

Linear Expansion Measurements of Polymers by Means of a Capacitance Technique

JOHN J. MAURER, *Enjay Laboratories*, and H. C. TSIEN, *Mechanical Division, Esso Research and Engineering Company, Linden, New Jersey*

Synopsis

The design, construction, and operation of a unit for measuring linear expansion properties of polymers is described. This unit utilizes a proximity transducer capacitance gauge to measure variations in capacitance caused by expansion of a sample of polymer held in an Invar (low expansion alloy) sample holder. Measurement of displacement and of temperature is continuously recorded on an X-Y recorder. The effect of operating conditions on the measurement of the linear expansion is described, and certain experimental artifacts are shown. In addition, the application of the instrument to polypropylene, styrene-butadiene rubber, butyl rubber, and to ethylene-propylene rubber is described. Distinct, nonlinear regions were found, above the normal glass transition temperatures, for butyl rubber and for ethylene-propylene rubber. In the former case, the effect is probably due to crystallinity; in the latter case, there are probably two minor transitions at about -35°C . and at about -5°C . in addition to the major transition at -67°C . These minor transitions may be due to atactic and stereoblock propylene segments, respectively.

INTRODUCTION

Linear expansion measurements are valuable in the study of polymers since they permit a determination of glass transition temperatures and of crystallinity effects. Also, since the transition which is observed at a particular temperature is accompanied by changes in other physical properties of the polymer, studies of this type are helpful in understanding the practical properties of elastomers and of plastics. Recent work¹ has indicated that this type of measurement may also be useful in determining the method of monomer addition in certain copolymers as well as in examining the microstructure of crystalline polymers made by stereospecific polymerization processes.

Dilatometers are frequently employed to determine transitions in polymers by measuring changes in volume as a function of temperature, but this method is tedious and time consuming. An apparatus described by Dannis² overcame some of these limitations by utilizing an optical lever system to obtain continuous measurements of linear expansion of a sample as a function of temperature, and extended the operating temperature range down to that of liquid nitrogen. However, this unit required baffles and shields to reduce stray light. This paper describes the design, con-

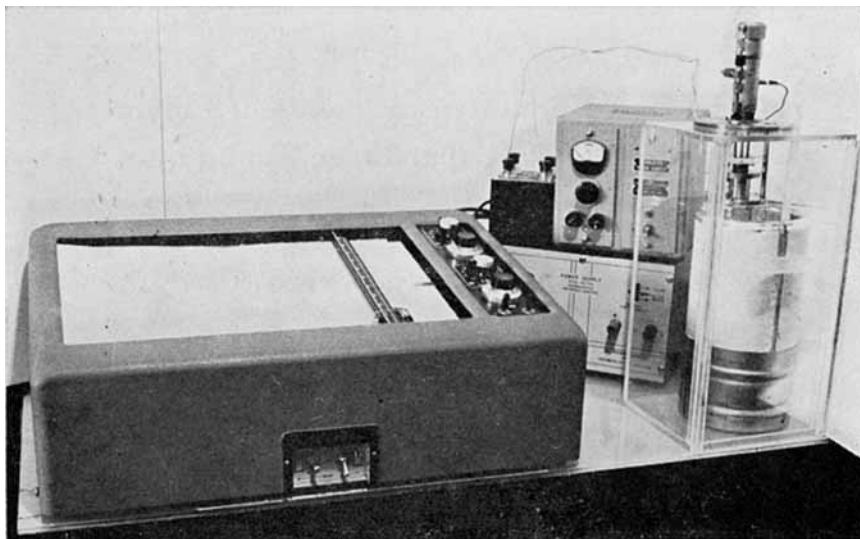


Fig. 1. Instrument layout for automatic recording of thermal expansion of polymers.

struction, and operation of an instrument (Fig. 1) which functions over a similar temperature range (-180 to $+25^{\circ}\text{C}$., or higher if desired), but which utilizes capacitance variations, rather than changes in light intensity, to measure linear displacement. The instrument is of high sensitivity and eliminates the problems encountered with the optical lever system due to stray light.

