

Characterization and effects of n-alkane swelling of polystyrene sheets

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Detailed penetration kinetics of a series of normal alkanes in 2 mm polystyrene sheets have been determined by an optical method over a broad range of temperatures encompassing the effective glass transition temperature of the resulting sheets. Whereas earlier thin film results, involving identical thermodynamic boundary conditions, have been characterized by ideal Case II transport, the results obtained here appear to be confounded at long times by a significant diffusional resistance in the swollen surface regions surrounding the unplasticized central core of these relatively thick sheets. At relatively low temperatures, the rate determining relaxations, at the boundary between swollen and unswollen polymer, are sufficiently slow to ensure ideal Case II transport over the entire course of the sorption history. These swelling experiments were complemented by Clash–Berg measurements of the temperature-dependence of the 10 sec torsional shear moduli of partly penetrated sheets, completely swollen sheets and unswollen sheets. The Clash–Berg results suggest that the T_g of the n-hexane swollen sheet is approximately 20°C and that the properties of the swollen regions of partly penetrated specimens are identical to the properties of the completely swollen sheet. A model based on the core-shell morphology, induced by the prior swelling, satisfactorily describes the observed mechanical properties of these swelling induced composites.

INTRODUCTION

Case II (relaxation-controlled) transport of organic vapours and liquids in polystyrene has been studied actively during the past decade^{1–6}. Although the experiments reported to date deal with a variety of system parameters including temperature, penetrant type, penetrant activity, polymer molecular weight, polymer orientation, and coblanding, the experiments have been largely confined to gravimetric sorption experiments in relatively thin films.

Although data have been reported for the series of n-alkanes from n-pentane to n-nonane^{1,2}, the experiments have concentrated on n-pentane and n-hexane penetration. Typically, the sorption kinetics are relaxation controlled (Case II) involving a linear relationship between the amount of penetrant sorbed and the contact time of the polymer and penetrant. At high penetrant activities, solvent induced crazing (microvoiding) accompanies the solvent penetration^{1,7}. These conditions permit independent optical determination of the velocity of the craze front and gravimetric adsorption kinetics⁶. These comparative experiments revealed that a step concentration profile does in fact develop in a swollen shell surrounding an essentially unpenetrated core. Phenomenologically, this result requires that diffusion of penetrant through the swollen shell to the relaxing boundary is extremely rapid compared with the rate-determining swelling induced relaxations. These results suggested, moreover, that a general optical technique could be developed whereby glassy polymers could be immersed in liquid penetrants containing appropriate dyes. Assuming that the dye diffuses to the relaxing boundary through the penetrant swollen outer shell, significantly more rapidly than the rate-

determining relaxations, the swollen regions would be highlighted by the dye, facilitating visible detection of the moving boundaries separating the swollen shells from the unpenetrated core. This technique could be applied quite simply to thick (>1 mm) sheet specimens.

The objectives of this investigation involved a general extension of the earlier experiments to include thick sheet specimens (approximately 2 mm). The penetration kinetics were determined optically using the dye highlight approach to characterize penetration from the liquid phase. The experiments involved detailed investigation of the n-alkane series, n-pentane through n-octane, over a temperature range 25° to 85°C.

The swelling experiments were complemented by Clash–Berg determinations of the T_g of the swollen specimens as well as Clash–Berg torsional mechanical characterization of the swelling induced composites. The T_g and mechanical results were analysed together with the independently determined penetration measurements.

EXPERIMENTAL

Materials

A polystyrene standard, designated as polystyrene-2 and supplied by the Polymer Supply Characterization Centre, Rubber and Plastics Research Association (RAPRA) of the United Kingdom, was used without further purification to form the hot pressed sheets. The number-average molecular weight, \bar{M}_n , was determined to be 151 000 by gel permeation chromatography analysis of a tetrahydrofuran solution of the polystyrene. The ratio of the weight-average molecular weight to the number-average molecular weight, \bar{M}_w/\bar{M}_n , was 2.36.

