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A THERMOMECHANICAL ANALYSIS OF POLYMER FOAMING

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A novel technique is described for studying the growth of foam from polymer melts containing thermally-decomposable blowing agents. A simple cylinder and plunger sample holder has been combined with a standard thermomechanical analyzer. This enables the recording of height i.e. volume vs. time or temperature at preselected rates for temperature scan. Demonstrations with foamable polyethylene and plasticized poly(vinyl chloride) have revealed the influences of heating rate, blowing agent type and concentration, blowing agent inhibitor, polymer viscosity and crosslinking agent on foam growth rate and final foam height i.e. foam density.

In the polymer field, thermomechanical analysis (TMA) has been widely applied to the study of thermal expansion and of transitons, i.e. the glass transition temperature and the melting point. The versatility offered by TMA to measure sample dimensions as a function of the temperature has been subsequently used for the study of a series of phenomena occurring under influence of external mechanical stresses, such as elongation of polymer fibers under tensile stress and the softening of amorphous polymers sensed by penetration and compressive stress.

In this paper we describe a new application of TMA for the study of polymer phenomena; the formation of foam from a polymer melt containing a thermally-decomposable blowing agent. This method differs from prior applications of TMA in which the sample remains in the solid state during the test or just reaches the mobile melt at the end of the test. In this new application, the polymer is in a liquid-like state during an essential part of the analysis. Therefore, the standard sample holder for linear expansion of a polymer solid is inapplicable. Instead, a cylinder and plunger type sample holder was developed to accommodate analysis of the polymer in both the solid and liquid like, i.e. foamed state. It has been shown that this new method provides reliable measurement of volume change for polymers foamed with chemical blowing agents.

For the study of foam formation, experiments with a temperature gradient across the sample are preferred to isothermal experiments for two reasons. First,

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the conditions in industrial practice are better simulated. Second, the influence of temperature on polymer foam growth can be revealed more readily by temperature programming than from a series of isothermal experiments which are also difficult to perform reliably.

The tests reported here provide direct information on polymer foam growth as a function of temperature for a range of experimental conditions and compositions. In addition, it has now been possible to show by this simple technique the relation between polymer foam growth and polymer viscosity. The blowing agent decomposition characteristics, the heating rate effects (temperature scanning speed) and the effect of pressure applied to the foam are also revealed.

In the first part of this paper, the apparatus and operating procedure are described. In the second, studies of the polyethylene foamability and of specific formulations of plasticized poly(vinyl chloride) foamable sheets are presented to demonstrate the capability of this novel measurement technique.

Polyethylene foams were produced by blending polymer melt with blowing and nucleating agents and heating the blend to blowing agent decomposition temperature. The quality of the foam depends on several of the parameters evaluated here.

Plasticized poly(vinyl chloride) foams are commonly utilized as coatings on fabrics or on substrates with a range of compositions. In some cases foams are produced to a uniform thickness; in others a surface of controlled variability in height is desirable. Several different processes may be used to produce this effect of variable foam thickness. A mechanical method is to pass the already-foamed sheet or mat between embossing metal rollers. Alternatively, foam growth may be controlled directly. In this case a poly(vinyl chloride) plastisol containing a chemical foaming agent may be cast into a film and gelled at sufficiently low temperature to prevent foaming agent decomposition. The sheet may then be coated with a restricting agent for the foaming process. On subsequent heating, the coated portions can foam noticeably less than noncoated portions.

The coating procedure for the production of embossed poly(vinyl chloride) sheets can be based on two distinct and mutually exclusive processes. For example, if the coat contains a crosslinking agent for plasticized poly(vinyl chloride), foam growth can be restricted by formation of a crosslink network in the system. This can occur even though the blowing agent thermal decomposition characteristics are uninfluenced. Foam growth control can also be achieved by an independent and alternate chemical method. This is accomplished by introducing a blowing agent decomposition inhibitor which need not have any influence on the polymer-plasticizer system. Therefore, it could be expected that the two chemical processes differ not only in the chemistry but also in respect to the foam growth pattern and mechanism. A goal of this study was to evaluate the mode of foam growth in the presence of a crosslinking agent and alternatively in the presence of an inhibitor for the chemical blowing agent.

