Exudation of Plasticiser from Vulcanised Rubbers

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A rather intriguing exudation process, termed sweating is described. This process which does not appear to be due to supersaturation effects, seems at first sight to contradict the thermodynamics of equilibrium swelling. Conditions and factors which affect this process in natural and synthetic rubber vulcanisates, previously swollen to equilibrium in dioctylphthalate, are discussed. It is suggested that the process could be due to surface tension effects caused by the presence of impurities or imperfections on the swollen rubber surface or simply contact of the swollen rubber with foreign substrates.

Rubber compounds contain a variety of ingredients which in some instances can include oils and plasticisers. These are usually incorporated into the rubber at moderately high temperatures because they then become more soluble in the polymer. When the compounded and subsequently vulcanised rubber is cooled to ambient temperatures, the solubility of some of the ingredients in the rubber becomes much reduced and they move to the rubber surface. This supersaturation model is applicable if the material does not precipitate out in the bulk of the rubber. If precipitation does occur, then a different mechanism which involves elastic stresses acting around the precipitates, provides the necessary driving force for the movement of the material to the rubber surface. Such is the case for wax blooming in rubber vulcanisates[1].

However, it has been found that such conditions are not always necessary. If a sheet of rubber, swollen to equilibrium in a high swelling non-volatile liquid at a particular temperature, is taken out of the liquid, its surfaces cleaned and left otherwise undisturbed at the same temperature, droplets of the liquid somewhat similar in character to beads of sweat, form on the surface of the rubber after some time. This phenomenon of 'sweating' is not unique to any type of liquid and many liquids which swell the rubber appreciably (e.g. plasticisers) show this behaviour. Nah[2] carried

out some studies on this phenomenon. He found that sweating occurred in both unextracted and acetone-extracted natural rubber (NR) vulcanisates and that the liquid which sweated to the rubber surface was virtually identical to the liquid in which the rubber was previously swollen except for minute traces of unidentified materials. Nah also observed that when a sample which had sweated for some time was re-immersed in the liquid, re-swelling occurred and the equilibrium swelling attained was virtually identical to the original[2].

The phenomenon is puzzling from the thermodynamic point of view. During the sweating process, the rubber is apparently in equilibrium with the liquid droplets on its surface, but this equilibrium is not the same as that found when the rubber is completely immersed in the liquid. The reason for this is not immediately obvious, and this paper reports and discusses investigations aimed at clarifying the mechanism.

MATERIALS AND METHODS

The liquid used for these investigations was dioctylphthalate (DOP) because it is sufficiently non-volatile and exhibits considerable sweating[2]. Acetone-extracted peroxide-cured natural and synthetic rubber vulcanisates were used. Such a cure system eliminates

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complications in the interpretation of results caused by vulcanisation ingredients and residues. The rubber formulations for the various rubbers used are given in *Table 1*.

TABLE 1. RUBBER FORMULATIONS

Vulcanisate	Amount (parts by weight)
NR	
NR (SMR L)	100.0
Dicumyl peroxide	2.0
BR	
BR (Europrene)	100.0
Dicumyl peroxide	0.6
IR	
IR (Cariflex IR 305)	100.0
Dicumyl peroxide	1.0
EPM	
EPM (Vistalon 404)	100.0
Dicumyl peroxide	2.5

All four rubber samples were vulcanised for 10 min at 100°C followed by 60 min at 160°C

Test samples, usually 50 mm square and about 0.6 mm thick were used. These were immersed in DOP and their weight regularly monitored until equilibrium swelling was reached. Once this was attained, the samples were cleaned with filter paper to remove the excess liquid on the rubber surface and then allowed to sweat under various experimental conditions. The amount of sweating was monitored by weighing the sample periodically after cleaning, using an analytical balance.

RESULTS AND DISCUSSION

Figure 1 shows typical swelling and sweating curves of the NR vulcanisate at (30 ± 0.2)°C and serves to illustrate the essential features of the sweating phenomenon. For this particular case, the swollen rubber was wrapped up in aluminium foil and allowed to sweat. The mass uptake (swelling) or loss (sweating) of plasticiser

per unit area, M_t, has been corrected for lateral increase in the dimensions of the testpiece, which usually occurs as a result of swelling. This is done by multiplying the weight change by $(v_r^{\frac{2}{3}}/A_o)$, where v_r is the volume fraction of rubber and A_o the total unswollen area of the sample.