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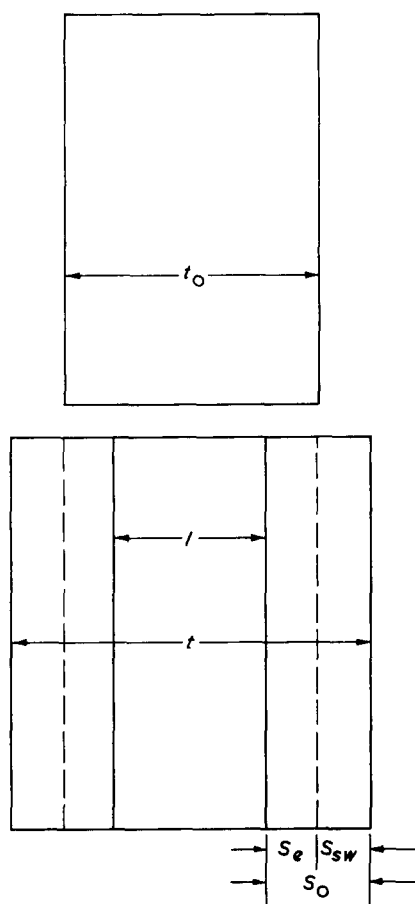


Figure 1 Schematic diagram of original and swollen sample cross-sections including symbolic designation of the relevant dimensions

Standard sheet specimens, 2 mm thick, were formed by compression moulding granules in teflon spray-coated moulds producing rectangular sheet specimens $130 \times 55 \times 2$ mm under a pressure of 5000–6000 p.s.i. at 200°C . The samples were maintained at these elevated temperatures for 30 min under pressure and then slowly cooled to room temperature, still under pressure. After attainment of room temperature, the pressure was relieved rapidly and the samples removed from the mould.

From each moulded specimen, 12 smaller samples, each $12 \times 50 \times 2$ mm were cut using a diamond knife. The sectioned samples were then thermally treated at 80°C for 40 h to release induced stress prior to further experimentation.

The normal alkanes (n-pentane, n-hexane, n-heptane and n-octane) reagent grade (Carlo Erba, SpA) were used without further purification in the sorption experiments.

Procedure

The penetration experiments were carried out by placing multiple $12 \times 50 \times 2$ mm samples in each of the n-alkanes studied. The liquid penetrants were maintained at a pre-determined temperature which varies less than $\pm 0.1^\circ\text{C}$ during the course of the experiment. The specimens were suspended in the solvent to avoid contact with the n-alkane-containing walls. At prescribed time intervals, samples were removed sequentially from the n-alkane. Immediately upon removal, the sample was quenched to -20°C and then fractured. The cross-section was viewed with a 'Stereoscan' optical reflectance microscope. A sharp boundary, easily detectable with the optical microscope, separated the apparently unpenetrated central core from morphologically altered, swollen

outer layers. The thickness of the central core and the overall specimen thickness were determined microscopically with a calibrated, Filar micrometer eyepiece. In some experiments, an n-alkane soluble dye was added to the penetrant to highlight the visual distinction between the swollen and unpenetrated polymer. The addition of dye (e.g. Sudan Red IV) was not required to determine the position of the boundary nor did it affect the kinetics of penetration. Mechanical tests were performed by using a Clash–Berg torsional stiffness apparatus. Untreated specimens, $60 \times 10 \times 2$ mm and samples previously immersed (and therefore swollen) in the n-alkane for various predetermined times, were subsequently tested over a broad range of temperatures.

The experiments were performed while the specimen was completely submerged in the respective n-alkane used previously to induce swelling in the outer layers. Clash–Berg experiments were commenced at -10°C and the temperature increased until the T_g was passed. Reference experiments were carried out with PS2 samples immersed in paraffin oil.

The torsion angle, α , was detected after 10 sec of application of the torque, M_t , according to the test protocols of Tobolsky⁸. The values of the shear moduli were calculated according to the following equation:

$$G = 917 \frac{M_t l}{u a b^2} \quad (1)$$

where a , b and l are respectively the width, thickness and length of the specimen and u is a parameter which depends upon the ratio a/b ⁹.

RESULTS AND DISCUSSION

The polystyrene sheets, as a result of the immersion in the various n-alkanes, increase in thickness. Moreover, the sectioned samples, after immersion, exhibit a clearly discernible boundary between swollen and unpenetrated polymer. The various dimensions used to characterize this concomitant expansion and penetration are presented in the schematic diagram of Figure 1. The symbol t_0 is used to describe the initial sheet thickness, S_e designates the depth of penetration of the advancing front at any time t , S_{sw} is used to abbreviate the linear increase in the half-sheet thickness, and S_0 is the apparent uncorrected depth of penetration, based upon the dimensions of the swollen specimen.