Experimental

Apparatus and procedure

In this study, a standard Perkin-Elmer Thermomechanical Analyzer, Model TMS-1, was used which consisted of an Analyzer unit, TMS-1 Control unit, a DSC-1B Control unit and a two pen recorder (Perkin Elmer Corp., Norwalk, Conn.). This apparatus enables the measurement of sample thickness under controlled temperature conditions including programming during heating or cooling. The sample thickness can be accurately measured from below a melting or softening point, that is, for appreciable polymer viscosity. The sample, in film form, is placed between a quartz bottom plate and the tip of a quartz probe. In expansion tests a larger tip diameter (0.145 in. = 3.68 mm) and a smaller probe loading (3g or less) are used to avoid penetration. In an alternate mode of operation, i.e. for penetration tests, a smaller tip diameter (0.035 in = 0.88 mm) and higher probe loading (10 g and more) are used to provide penetration of the probe in the sample above polymer transition, such as glass transition and melting points. To exclude penetration and thus to study accurately the foaming through expansion, a special sample holder was used as shown in Fig. 1. A cylindrical sample is inserted between two tungsten carbide plungers surrounded by an aluminum barrel. This sample holder is placed into the standard quartz sample tube. The quartz probe is moved upwards at low fraction by sample expansion during the heating. The contraction of the sample may also be followed during cooling with the recorder reflecting absolute changes in sample thickness. The movement of the probe is sensed by a transducer. The electrical signal is modulated, amplified and recorded. A sensitivity (X) means that full scale deflection of a 10 mV recorder

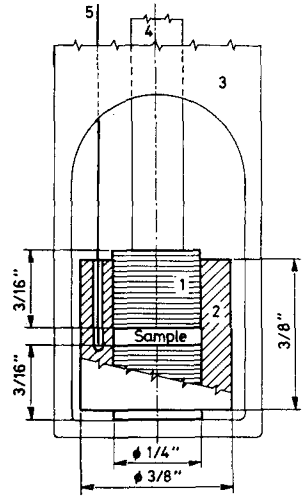

Fig. 1. Sample holder: 1-tunston carbide plunger; 2-aluminum barrel; 3-standard quartz sample tube; 4-quartz probe; 5-thermocouple

is obtained when the probe is moved X thousands of an insh. Smaller values of X correspond to proportionately higher sensitivities.

Controlled heating is provided by a small Perkin-Elmer electrical furnace controlled by the programmer incorporated in the DSC-1B Control unit. The standard temperature calibration consists in setting the two potentiometers of the TMS Control unit to balance the programmer reading and the sample thermocouple at thermal equilibrium.

The test is initiated by introduction of a cylindrically cut sample of 0.25 in diameter into the holder (see Fig. 1) which is then placed in the sample tube. The sample was cut from sheet of about 20 mil thickness. The system is then brought to thermal equilibrium, followed by zeroing the dilatation indicator and adjusting for desired dilatation measurement sensitivity, temperature scan rate and recorder

Table 1

Composition of foamable polyethylenes prepared for study (parts by weight)

Sample, No.	1	2	3	4	5	6	7	8	9	10	11
Low density polyethylene (higher melting point)	100	100	100						100		
Low density polyethylene (lower melting point)				100	100	100	100	50		100	50
High density polyethylene (PE–C)								50			50
Blowing agent, p, p'-oxy bis (benzene sulfonyl hydrazide) (decomposition temperature 150–160°C)				1	2	3			2	2	
Blowing agent, p-toluene sulfonyl semicarbazide (decomposition temperature 213–225°)	1	2	3				2	2			2
Nucleating agent, zinc octoate, 18 % Zn	2	2	2	2	2	2	2	2	2	2	2
Xylene	1	1	1	1	1	1	1		1	1	
Decalin								1			1
Crosslinker, tertbutyl perbenzoate									0.25	0.25	0.25

chart speed. The temperature program is then initiated. At the desired maximum temperature, the quartz sample tube is removed from the furnace and the subsequent contraction can be recorded during cooling.

Materials

Foamable polyethylenes. Eleven different foamable polyethylene samples were prepared by blending in an extruder at the following temperatures: rear 110°; front 120°; die 110°. The composition of the sample is given in Table 1.

Foamable plasticized poly(vinyl chlorides). Seven samples were prepared by casting plastisols and gelling at 140° for 2 min, see Table 2.

Table 2

Composition of foamable plasticized poly(vinyl chlorides) prepared for study

Sample Number	Composition
1	Plastisol A sheet
2	Plastisol A sheet coated with a crosslinking agent
3	Plastisol B sheet
4	Plastisol B sheet coated with an inhibitor for blowing agent thermal decomposition
5	Plastisol C sheet
6	Sheet made from plastisol C containing 1 % benzoyl peroxide
7	Sheet of plastisol C containing 1 % of fumaric acid

Rheological characterization

The three polyethylenes used for foamable sample preparation were tested in a Weissenberg Rheogoniometer R-17 in steady and oscillatory (dynamic) experiments using a cone and plate of 1.0 inch diameter and 4° cone angle.

