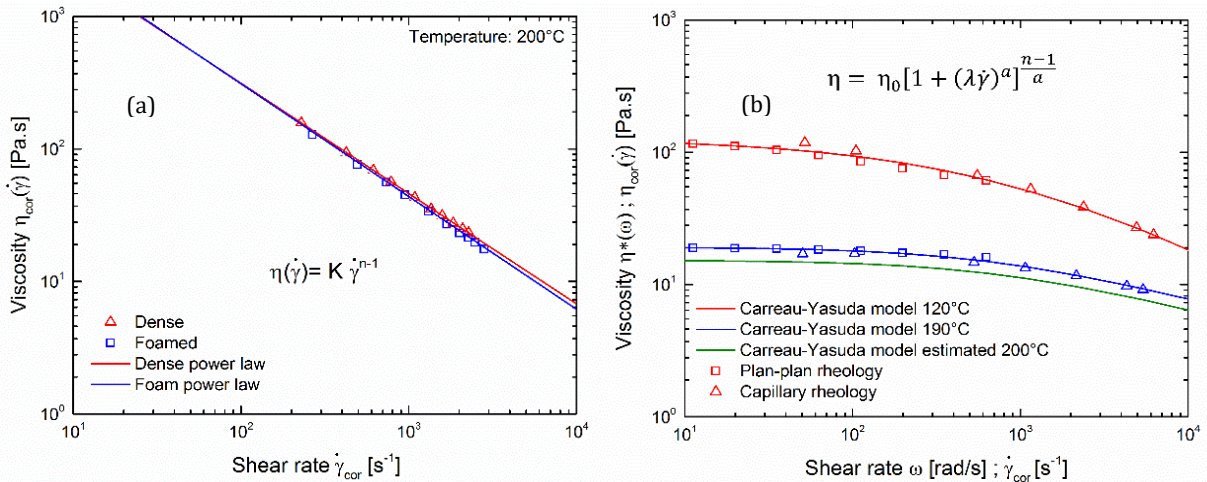

FIGURE 1. (a) Master curve at 200°C of viscosity determined by rheometric slit die and power law fitting model. (b) Experimental data from plan-plan rheology and capillary rheology with Carreau-Yasuda 4 parameters fitting model.

TABLE 3). Material rheology behavior at 200°C

Material	K Consistency [Pa.s^n]	η_0 viscosity at zero shear rate [Pa.s]	λ relaxation time [s]	n Pseudo-plastic index [-]	a [-]	Ea Activation energy [kJ.mol^{-1}]
TPE-V	14538	/	/	0.167	/	11.3
TPE-V + 0.65% TEM	15030	/	/	0.155	/	11.3
EVA	/	15.30	0.0013	0.678	0.868	41.1

2.2   Method and Results

Pressure Drop Threshold Measurements

This experiment was inspired by Kawaguchi et al. [23]. We subjected TEMs inside a masterbatch to high pressure at 205°C. Expansion does not occur after 10 minutes at 60 bar. Then, experiments were carried out with PDE 1700 MD apparatus equipped with pressure transducer and thermocouple developed by Eurotechnica GmbH. Acquisitions were done by a CCD camera and LabVIEW software. Samples were placed in a 10x10x20 mm cuvette, inside the pressurized cell. The pressure was controlled by N_2 flow. The area taken by MBTEM samples is measured by image processing (i.e., imageJ software). The expansion ratio is normalized by the highest level of area taken by the sample during the experiment. The pressure drop is controlled manually around 0.1 bar/s. Figure 2 shows clearly a pressure threshold around 10 bar below which the expansion is increasing widely. In case of TPE-V extrusion, the expansion starts when the pressure is around 10 bar. Inside the extrusion unit, a sufficient elevated temperature and low pressure is only achieved at the end of the die. Experiments do not show any variation in dimension of the sample after the die. It suggests expansion may occur mostly before the die exit.
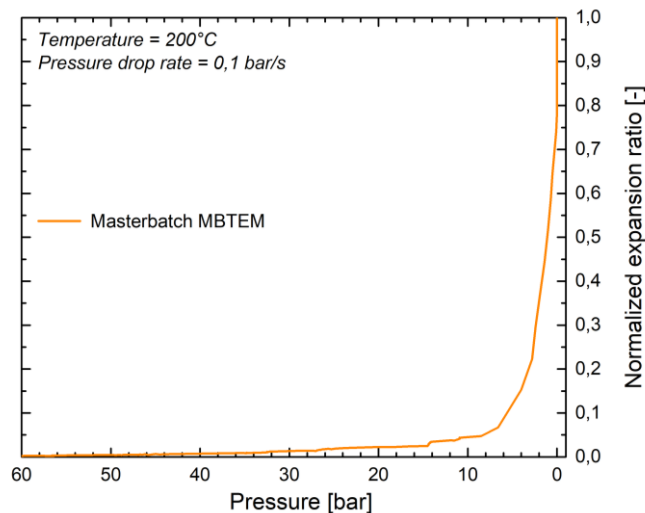

FIGURE 2. *Expansion of MBTEM at 200°C in pressurized cell*

Pressure Drop Rate Study

Following the previous study, we investigated various die conditions to study their influence on foaming microstructure. 9 slit dies were calculated numbered from 11 to 33: 3 groups of 3 dies to apply 3 different pressure drop rate (32 bar/s, 76 bar/s and 110 bar/s, respectively) and different time residence (1.4 to 0.2 s). Every die has a width versus thickness ratio higher than 10 to neglect wall shear rate and stress effects [24].