The temperature-dependence of the kinetics of liquid n-hexane penetration of these relatively thick (2 mm) sheets are presented in plots of penetration depth (referred to the original sample dimensions) S_e versus time in Figure 2.

Qualitatively similar plots were obtained for n-heptane and n-octane penetration over the temperature range $25^\circ - 80^\circ\text{C}$. In all cases, the plots deviate from linearity at relatively short times. Similar plots describing n-pentane penetration are presented in Figure 3. The penetration rate for n-pentane at 25°C (the lowest temperature studied in this work) was, in contrast, constant over the entire period of penetration.

These results suggest that, after initial Case II penetration, significant diffusional resistances are developed in the swollen outer regions of the sheet providing an increasing diffusional resistance to continuing absorption as the swollen outer shell becomes progressively thicker. The initial rates of penetra-

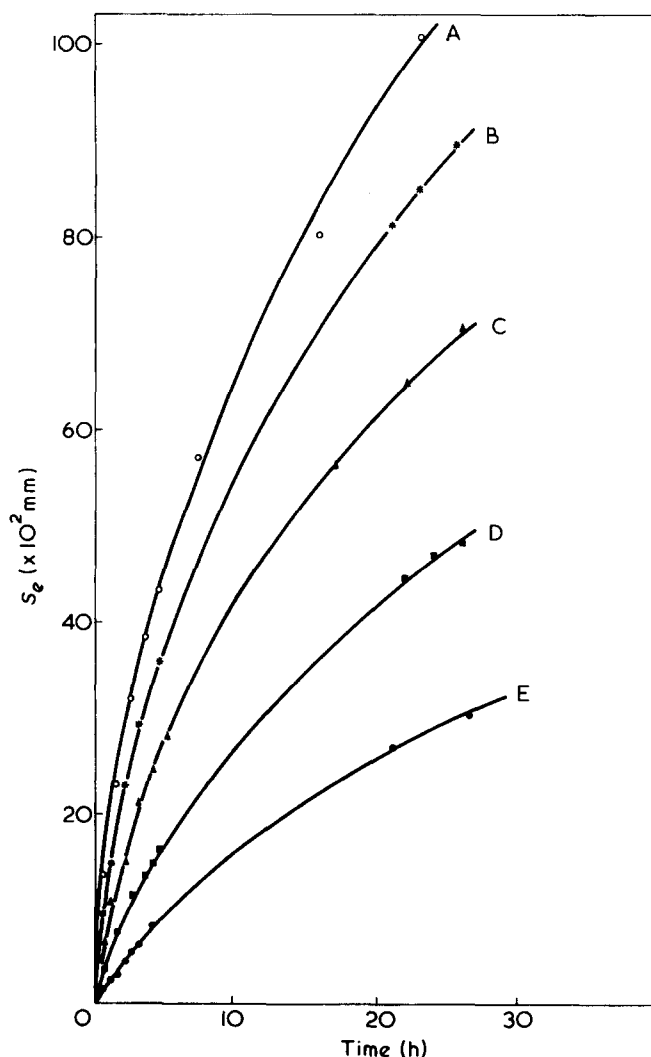


Figure 2 Temperature dependence of *n*-hexane penetration of polystyrene sheets. A, $T = 55^\circ\text{C}$; B, $T = 50^\circ\text{C}$; C, $T = 45^\circ\text{C}$; D, $T = 40^\circ\text{C}$; E, $T = 35^\circ\text{C}$

tion determined in these thick sheets are quite similar to the penetration rates calculated from the absorption data presented earlier by Jacques and Hopfenberg⁶ for liquid *n*-hexane penetration of thin polystyrene films. Specifically, Jacques and Hopfenberg reported a penetration velocity (calculated from gravimetric absorption data assuming perfect step concentration profiles) of 4.5×10^{-5} cm/min at 35°C in 1.5 mil polystyrene films. The initial slope of the penetration–time plot (see Figure 2) characterizing sorption in the 2 mm sheets corresponds to a penetration velocity of 3.7×10^{-5} cm/min at the same temperature. The gratifying similarity between these optically determined initial penetration rates and the calculated front velocities obtained from gravimetric sorption experiments in thin films, strongly suggests that limiting Case II sorption does indeed control the initial penetration of these thick sheets.