The swelling curve *(Curve A)* in *Figure 1* has the general features of a diffusion-controlled process from which an average diffusion coefficient can be calculated. Since the rubber swells considerably, the mutual diffusion coefficient[3], D^v, is probably more appropriate although it is realised that this quantity, appropriate for diffusion in one dimension only, is not strictly applicable to isotropic swelling. For this NR vulcanisate which had a shear modulus, G, of 0.5 MPa, the weight uptake of DOP at 30°C was 120% and its mutual diffusion coefficient 1.5×10^{-12} m²s⁻¹.

Curve B in *Figure 1*, the sweating curve, shows an initial linear relationship between M_t and $\sqrt{t}$ where t is the time for which the sample has been allowed to sweat. This coupled with the fact that the sweating rate was independent of the sample thickness[2] suggest that the process is diffusion-controlled. However, at longer times, this curve tends to become convex to the $\sqrt{t}$ axis probably due to oxidation of the highly swollen rubber and its removal during the cleaning process prior to weighing. The initial sweating rate was 4.1×10^{-6} kg m⁻²s⁻¹ while the swelling rate was 9.2×10^{-5} kg m⁻²s⁻¹. This suggests a much lower diffusion coefficient *(D)* of the DOP during the sweating process. The low D during sweating is however, not due to concentration effects on D since the asymptotic D of the plasticiser, near equilibrium swelling, was similar to that calculated from the initial slope of the swelling curve, both being about 2×10^{-12} m²s⁻¹. It should be noted that after twenty-seven days, the amount of material that had exuded to the surface of the rubber was only about 3% of the equilibrium plasticiser uptake and the process persisted even after three months by which time the rubber sample had also become quite sticky.
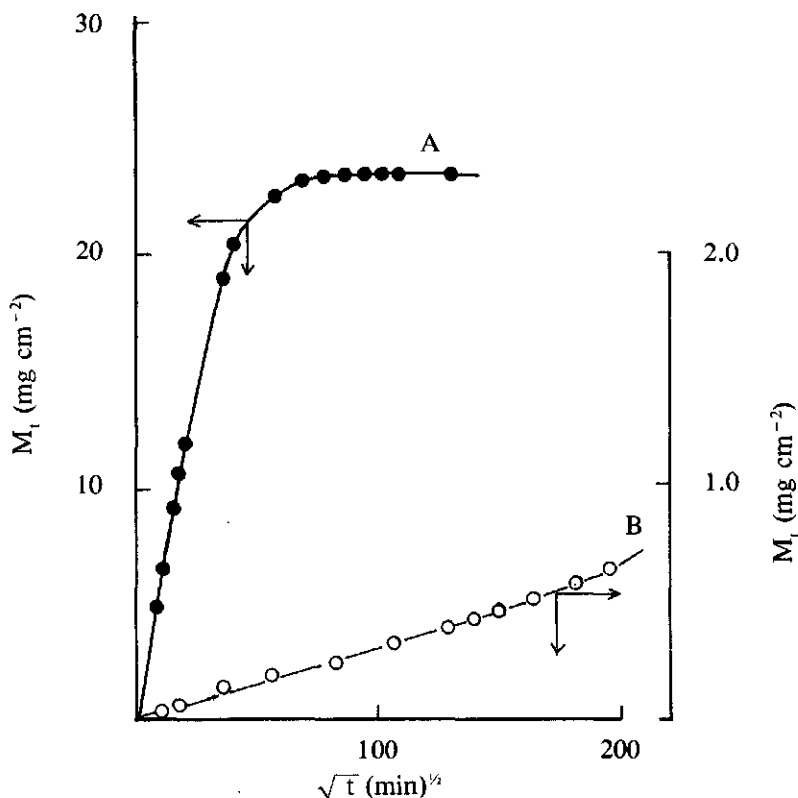
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Figure 1. Swelling A and sweating B curves of dioctylphthalate in vulcanised natural rubber (2.0 p.p.h.r. DCP) at 30°C.