Thermogravimetric characterization

The two blowing agents used to prepare foamable polyethylenes were separately tested in the Perkin Elmer TGS-1 Thermobalance.

Results and discussion

Figure 2 is a typical record for both the dilatation and the sample holder temperature for polyethylene sample number 4 at 20°/min, see Table 1 for sample designations. The dilatation curve exhibits a sigmoidal shape. The foam growth

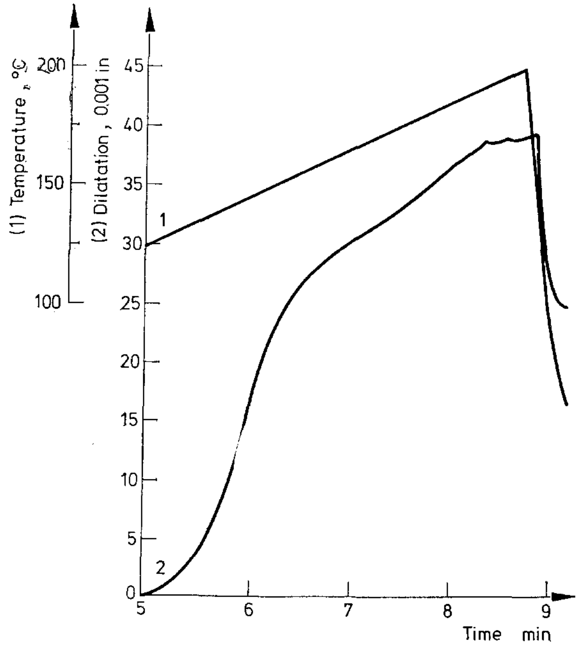

Fig. 2. Dilatation curve for polyethylene sample number 4 at the heating rate shown

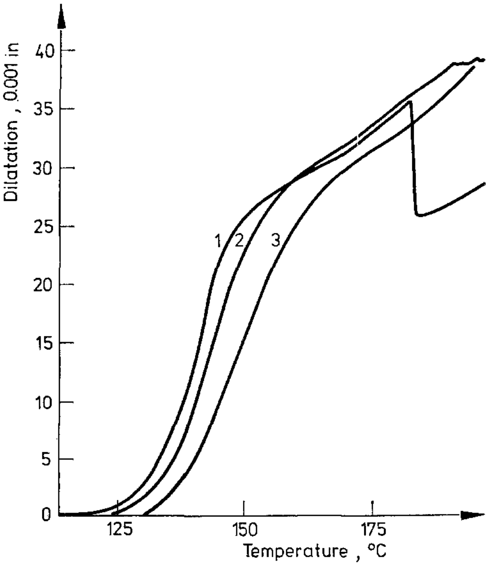

Fig. 3. Dilatation curves for polyethylene sample number 4 at heating rates of 10, 20 and 40°/min for curves 1, 2 and 3 respectively

starts at a well-defined temperature and continues to grow smoothly to a critical height characterized by "bubbling". This term is our identification for the development of an irregular recorder trace, probably caused by percolation of gross bubbles against the detector probe.

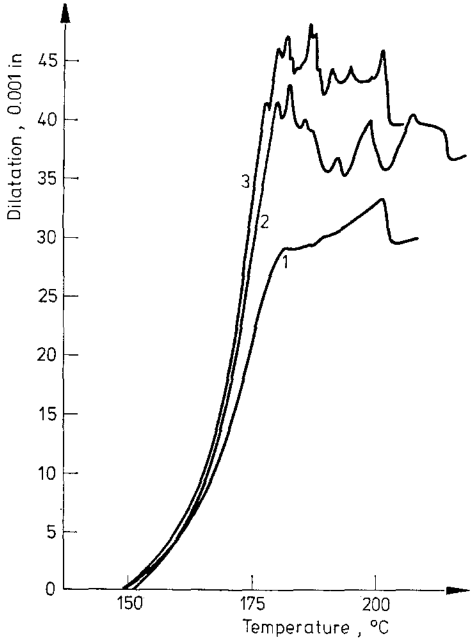

Fig. 4. Three repeat dilatation curves for polyethylene sample number at a heating rate of 20°/min

Figure 3 presents dilatation curves on the same starting sample at different heating rates. It can be seen that the temperature at which foam growth begins is higher at higher temperature scan rates. The foam growth rate measured at the dilatation curve midpoint, and expressed in per cent of the original sample thickness per min, e.g. as $(100\,\Delta V)/(V\Delta t)$, increases with scan rate. But if expressed per °C, e.g. as $(100\,\Delta V)/(V\Delta T)$, the foam growth rate apparently decreases with the temperature scan rate. The critical foam height for "bubbling" as measured after cooling to the room temperature, represents in all cases from 200–250% of the original thickness of the foamable sheet, regardless of scan speed.