At relatively low temperatures (e.g. *n*-pentane penetration at 25°C) the rate-determining relaxations, at the boundary between swollen and essentially unpenetrated polymer are sufficiently slow to ensure ideal Case II transport over the entire course of the sorption history. The relatively high activation energy for these swelling induced relaxations ($\sim 45\text{--}55$ kcal/mol) ensures that, at the relatively low temperatures, the relaxation processes are markedly retarded

compared with the less activated diffusional processes. Diffusion to the relaxing boundary remains relatively rapid, therefore, compared with the rate-determining swelling induced relaxations. Case II transport, not altered by a noticeably increasing diffusional resistance is only observed, therefore, in relatively thin films or for penetration of thick sheets at relatively low temperatures.

Assuming that Case II transport does indeed control initial penetration of these sheets, the initial slopes of the penetration–time plots (e.g. Figure 2) would be proportional to the respective Case II relaxation constants. The initial penetration rates, V_0 , are therefore plotted in Arrhenius form in Figure 4. The activation energies describing the Case II absorption of the individual *n*-alkanes in polystyrene, are calculated directly from the slopes of the Arrhenius plots in Figure 4 and are reported in Table 1.

The magnitude of the activation energies determined here are in good agreement with related values for the respective *n*-alkanes reported previously by Hopfenberg, Holley and Stannett². In addition, by varying the penetrant activity for a given alkane, Hopfenberg *et al.*² demonstrated that the activation energy for Case II transport increases with the

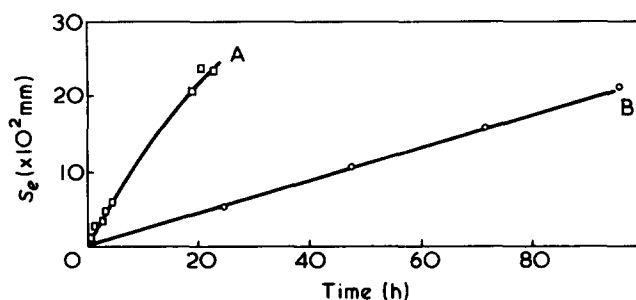


Figure 3 Temperature dependence of *n*-pentane penetration of polystyrene sheets. A, $T = 30^\circ\text{C}$; B, $T = 25^\circ\text{C}$

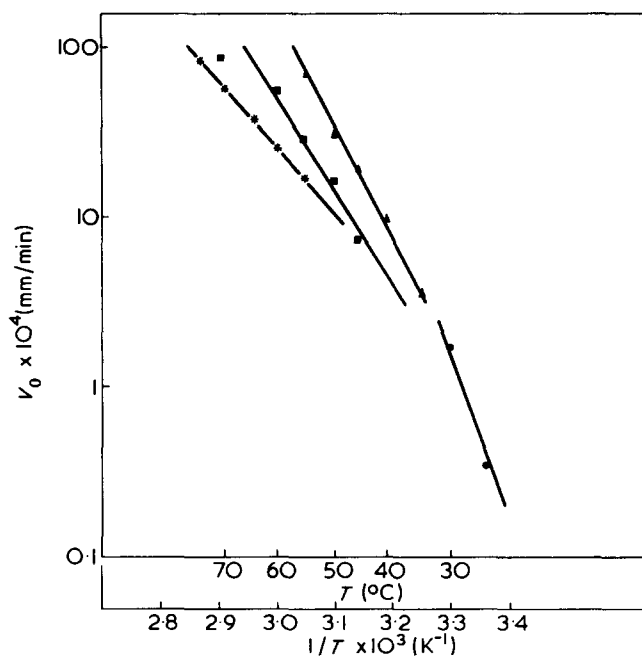


Figure 4 Arrhenius plots of the temperature dependence of the initial penetration velocity of a series of *n*-alkanes in polystyrene sheets. ●, *n*-pentane; ▲, *n*-hexane; ■, *n*-heptane; *, *n*-octane

Table 1 Activation energies describing Case II penetration of *n*-alkanes in polystyrene sheets

Penetrant	Activation energy (kcal/g mol)
<i>n</i> -Pentane	52
<i>n</i> -Hexane	42
<i>n</i> -Heptane	29
<i>n</i> -Octane	15