Effect of Materials in Contact with the Swollen Rubber

Samples of the NR vulcanisate, swollen to equilibrium in DOP at $(30 \pm 0.2)°C$, were allowed to sweat at the same temperature under the following conditions: a) wrapped up in aluminium foil; b) sandwiched between two Whatman Qualitative No. 1 filter papers; c) dusted with ballotini No. 15 (*i.e.* glass beads whose diameters were between $60 \mu m$ and $95 \mu m$) and then wrapped up with aluminium foil; and d) ballotini-treated as in c) but the sample was sandwiched between two of the same filter papers as above. After weighing, all the rubber samples were either wrapped up with clean aluminium foil or sandwiched between clean filter papers, as necessary, before being returned to the oven at $(30 \pm 0.2)°C$. For

samples treated with ballotini, fresh ballotini was dusted onto the rubber surfaces before the samples were re-wrapped. *Figure 2* shows the results of this experiment.

For low sweating rates (*Curves C* and *D*), the initial linear region extends for a long time, up to about twenty-five days while for high sweating rates (*Curves A* and *B*), the linear regions extend either for a short time or are virtually non-existent. The amount of sweating is greater when the swollen rubber is in contact with filter paper than with aluminium foil, especially at longer times. *Figure 2* also shows that dusting the samples with ballotini effectively reduces the amount of sweating.

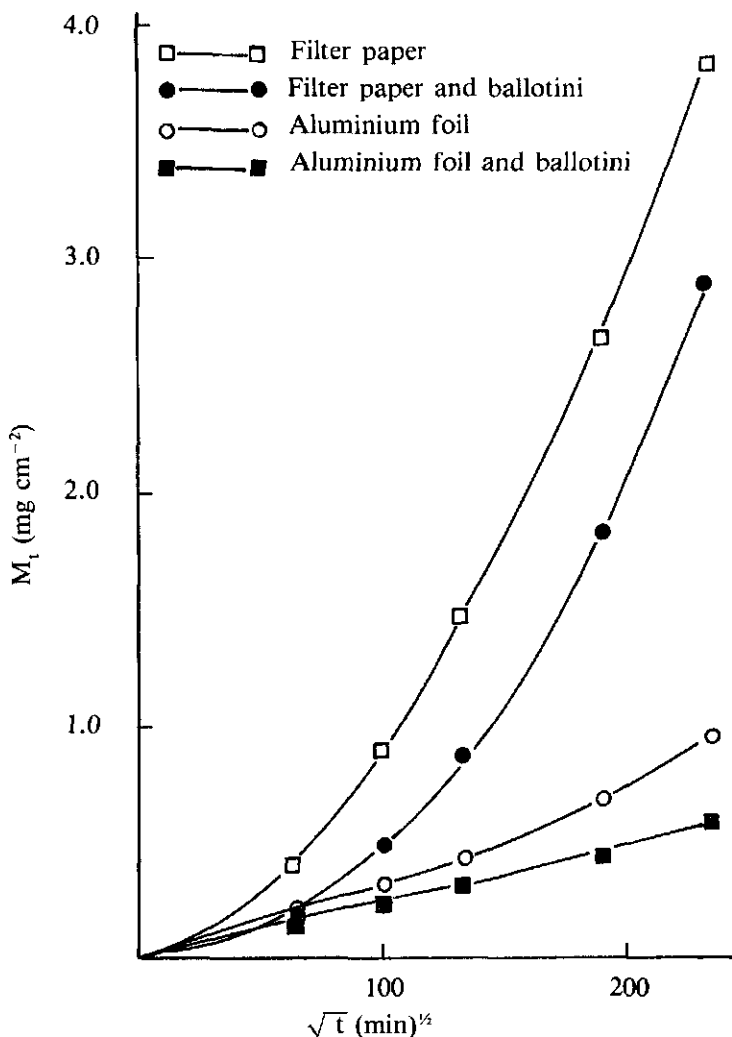If it is assumed that the mechanism of sweating is due to surface tension forces at

Figure 2. Effect of surface contact conditions on the sweating rate of DOP from a NR vulcanisate (2.0 p.p.h.r. DCP) at 30°C.

points of contact between the rubber and any foreign material such as dust, filter paper debris, filter paper or aluminium foil, then the above results imply that these points of contact are fewer when the swollen sample is wrapped up with aluminium foil than with filter paper. However, the surface tension hypothesis does not provide an explanation why the process continues over such long periods even after the amount of liquid exuded is more than sufficient to saturate the foreign material[4].