In Fig. 4, the traces for polyethylene samples 1 to 3 indicate a more rapid foam growth and a greater final height with increasing blowing agent content.

Figure 5 shows the influence of the blowing agent type. Polyethylene samples 5 and 7 differ only in blowing agents whose thermogravimetric curves are given in Fig. 6. The pattern of foam growth reflects the difference in blowing agents decomposition temperature.

Figure 7 demonstrates the pronounced influence of the polymer melt viscosity on foam growth. The viscosities of two polyethylenes used to prepare samples 9 and 10 are given in Fig. 8. The foam growth of the higher viscosity polyethylene

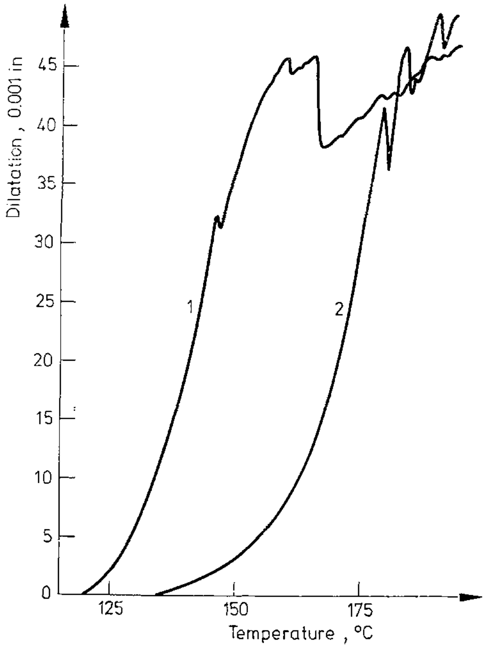

Fig. 5. Dilatation curves for polyethylene sample number 5 (curve 1) and number 7 (curve 2) at a heating rate of 20°/min

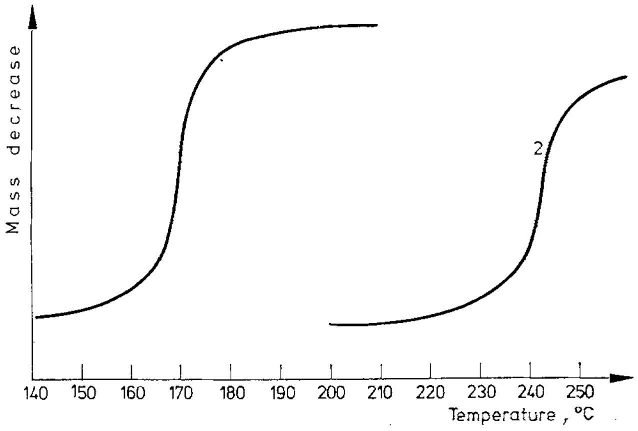

Fig. 6. Mass decrease (arbitrary units) for *p,p*'-oxy bis/benzene sulfonyl hydrazide (curve 1) and *p*-toluene sulfonyl semi-carbazide (curve 2) at a heating rate of 20°/min

begins at about 30° higher temperature than of the lower viscosity polyethylene. There is also a noticeable influence on final foam height which is bigger for lower viscosity polyethylene.

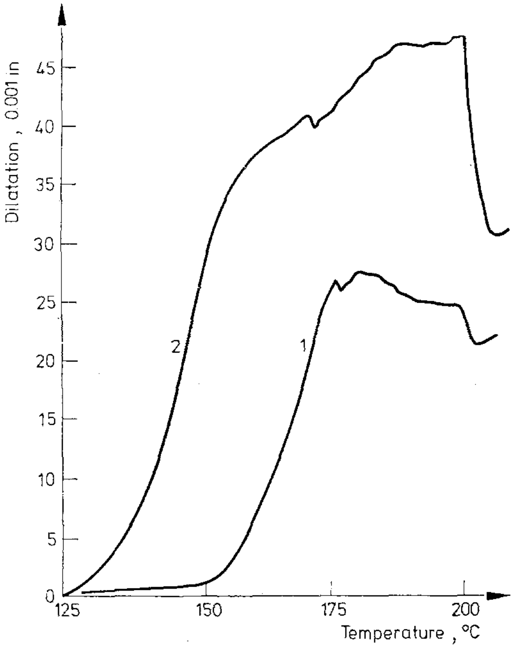

Fig. 7. Dilatation curves for polyethylene samples number 9 (curve 1) and 10 (curve 2) at a heating rate of 20°/min