EXPERIMENTAL

Description of the Unit

The components used in the construction of this unit are listed in Table I.

The portion of the instrument (Fig. 2) in which the expansion of the sample takes place consists of an Invar (low expansion alloy) framework which suspends a sample holder from the top of a Lucite box. A proximity transducer capacitance gauge is screwed into the top Invar plate and penetrates into the box, while the micrometer head of the transducer remains outside the box. An Invar electrode, attached to the transducer, serves as the fixed upper plate of a variable capacitor. The lower movable plate of the capacitor rests on the polymer sample which is placed at the bottom of the framework. A thermocouple, sealed into the Invar with epoxy resin, penetrates into the sample and permits temperature evaluation during expansion. During measurements, a Dewar flask is raised around the sample holder, and a close fitting door covers the front of the box. Cooling of the system is accomplished by pressuring liquid nitrogen into the flask via a polyethylene tube, and addition of the coolant is regulated with a level-

TABLE I
Components for Linear Expansion Apparatus

Component	Source
Invar 36 (free cut)	Carpenter Steel Co., Reading, Pa.
Proximity transducer capacitance gauge (PT-5)	Photocon Research Products, Pasadena, Calif.
Chromel-constantan thermocouple (Type HT)	Baldwin, Lima, Hamilton Co., Waltham, Mass.
Boxer epoxy resin system (EP-1000)	Union Labs, Inc., Morganville, N. J.
Dewar flask (Type B, JF2570)	Scientific Glass Co., Vineland, N. J.
Liquid nitrogen level control unit	Almac Cryogenic Air Co., Oakland, Calif.
Dynagage (DG-600) and power supply (PS-600)	Photocon Research Products, Pasadena, Calif.
Moseley autography X-Y recorder (Model 25)	F. L. Moseley Co., Pasadena, Calif.
Pyrotest model 9-B millivoltmeter	Technique Assoc., Indianapolis, Ind.
Thermocouple reference junction (PRJI) and power supply (PSI)	Joseph Kaye & Co., Inc., Cambridge, Mass.

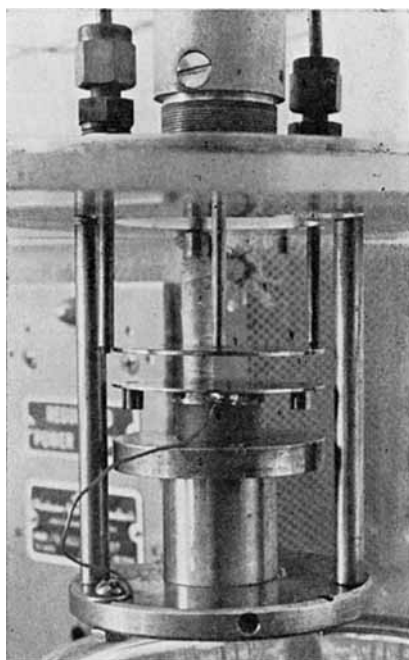


Fig. 2. Sample holder and cell (showing positioning of sample).

sensing device in combination with solenoid valves. To prevent frost formation on the capacitor plates, a stream of dry nitrogen is blown into the system during the run.

The capacitor described above, in conjunction with an inductance built into the transducer, forms a tuned radio frequency circuit which is link-coupled to a Dynagage oscillator-detector circuit. Thus, small capacity changes due to expansion of the sample produce relatively large changes in the detector impedance. The output from this detector is fed through a cathode follower to the *Y*-axis of an *X*-*Y* recorder. Temperature measurements are displayed on the *X*-axis. The *Y*-axis was calibrated at the start and at the end of each run to permit the detection of any flow of the sample. Calibration data supplied by the manufacturer were used in conjunction with the chromel-constantan thermocouple. An ice-water junction was used as a reference.