The higher sweating rate observed with filter paper could be due to it being absorbent but this effect cannot be large since droplets of DOP were still seen on the rubber surface. This suggests that intimate contact was lacking between paper and rubber and placing a light load on the paper did indeed increase the sweating rate and there were many fewer discrete DOP droplets seen on the rubber surface. This increased sweating over the 'no-load' condition is shown in *Figure 3*, where
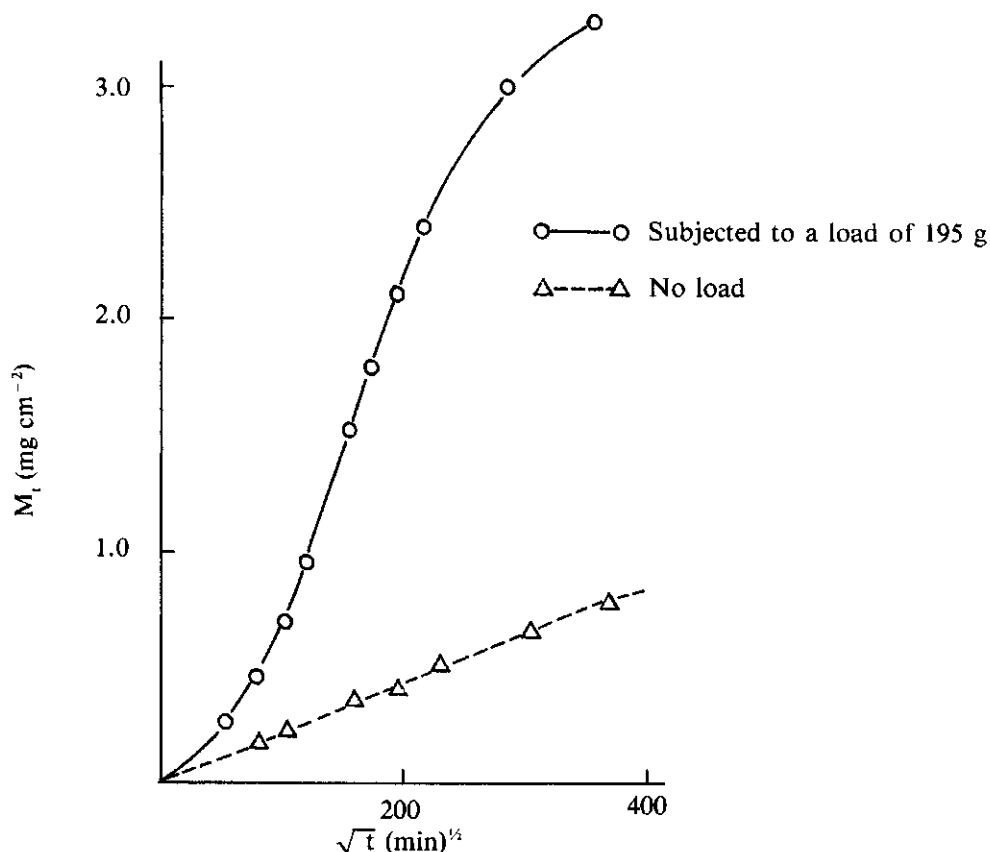
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Figure 3. Sweating of DOP from swollen NR vulcanisate (1.6 p.p.h.r. DCP). Rubber sandwiched between two Whatman No. 42 filter papers.

a load of 195 g was evenly applied to the filter paper/rubber sandwich. The hydrostatic pressure required to change the equilibrium swelling in the rubber by the amount of DOP that had sweated out from these rubbers after three months was calculated from the Flory-Huggins equation[5] and was found to be 0.09 MPa. This value is one hundred times higher than the pressure acting on the sample due to a load of 195 g. Thus, the increased sweating must be associated with a more intimate contact between the fibres in the filter paper and the swollen rubber. This would give rise to more points of contact between the two which, according to the surface tension hypothesis, would result in more sweating.