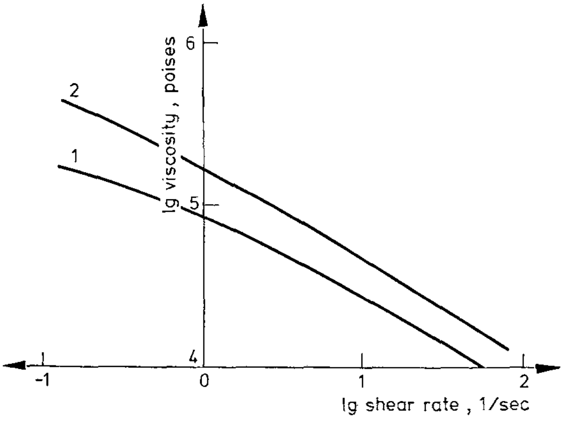

Fig. 8. Viscosities of the two polyethylenes used to prepare foamable sheets; curve 1 lower melting polyethylene, curve 2 the higher melting polyethylene

In the case of plasticized poly(vinyl chloride) foamable sheet, Fig. 9 shows that both samples 1 and 2 start to foam at the same temperature of about 185°. However, the foam growth of the sample 2 stops earlier, consistent with crosslinking restriction of foaming.

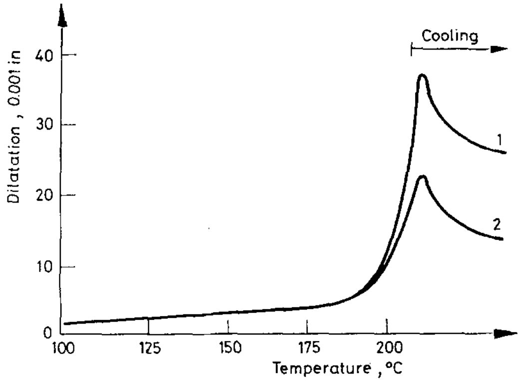

Fig. 9. Dilatation curves for plasticized poly(vinyl chloride) samples number 1 (curve 1) and 2 (curve 2) at a heating rate of 20°/min followed by cooling

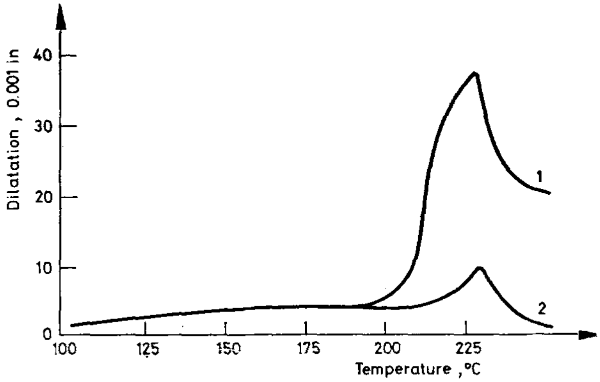

Fig. 10. Dilatation curves for plasticized poly(vinyl chloride) samples number 3 (curve 1) and 4 (curve 2) at a heating rate of 20°/min followed by cooling

Comparison of traces for poly(vinyl chloride) in Fig. 10 reveals that foam growth of sample 4 begins at a temperature about 20° higher than the corresponding temperature for sample 3, i.e. the same but without the inhibitor.

The curves in Fig. 11 are a further substantiation of these prior results and conclusions. The fumaric acid inhibits the thermal decomposition of the blowing agent and benzoyl peroxide acts as a crosslinking agent for the polymer.

Finally, it should be mentioned that the same method can be used in the derivative mode, as shown for polyethylene sample number 4 in Fig. 12. The recorded curve represents in this case foam growth rate vs. time.