Experimental Procedure

Cylindrical samples (0.5 × 3/4 in.) of polymer were prepared in a standard mold used for the preparation of slugs for the Yerzley oscillograph. Prior to expansion measurements, the samples were allowed to relax overnight at room temperature. For uncured samples or for cured samples of low molecular weight, additional relaxation time was required so that sample creep did not influence the expansion measurements. In

TABLE II
Preparation of Samples

Sample	Conditions of preparation
Polypropylene	Annealed 6 hr. at 120°C., then cooled (6°C./hr.) to room temperature.
Natural rubber	Recipe: 100 rubber, 0.5 phr Captax, ^a 2.5 phr sulfur, 5.0 phr ZnO, 1.5 phr stearic acid. Curing conditions: 10 min. at 307°F.
Styrene-butadiene rubber (SBR-1500)	Recipe: 100 rubber, 2 phr sulfur, 5 phr ZnO, 2 phr stearic acid, 1.2 phr phenyl β-naphthylamine, 1.5 phr Altax, ^b 0.1 Cumate. ^c Curing conditions: 20 min. at 307°F.
Butyl rubber	Recipe: 100 rubber, 1.0 phr Tuads, ^d 1.0 phr sulfur, 1.0 phr ZnO. Curing conditions: 30 min. at 307°F.
Ethylene-propylene rubber (A) 73 mole-% C ₂ , $\bar{M}_v = 90,000$ (B) 33 mole-% C ₂ , $\bar{M}_v = 280,000$	Recipe: 100 rubber, 1 phr Ca stearate, 2.6 phr DiCup, ^e 0.3 phr sulfur. Curing conditions: 30 min. at 320°F. Annealed under same conditions as polypropylene.

^a 2-Mercaptobenzothiazole.

^b Di-2-benzothiazyl disulfide.

^c Copper dimethyl dithiocarbamate.

^d Tetramethyl thiuram disulfide.

^e Dicumyl peroxide.

these cases, the sample was placed in the unit and allowed to relax at room temperature until no further flow was detected. The unit was then re-balanced before cooling was started. In all of the runs reported in this paper, no flow of the sample during the run was detected.

Liquid nitrogen addition was performed slowly in order to avoid rapid cooling of the sample. A total cooling time of 1-1/2 hr. was generally used, but this can be varied as desired. The linear expansion properties of the polymers were obtained during warming of the samples because it was easier to reproduce slow warming rates than it was to obtain slow cooling. Agreement between the two methods has been obtained, however, as is shown in the SBR data. The average warming time for a total expansion curve was about 6 hr.

To compensate for any capacitance changes not due to the elastomer, a sample of Invar of the same dimensions as the polymer samples was placed in the unit and a standard curve was obtained under the conditions used to measure the polymers. This curve was then used to construct differential linear expansion plots. There is a very small error introduced by this technique but it is not significant enough to alter the conclusions drawn from any corrected expansion curves.