The effect of ballotini on the sweating rate, shown in *Figure 2,* is a little puzzling. It is possible that the presence of the glass beads causes a nett reduction in the surface tension forces acting on the liquid in the rubber since these beads will generally be larger than dust particles. However, why there should be a difference in sweating rates of ballotini-dusted samples that were wrapped up in aluminium foil and those sandwiched between filter papers is not entirely clear. Since it was observed that in the latter case the bottom filter paper always tended to have more DOP stains that the top one, it is suggested that the sweated liquid runs down the spaces between the glass beads and is subsequently absorbed by the bottom filter

paper giving rise to the observed higher sweating.

This investigation shows that the sweating rate can be altered by changing the physical conditions at the surface of the swollen rubber suggesting that the phenomenon is merely due to surface effects. It is therefore in accord with the hypothesis suggested above, which is that the driving force for the phenomenon is derived from surface tension effects acting on the liquid near the surface of the rubber caused by the presence of foreign contacts on the swollen rubber surfaces.

Sweating in Other Rubber Vulcanisates

So far, the discussion of sweating has been limited to NR. However, this phenomenon is also observed in other rubber vulcanisates and results are presented for synthetic cis-polyisoprene (IR), cis-polybutadiene rubber (BR) and ethylene propylene copolymer (EPM). These polymers were chosen because of the specific differences over NR. IR is a synthetic analogue of NR but has a much lower impurity content. BR affords a higher mobility to DOP while EPM is relatively more resistant to oxidation than NR.

Acetone-extracted samples of the synthetic vulcanisates, 0.5 mm thick and 5 mm square, were swollen to equilibrium in DOP at 21°C and then allowed to sweat wrapped up in aluminium foil at the same temperature. The swelling curves for the three vulcanisates are shown in *Figure 4.* From such curves,
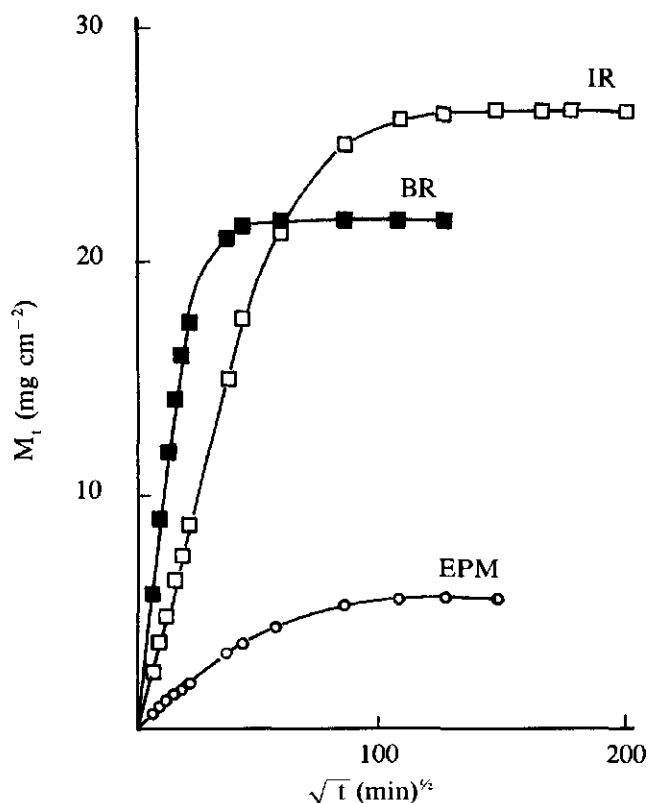

Figure 4. Swelling of some synthetic rubbers in DOP at 21°C.