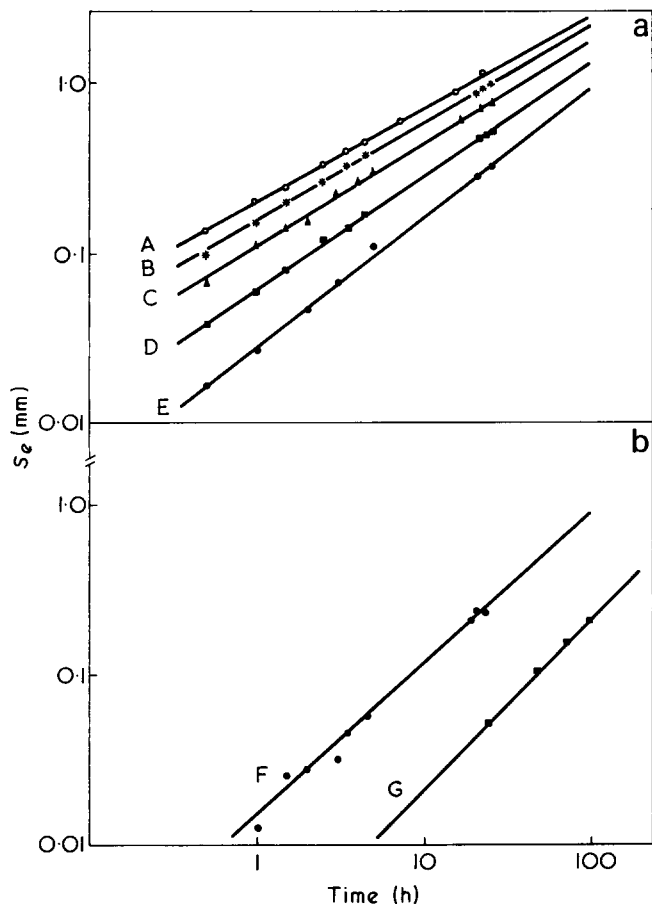


Figure 5 Logarithmic plots of the time dependence of penetration in polystyrene sheets of (b) *n*-hexane: A, 55°C; B, 50°C; C, 45°C; D, 40°C; E, 35°C. (a) *n*-pentane: F, 30°C; G, 25°C

increasing rate of penetration associated with sorption at the higher activities. The results of *Figure 4* and *Table 1* also indicate that the activation energies for the more rapid processes are higher than the corresponding activation energies for the slower penetration. In contrast, most activated processes (e.g. diffusion or chemical reaction) exhibit so-called compensation involving a lower activation energy (barrier) for the inherently more rapid process. Hopfenberg *et al.*² suggested earlier that the more rapid absorption is a consequence of larger polymer segments cooperating in the rate-determining relaxation and, therefore, a higher activation energy is reasonably associated with the more rapid penetration under conditions which lead to limiting Case II (relaxation controlled) absorption.

Wang, Kwei and Frisch¹⁰ have presented an approximate relationship, based upon a model describing coupled diffusional and relaxation processes, for the time dependence of the position of the moving boundary for Case II transport altered by diffusion. Their result is presented as equation (2):

$$S_e = 2k(Dt)^{1/2} + vt \quad (2)$$

where: S_e is the position of the moving boundary relative to the initial position of the unswollen sheet surface; k is a constant; D is the diffusion coefficient; t is time and v is the velocity of the moving boundary under conditions of limiting Case II transport.

The two special cases of $D \ll v$ and $D \gg v$ correspond to Fickian diffusion and Case II transport, respectively. Typically, $D \ll v$ suggests a rubbery system wherein relaxations, characterized by the parameter v are very rapid. The assumptions inherent to limiting Case II transport require that slow relaxations are rate determining. It is convenient, therefore, to model intermediate processes by the phenomenological equation:

$$S_e = at^n \quad (3)$$

The exponent, n , would be equal to 1.0 for limiting Case II transport and would equal 0.5 for limiting Fickian diffusion. Intermediate behaviour would be characterized by values of n which lie between 0.5 and 1.0.