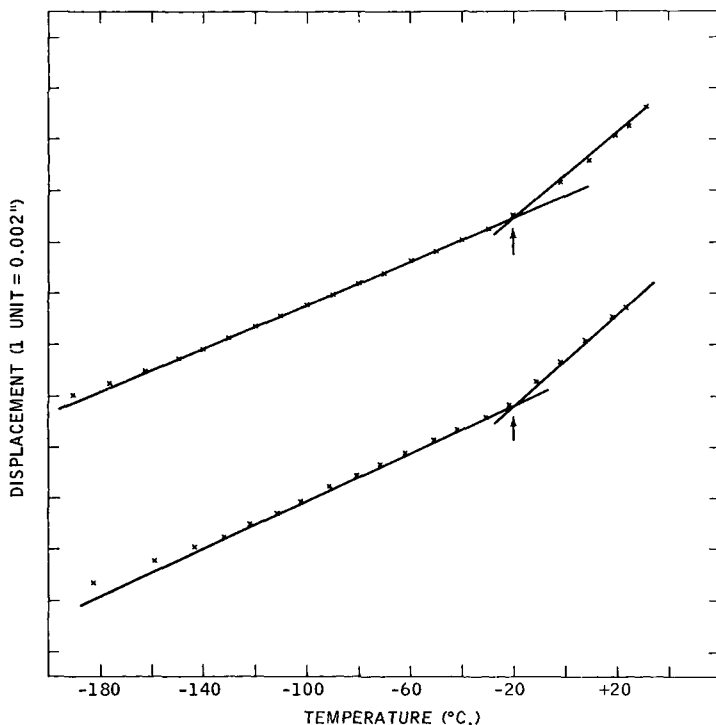


Fig. 3. Linear expansion plots for polypropylene showing reproducibility of the measurements (curves arbitrarily displaced).

RESULTS AND DISCUSSION

These examples illustrate the types of valid expansion curves obtained, certain artifacts due to experimental procedure, and the application of the method to two samples of ethylene-propylene rubber. The preparation of the samples is described in Table II.

Polypropylene

This sample was machined from a plug of polymer taken from a molding operation, and was annealed before measurement of its expansion properties. The density of this sample was 0.9085 g./cc. The glass transition in both runs (Fig. 3) was observed at about -20°C . A slight indication of an additional transition in the -140 to -160°C . region was noted, but none was seen in the -70°C . region previously reported.²

Natural Rubber

Figure 4 (curve 1) shows a curve typical of the behavior of this material after slow cooling. Several runs were required to obtain a good estimate of T_g ($-71 \pm 2^{\circ}\text{C}$.) because the curve passed from the glass transition interval directly into a crystallization interval, and thus caused difficulty in the proper selection of the correct intersection temperature (T_g).

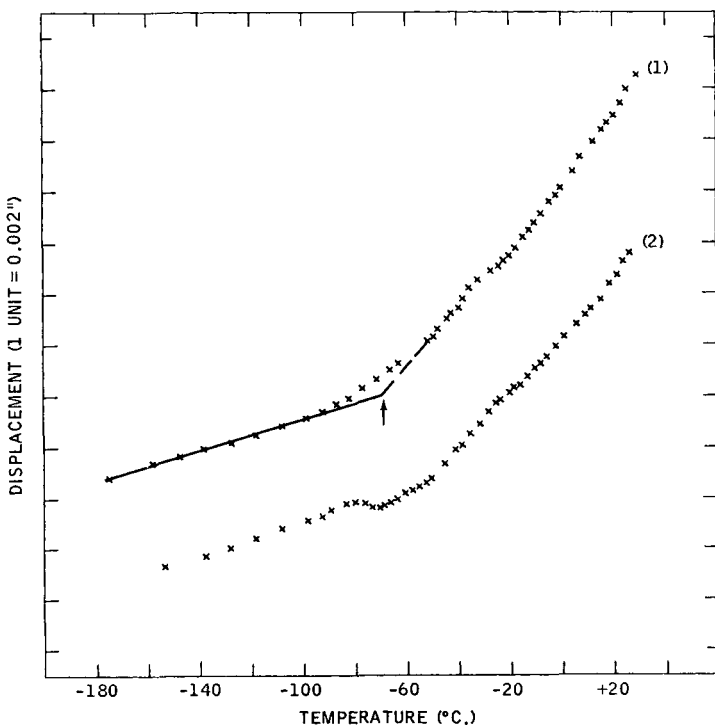


Fig. 4. Effect of cooling rate on linear expansion plots for natural rubber: (1) slow cooling; (2) shock cooling (curves arbitrarily displaced).