TABLE 2. SWELLING PARAMETERS OF VARIOUS RUBBER VULCANISATES
IN DIOCTYLPHTHALATE AT 21°C

Rubber	Shear Modulus G (MPa)	Equilibrium uptake (%)	v_r	X	$D^v \times 10^{12}$ $(m^2 S^{-1})$
BR	0.46	135	0.446	0.44	4.6
IR	0.29	146	0.428	0.52	0.8
EPM	0.28	23	0.835	1.33	0.4
NR[a]	0.30	119	0.411	0.47	1.2

[a] Refers to data calculated from Nah's results[2] for a NR vulcanisate cured with 1.0 parts of DCP per 100 parts of rubber.

v_r is the volume fraction of rubber at equilibrium DOP uptake. G is the shear modulus of the unswollen vulcanisate and X the rubber/DOP interaction parameter.

the mutual diffusion coefficient, D^v, was calculated. These, together with the interaction parameter X, equilibrium uptake and shear modulus G, are presented in *Table 2*. As expected, the diffusion coefficient of DOP in BR was significantly greater than in the other two vulcanisates. At equilibrium, EPM absorbed less than 20% of the DOP uptake in the other rubbers.

The sweating curves of the vulcanisates when the swollen samples were wrapped up in aluminium foil are shown in *Figure 5 (a)*. The sweating curves are initially linear and this linearity extends over much longer times for BR and IR than it does for EPM. Although IR absorbed more DOP at equilibrium than BR, the sweating rate in the latter is higher, perhaps due to the higher diffusion coefficient of DOP in BR. However, the difference is not as large as would be expected from the diffusion coefficients of DOP in these two rubbers *(Table 2)* and could be attributed to a dissimilar increase in the size or number of contact regions between the rubbers and the aluminium foil due to the difference in their moduli. The amounts of DOP sweated out after 120 days in BR, IR and EPM were 8%, 6% an 1.1% by weight respectively, which are small relative to their equilibrium DOP uptake.

Figure 5 (b) shows the sweating curves when the swollen rubbers were sandwiched between filter papers (Whatman Paper No. 42) and a

load of 195 g evenly applied to the assembly. It shows that the amount of sweating was greatly increased, by between 1.5 and 5 times the sweating rate when the samples were in contact with aluminium foil. It is interesting to note that in *Figure 5 (b)*, the curves for BR and IR are non-linear while that of EPM remains linear even beyond $\sqrt{t}$ of 200 min$^{1/2}$.

This investigation shows that IR, BR and EPM also exhibit the sweating phenomenon. That the process occurs in acetone-extracted IR suggests that sweating in NR vulcanisates is not due to its non-rubber impurities since IR is a much cleaner rubber containing very low non-rubber constituents. Furthermore, infra-red analysis of the sweated liquid from the IR vulcanisate showed that it was virtually identical to the original DOP used to swell the rubbers except for a small amount of unidentifiable 'dirt' which was detected mainly between 300 mm^{-1} and 350 mm^{-1}. Oxidation could not be the cause of sweating since this is also observed in the EPM which has a high resistance to oxidation.