The exponents are conveniently determined by evaluating the slope of a log-log plot of S_e versus t . All the data, for the temperature range 25°–80°C, have been included in the log S_e versus log t plots of *Figures 5* and *6*. In this manner, the exponents, n , which characterize the form of the penetration kinetics, can be determined for each penetrant at

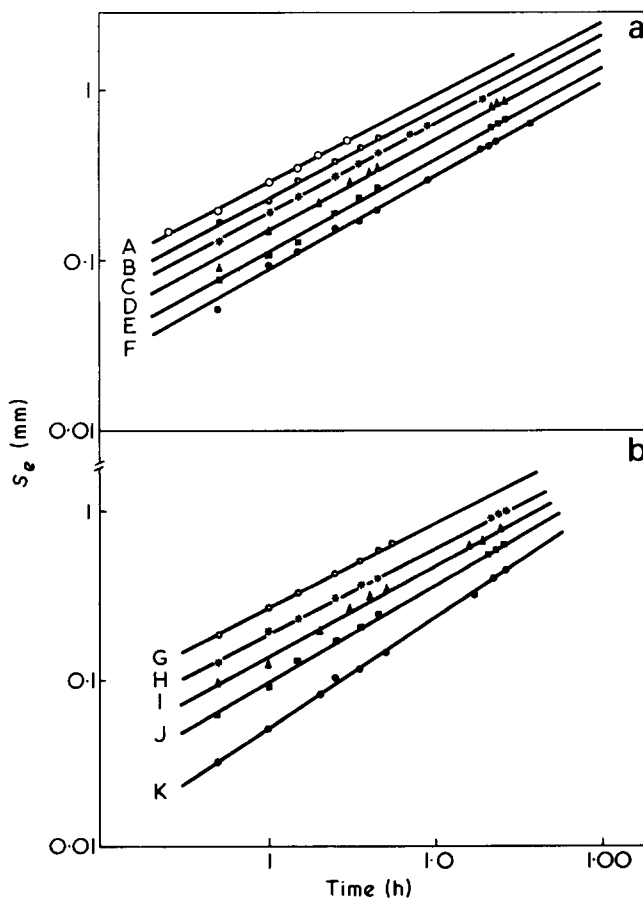


Figure 6 Logarithmic plots of the time dependence of penetration in polystyrene sheets of (b) *n*-octane: A, 80°C; B, 75°C; C, 70°C; D, 65°C; E, 60°C; F, 55°C. (a) *n*-heptane: G, 70°C; H, 60°C; I, 55°C; J, 50°C; K, 45°C

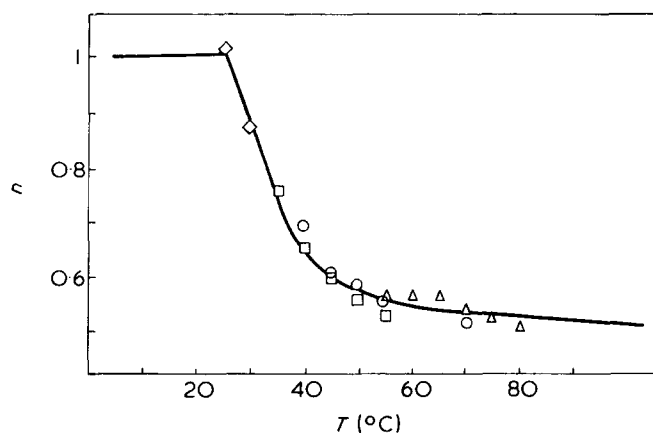


Figure 7 Relationship between exponent, n , in equation; $S_e = at^n$ and temperature, describing penetration of the *n*-alkane series pentane through octane in polystyrene sheets. Symbols: \diamond , *n*-pentane; \square , *n*-hexane; \circ , *n*-heptane; \triangle , *n*-octane

each temperature studied. The temperature dependence of the exponent, n , is presented in Figure 7; results derived from each penetrant are designated separately by a distinctive symbol.

The exponent n varies monotonically from a low temperature limit of 1.0, (corresponding presumably to Case II transport) to a high temperature asymptotic value of 0.5 (resulting presumably from relatively rapid relaxations and, therefore, diffusion controlled penetration). Quite strikingly, the value of the exponent is essentially independent of the molecular weight of the specific penetrant. This independence presumably derives from the comparable volumetric swelling achieved with the various *n*-alkanes². Limiting Case II penetration is apparently achieved as the temperature is reduced to approximately 20°C. This limiting transport behaviour is approached at a temperature which is quite similar to the value of the glass transition temperature, T_g , determined by the inflection point in the Clash–Berg plot reported in Figure 8 for the sheet specimen which was previously swollen completely with *n*-hexane. Data for 10 sec shear moduli, $G(10)$, are also presented in Figure 8 for previously untreated samples as well as for swelling induced composites, prepared by immersing the sheets in *n*-hexane at 50°C for 1, 3, and 20 h prior to torsional testing.