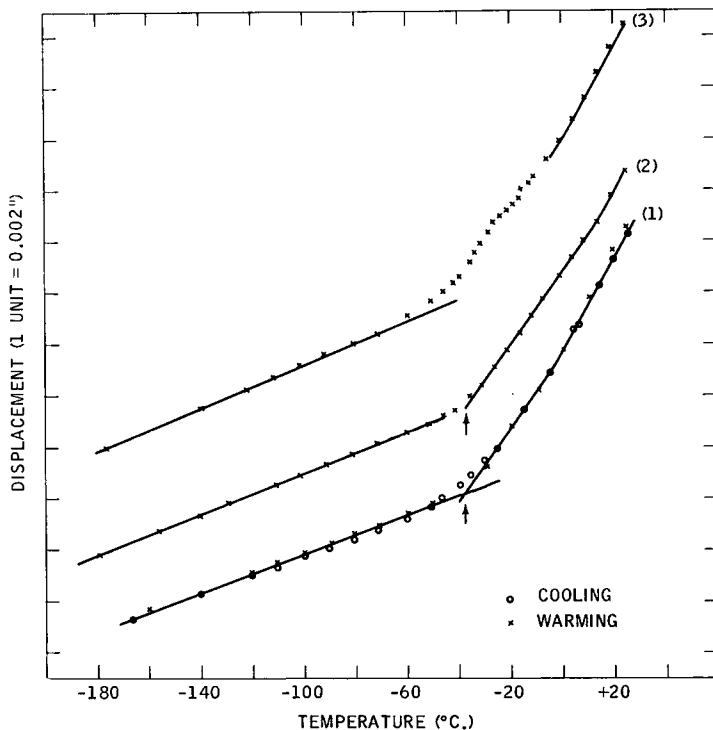


Fig. 5. Effect of experiment variables on linear expansion plots for styrene-butadiene rubber: (1) slow cooling, sample aged at 25°C.; (2) slow cooling, sample aged at 60°C.; (3) rapid cooling, sample aged at 25°C. (curves arbitrarily displaced).

Curve 2 of Figure 4 represents a typical pattern obtained when a sample is shock-cooled in such a way that it is contacted by the liquid nitrogen. This treatment causes an apparent melting region which peaks at -80°C . and a second minor apparent melting region peaking near -60°C . After this, the curve again traces out a "normal" crystallinity peak near -25°C .

Although not shown here, it has been found that a cooling rate intermediate between those used in obtaining curves 1 and 2 will result in a plateau in the expansion curve prior to T_g . This is similar to the effect described by Dannis,² but was observed only when fairly rapid cooling of the sample took place.

Styrene-Butadiene Rubber

The curves in Figure 5 illustrate the effect of several experimental variations on the expansion properties of SBR. Curves 1 and 2 of Figure 5 show that 60°C . aging of the sample did not change T_g or another transition which occurs about $+5$ to $+10^{\circ}\text{C}$. No crystallinity effects are discernible in these curves, but the presence of crystallinity is suggested by curve 3, which is the same run in which the cooling portion of curve 1 was obtained. These data show that experimental artifacts can arise even in a fairly well behaved system.

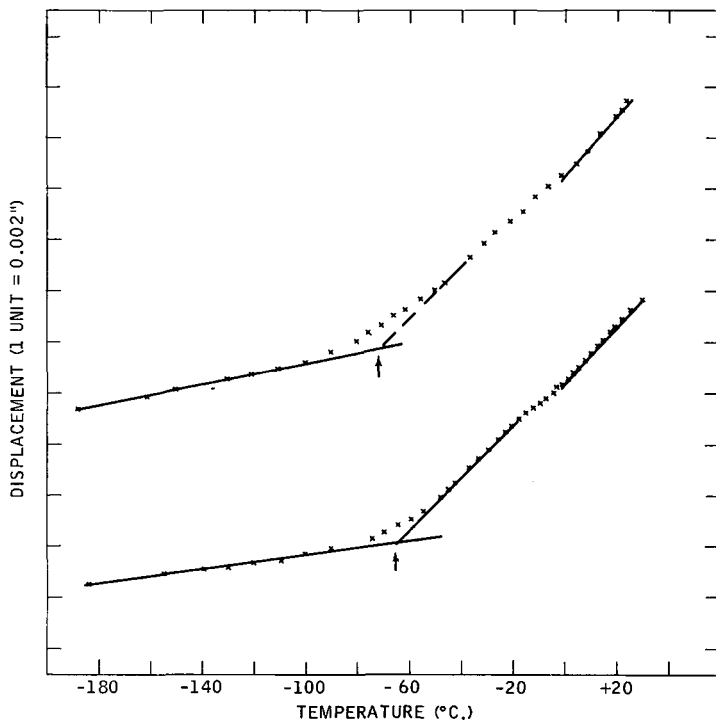


Fig. 6. Linear expansion plots for butyl rubber showing reproducibility of nonlinearity above the glass transition temperature (curves arbitrarily displaced).