CONCLUSIONS

A variety of rubber vulcanisates, previously swollen to equilibrium in a plasticiser such as dioctylphthalate, exhibit a rather puzzling exudation phenomenon. This process, called sweating, is not due to supersaturation effects caused by temperature variation or impurities
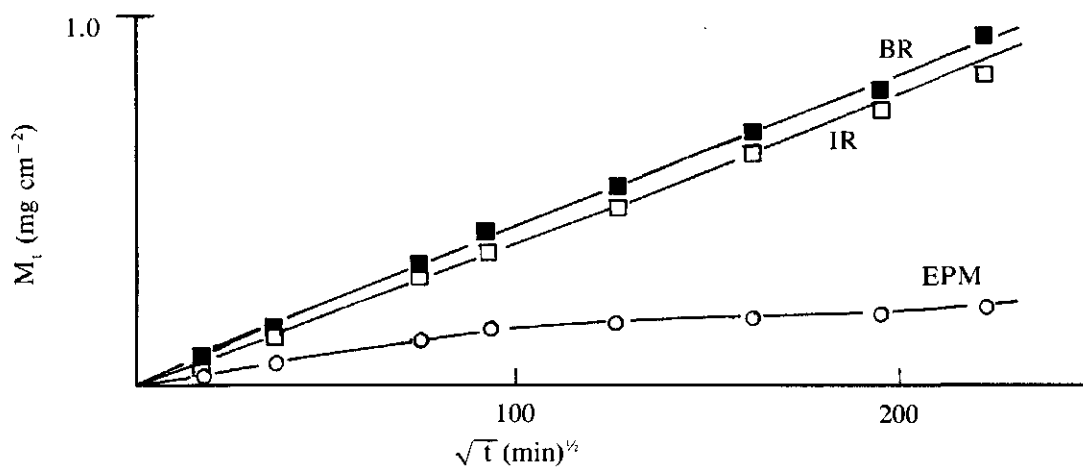
(a) Wrapped up in aluminium foil.
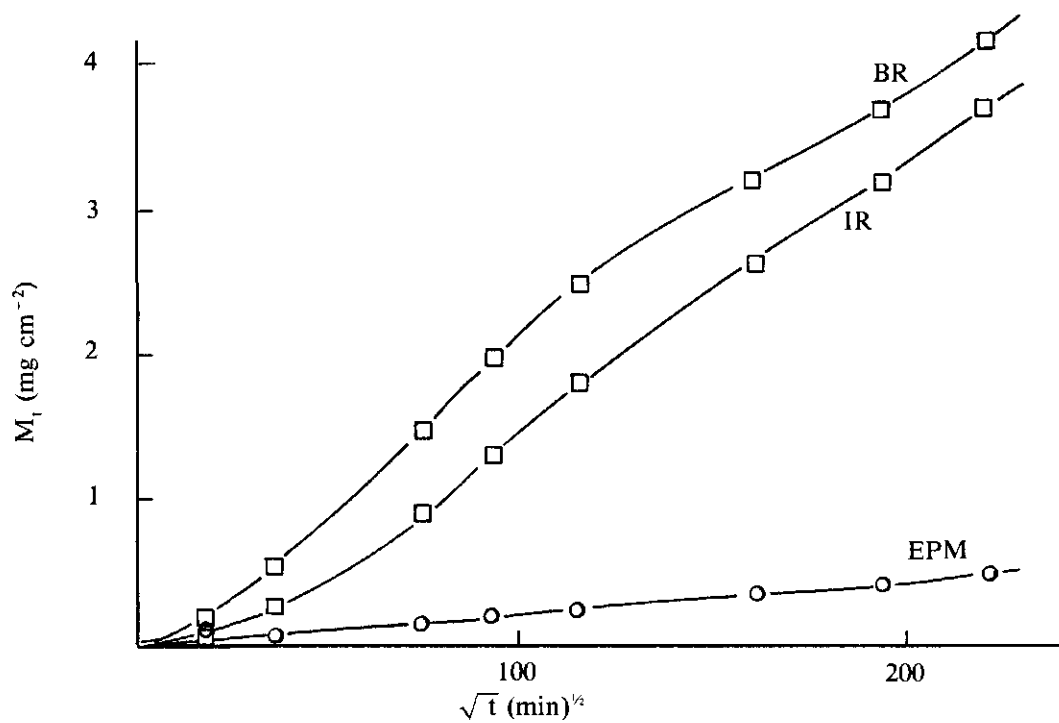
(b) Sandwiched between two Whatman No. 2 filter papers No. 42 and subjected to a compressive load of 159 g.

Figure 5. Sweating of DOP from synthetic rubbers at 21°C.

present in the rubber. It is also known that when a sample, after it has sweated for some time, is re-immersed in the liquid at the same temperature, it re-swells to approximately the same equilibrium value. These observations are rather difficult to reconcile with the thermodynamics of equilibrium swelling.

It has been shown that the amount of sweating can be significantly altered by varying the physical conditions at the surface of the rubber. Furthermore, the intimacy of contact at the swollen rubber surface is an important feature and strongly influences the kinetics of the sweating process. These observations suggest that the process is primarily due to surface effects.

It is postulated that sweating in a highly swollen rubber is caused by surface tension effects due to the presence on the rubber surface of extraneous debris (e.g. dust) or microscopic surface irregularities or simply due to contact with other substrates. Surface tension forces will cause the liquid near the rubber surface to move to the surface forming droplets in regions where such forces exist. If

the process can be modelled along the lines where dust particles or imperfections at the rubber surface act as small isolated sinks for the plasticiser, then it is possible to explain, at least qualitatively, the slow rate of migration of the liquid during sweating and the observed effects of perfection of contact at the swollen rubber surface.

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