The data presented in Figure 8 for the swelling-induced composites have been compared with a predictive model which has been derived by considering the partly penetrated sheets as a composite of a rigid core surrounded by uniformly swollen and sharply defined outer layers, consistent with the schematic diagram of Figure 1. Values of the shear moduli for the core and shell have been determined from the experimental values of the shear moduli of the untreated and completely swollen specimens, respectively. The temperature dependence of the moduli are presented in Figure 8 as curves B and F for the untreated and completely swollen samples, respectively. The experimental data have been connected simply by a broken line. The solid curve C, D and E in Figure 8 have been derived, however, from a simple linear model which states that:

$$G_c = AG_1 + BG_2 \quad (4)$$

where: G_c is the shear modulus of the composite; G_1 is the shear modulus of the core and G_2 is the shear modulus of the swollen shell and

$$A = \frac{a_1 b_1^3 u_1}{a_c b_c^3 u_c} \quad \text{and} \quad B = 1 - A$$

where a and b are the width and thickness characterizing the dimensions of the core in the overall composite and u is a parameter which depends upon the ratio a/b . The subscript 1 refers to the core and the subscript c refers to the total composite. The appropriate dimensions have been determined from the penetration and swelling measurements.

The excellent agreement between the experimental data for the partly penetrated sheets and the model embodies in equation (3) provides support for the assumptions inherent in the model. Specifically, the penetrated shells are compared with the core and the boundary between swollen and unpenetrated polymer is distinct.

Curves C, D and E all exhibit an inflection in the vicinity of 20°C consistent with the T_g of the completely swollen polymer. The limiting modulus of the swelling-induced composites in the temperature range immediately above 20°C, decreases systematically, however, as the ratio of swollen to unpenetrated polymer increases. The inflection apparent in the Clash–Berg plots for the swelling-induced composites and for the completely swollen sheet provides additional evidence that the properties of the shell are quite similar to the properties of the completely swollen sheet. Qualitatively identical results relating Clash–Berg determinations with penetration measurements were obtained with the other *n*-alkanes studied.

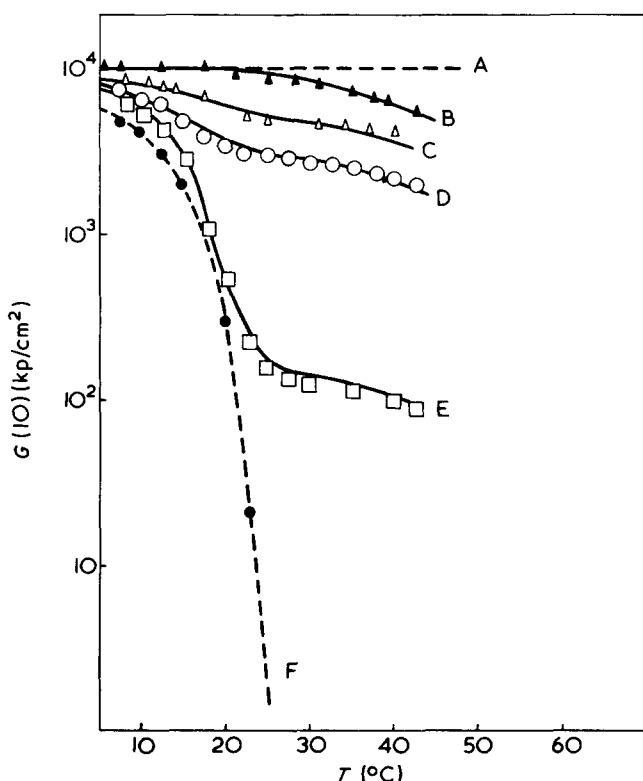


Figure 8 10 sec shear moduli determined by the Clash–Berg technique⁸ for polystyrene sheets which have been previously immersed in *n*-hexane under various conditions. \blacktriangle , previously unpenetrated; \triangle , immersed 1 h at 50°C; \circ , immersed 3 h at 50°C; \square , immersed 20 h at 50°C; \bullet , previously immersed at 50°C to ensure that sample is uniformly and completely swollen

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