Butyl Rubber

The glass transition temperatures for the two runs were -66 and -70°C . (Fig. 6), which are close to the value previously reported (-71°C .) for uncured Enjay Butyl 218.³ Above the glass transition region, there is definite nonlinearity in the expansion plot, and thus a possible indication of crystallinity in the sample, with the peak about -20 to -30°C . This was unexpected, since it has previously been shown that it is extremely difficult to crystallize unstretched butyl rubber. The nonlinearity of the plots is quite apparent, however, and is also reproducible. The present limited data do not permit further analysis of this observation.

Ethylene-Propylene Rubber

The expansion curves presented (Fig. 7) are very similar in appearance although they represent two very different polymers. Curve 1 of Figure 7 represents a low molecular weight polymer with a high ethylene content and with narrow distributions of both molecular weight and ethylene content; curve 2 represents a high molecular weight polymer, with a lower average ethylene content and with broad distributions of both molecular

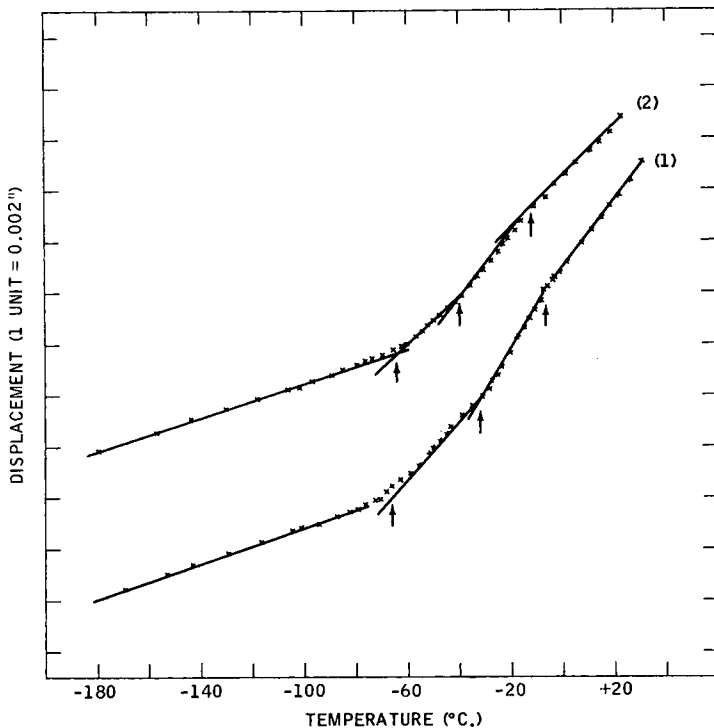


Fig. 7. Linear expansion measurements for ethylene-propylene rubbers of different compositions: (1) low molecular weight, uniform ethylene composition; (2) high molecular weight, broad distribution of ethylene composition (curves arbitrarily displaced).

weight and of ethylene content. Both samples were annealed prior to the determination of their expansion properties. The same general behavior was also found in unannealed samples.

The appearance of the curves above T_g again poses the problem of deciding whether the curve indicates crystallinity or whether there are additional transitions above the major T_g . In addition, the similarity of the two T_g values is interesting. Based on ethylene content, the sample of curve 2 should have a T_g near -40°C ., but the value is actually depressed by about -25°C . Solvent contamination was found not to be an apparent factor in this problem. In any event, the observed T_g value is much too low rather than too high, as has sometimes been observed in crystalline polymers.⁴ A gum vulcanizate of this sample, cured with peroxide and sulfur, showed no crystallinity to x-rays even after an elongation of 800%. Further, neither of the polymers showed any crystalline peaks in the infrared spectrum either before or after annealing. Finally, it was found that sample 2 was essentially completely soluble in *n*-heptane after 1 hr. at 70°C . This suggests that there was no crystalline component in the original sample.