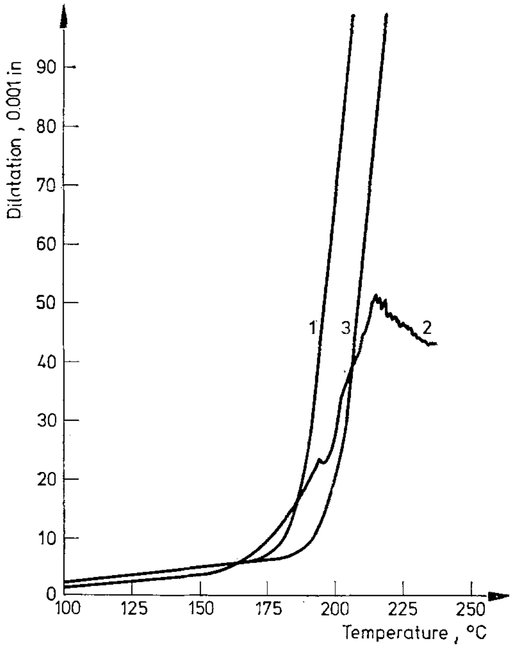

Fig. 11. Dilatation curves for plasticized poly(vinyl chloride) samples number 5 (curve 1), 6 (curve 2) and 7 (curve 3)

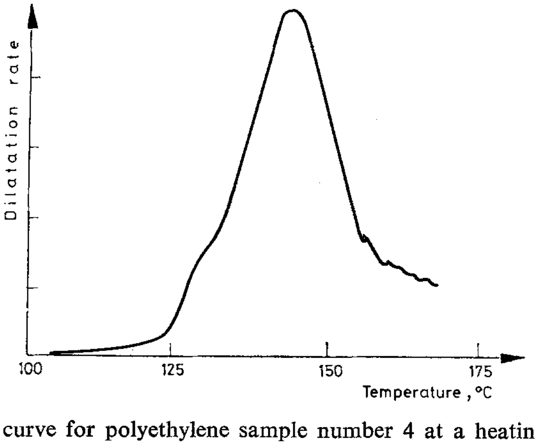

Fig. 12. Dilatation curve for polyethylene sample number 4 at a heating rate of 20°/min, recorded in derivative mode (arbitrary units)

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Résumé — On décrit une nouvelle technique pour étudier la formation de mousse dans les polymères fondus qui contiennent des agents de soufflage décomposables par voie thermique. On a associé un simple cylindre et un porte-échantillon d'immersion à un analyseur thermomécanique standard. Cela permet d'enregistrer la hauteur, c'est-à-dire le volume, en fonction du temps ou de la température, à des vitesses de montée en température présélectionnées. Des démonstrations avec du polyéthylène et du chlorure de polyvinyle plastifié pouvant mousser ont mis en évidence les influences respectives de la vitesse de chauffage, du type et de la concentration de l'agent de soufflage, de l'inhibiteur de l'agent de soufflage, de la viscosité du polymère et de l'agent de réticulation sur la vitesse de formation de la mousse et sur sa hauteur finale, c'est-à-dire la densité de la mousse.

Zussammenfassung — Eine neue Technik zur Untersuchung der Schaumbildung aus Polymerschmelzen, welche thermisch zerstörbare Schaumbildner enthalten, wird beschrieben. Ein einfacher Zylinder und ein Tauchprobenbehälter wurden mit einem thermomechanischen Standardanalysator gekoppelt. Dies ermöglicht das Registrieren der Höhe, d.h. des Volumens als Funktion der Zeit oder Temperatur, bei vorgewählten Geschwindigkeiten für die Temperaturabtastung. Versuche mit schäumungsfähigem Polyäthylen und plastizisiertem Poly(Vinylchlorid) zeigten die Einflüsse der Aufheizgeschwindigkeit, des Typs und der Konzentration des Schaumbildners, des Inhibitors des Schaumbildners, der Viskosität von Polymer und Quervernetzer auf die Geschwindigkeit der Schaumbildung und auf die Endhöhe des Schaumes, d.h. die Schaumdichte.

Резюме — Описана новейшая техника для изучения роста пены из полимерных расплавов, содержащих термически разлагающиеся газообразующие вещества. Простой цилиндр и поршневой держатель образца были соединены с стандартным термомеханическим анализатором. Это позволило регистрировать высоту т. е. объем против времени или температуры при заранее выбранных скоростях температурной развертки. Опыты с пенообразующим полиэтиленом и пластифицированным поливинилхлоридом показали влияние скорости нагрева, типа газообразующего вещества и его концентрации, ингибитора газообразующего вещества, вязкости полимера и поперечно-связывающего вщества на скорость роста пены и конечную высоту пены т. е. плотность пены.