Temperatures were fixed at 205°C ± 2°C. The flow rate was fixed at 13500 ± 200 mm^3/s. Rheological models presented above are applied as reference to calculate and to correct rheological values. TPE-V melt density was determined by PVT measurements. Assumption is made to calculate the melt density in case of foaming: the porosity proportionally decreases the melt density. Corrected viscosity was evaluated from pressure measurement inside the slit die and by considering Rabinowitsch effect as described by Macosko [26]. Figure 3 presents the 4 main parameters variations in function of pressure drop rates. Average porosity achieved with 0.65% of TEMs is 8.5%. Every pressure drop rate corresponds to a material viscosity level. The dispersion is not fully homogeneous. The average size of porosities is 40 µm. The 4 parameters analyzed do not described any trend due to pressure drop rate or time residence. In the range analyzed, die design does not affect the TEM expansion during extrusion process.
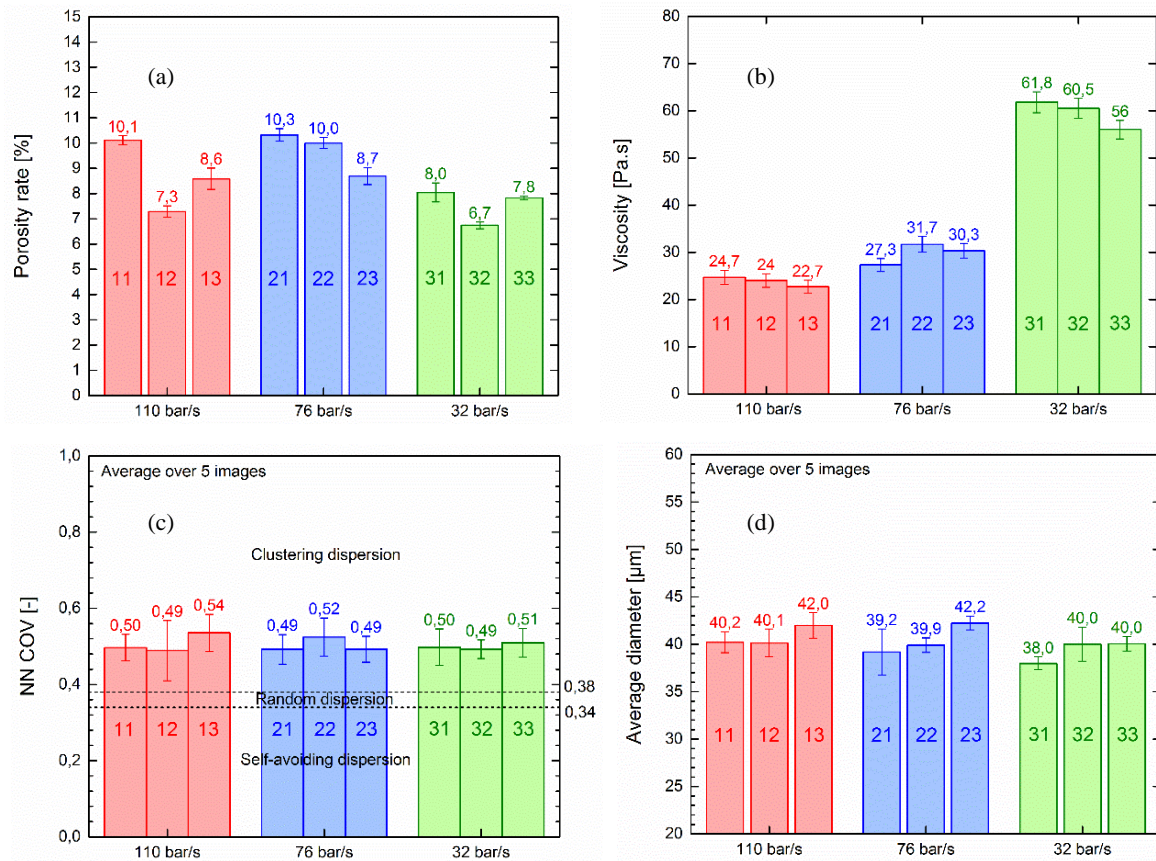
FIGURE 3. (a) Porosity rate calculated from density measurements. (b) Corrected viscosity of foam TPE-V, calculated from Rabinowitsch and thermo-dependency corrections. (c) 2D porosity dispersion parameter calculated as presented by Yang [25]. (d) Average diameter is calculated from apparent area of TEMs.

Conclusion

In this work, TEMs expansion phenomena localization during extrusion process was investigated. A masterbatch was created with an EVA matrix which roughly exhibits similar rheology of TPE-V during extrusion. At low pressure drop we measured a pressure threshold at around 10 bar under which the expansion can occur. In classic automotive sealing system extrusion, conditions that enable expansion can only be achieved inside the die.

That is why, we have designed multiple dies corresponding to three pressure drop rates and various residence times. Each die section applies a shear rate on melt which corresponds to a viscosity. The measured dispersion is not homogeneous, microcapsules tend to form clusters. It could be attributed to the original masterbatch pellets or a too short extrusion unit. Under these conditions, TPE-V syntactic foam microstructures are roughly the same. Die design does not affect the extrusion foaming process. This is an interesting result regarding an industrial production. In fact, the foaming process, with TEMs, seems to be stable whatever the extruder system for TPE-V syntactic foam in the range of sealing system extrusion conditions. Rheology of microcapsule shells need to be investigated to compare with the rheology of the surrounded TPE-V polymer matrix. Indeed, if TPE-V viscosity is far lower compare to microcapsule shell rheology, a variation of TPE-V viscosity could be neglected and as a result the foaming behavior would be roughly the same.

Acknowledgments

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