If the observed nonlinearity in the expansion curve above T_g is not due to crystallinity, then it probably reflects the presence of two additional, minor transitions at about -35 and -5°C . These may correspond to the glass transitions attributed to atactic propylene and to stereoblock propylene segments, respectively.¹ Further work, including differential thermal analysis, is in progress to attempt a resolution of this problem.

References

1. Knox, J. R., paper presented at 140th Meeting of the American Chemical Society, Chicago, Illinois, Sept. 3-8, 1961.
2. Dannis, M. L., *J. Appl. Polymer Sci.*, **1**, 121 (1959).
3. Kell, R. M., B. Bennett, and P. B. Stickney, *Rubber Chem. Technol.*, **31**, 499 (1958).
4. Howard, W. H., *J. Appl. Polymer Sci.*, **5**, 303 (1961).

Résumé

On décrit la construction et la manipulation d'un appareil pour mesurer le coefficient d'expansion linéaire des polymères. Cette unité utilise une jauge de capacitance de proximité qui mesure les variations de capacitance causées par l'expansion de l'échantillon tenu dans une pince en Invar (alliage à faible coefficient d'expansion). On mesure simultanément et continuellement le déplacement et la température grâce à un enregistreur X-Y. On décrit l'effet des conditions opératoires sur la mesure du coefficient linéaire d'expansion et l'on montre certains artifices expérimentaux. De manière subséquente on montre que cet instrument peut servir à l'étude du propylène du caoutchouc ou styrène-butadiène du caoutchouc au butyle et du caoutchouc à base de copolymère éthylène-propylène. On trouve des régions non-linéaires distinctes à des températures supérieures au point de transition vitreuse pour le caoutchouc au butyle et le copolymère éthylène-propylène. Dans le premier cas, cet effet est probablement dû à la cristallinité; dans l'autre cas il est fort probable qu'il existe 2 transitions secondaires à des températures voisines de -35°C et de -5°C en plus de la transition principale située à -67°C . Ces transitions secondaires seraient respectivement attribuables à des segments atactiques et à des stéréoblocs de propylène.

Zusammenfassung

Es werden Planung, Aufbau und Arbeitsweise eines Gerätes zur Messung linearer Expansioneigenschaften von Polymeren beschrieben. Dabei wurde eine Messeinrichtung mit einem Abstands-Kapazitäts-Umwandler zur Messung der Kapazitätsänderungen verwendet, die durch die Ausdehnung der in einem Probenhalter aus Invar (Legierung mässiger Ausdehnung) gehaltenen Polymerprobe hervorgerufen werden. Die Messung von Ausdehnung und Temperatur wird durch einen X-Y-Schreiber kontinuierlich registriert. Der Einfluss der Versuchsbedingungen auf die Messung der linearen Expansion wird beschrieben und gewisse experimentelle Kunstgriffe angegeben. Ausserdem wird die Anwendung des Geräts auf Polypropylen, Styrol-Butadien-Kautschuk, Butylkautschuk und Äthylen-Propylen-Kautschuk beschrieben. Bei Butylkautschuk und Äthylen-Propylen-Kautschuk wurden oberhalb der normalen Glasumwandlungstemperatur ausgeprägte nichtlineare Bereiche festgestellt. Im ersten Fall wird dieser Effekt wahrscheinlich durch Kristallinität hervorgerufen. Im zweiten Fall treten wahrscheinlich ausser der Hauptumwandlung bei -67°C noch zwei Nebenumwandlungen bei etwa -35°C und -5°C auf. Diese Nebenumwandlungen dürften auf ataktische bzw. Stereoblock-Propylensegmente zurückgehen.

Received June 27, 1963

Revised August 16, 1963