Studies on membranes composed of polymer–bitumen blends

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A computer-controlled bending system has been constructed for characterizing the bending properties of commercial membranes composed of polymer–bitumen blends supported by a non-woven polyester type base. The system allows the bending elasticity and yield point to be obtained for a membrane, and also permits the stress relaxation after a distortion to be characterized. These properties are related to the polymer present in the bitumen.

(Keywords: polymer–bitumen blends; bending tests; elasticity; yield point; stress relaxation)

INTRODUCTION

Membranes consisting of a non-woven polyester or glass mat that are impregnated with a blend of bitumen, a limestone filler and either atactic polypropylene (APP), a styrene–butadiene triblock (SBS) polymer, or low density polyethylene (LDPE) are used in the waterproofing of flat rooves. The membranes are fabricated in a factory, and are applied to the roof with the aid of a gas torch, which melts the blend, and causes the article after cooling to adhere to the roof and to form a waterproof joint with any adjacent and previously laid strip[1].

One important feature of the blends is their sudden drop in viscosity on heating above a certain temperature: blends of bitumen with SBS rubbers flow when the polystyrene domains melt and disperse[2], and blends with APP begin to flow at ~155°C upon the melting of the minor fraction of crystalline material that is present[3]. Blends incorporating LDPE[4] probably behave in the same manner, but begin to flow at a lower temperature (~120°C). A typical membrane is based on a non-woven polyester membrane weighing $180\,g\,m^{-2}$, which is ~0.85 mm thick, together with upper and lower layers of polymer–bitumen blend of, respectively, 1.2 and 1.8 mm thickness. The upper surface is coated with a layer of sand or some other finish, and the lower surface with a thin film of isotactic polypropylene*. A blend used in preparing the membrane may consist of 71 wt% of 200 penetration grade bitumen, 24 wt% APP and 5 wt% of calcium carbonate filler. A second feature of these membranes is their ability to distort under minor disturbances, both before and after being laid. Their physical properties under ambient conditions may be controlled by the presence of the polymer in the blend, and will determine the performance of the membrane system. Our measurement system is designed to characterize the membranes when distorted by bending, as this mode is more sensitive to the properties of the blend. Extension of the membrane would be controlled by the polyester non-woven base.

BENDING MEASUREMENT SYSTEM

We have considered a simple system for performing bending measurements upon sample strips of the roofing membranes, and have examined three aspects of their bending behaviour: their elasticity when bent through a small angle, the force which is required to cause them to yield when bent around a mandrel of a certain size, and the stress relaxation following a bending distortion. The measurement system comprises a strip bending arrangement (*Figure 1*) linked to a load cell, a BBC microcomputer for data recording, a visual display unit and a printer. Samples 20 mm wide and 160 mm long were cut by pressing parallel knives through a membrane, and were annealed by heating to 60–70°C for 30 min, followed by overnight cooling in an oven. Samples were placed in the measurement head as shown in *Figure 1*, were attached to the load cell extension by a clip, and were bent by rotating the driving cylinder, M2, progressively around the first mandrel, M1, at a constant angular rate of $9^\circ\ \mathrm{min}^{-1}$. The force produced was measured by the load cell, and recorded with a BBC microcomputer for a predetermined period[5]. The load cell had been calibrated to measure forces acting along the line x. The stored data could be listed for analysis and plotted. Such measurements were made between 15°C and 25°C at ambient temperatures, and at low temperatures, between −17°C and −25°C, in a refrigerator. For low temperature measurements the metal mandrel and the driving cylinder were cooled before the sample was placed in contact with them in the measurement head, and then all were placed in a refrigerator. The distance between the mandrel, M1, and the load cell extension was always 20 mm. The diameters of the driving cylinder, d_{M2}, of the mandrel, d_{M1}, and the

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*The blend was formed at 180°C by stirring for >4 h. The bitumen consisted of asphaltenes, resins, aromatics and aliphatics in the proportions of 54, 14, 17 and 15. The membrane was dressed with sand, talcum powder, slate particles or aluminium flakes

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distance between their centres, s, were styled in series as $d_{M2}/d_{M1}/s$.

BENDING MEASUREMENTS

A typical plot of force *versus* angle is shown in *Figure 2*. Measurements were made with the mineral finish on the convex side of the curve to prevent its incompressibility affecting the results. The elasticity of the membrane in the bending mode, E_b, was measured from the initial slope, and the force applied when the membrane failed in bending was obtained from the maximum force measured, Y_b, as shown. The values reported depend upon the geometry of the sample and the measurement system, factors which are recorded, but not explored further here. The reproducibility of measurements is demonstrated by the six performed on a membrane made of an APP–bitumen blend coated with talcum powder where $E_b = 0.22 \pm 0.4$ N deg^{-1} and $Y_b = 2.0 \pm 0.2$ N.

We can see from *Table 1* that the elasticity and yield strength of the membrane formed from the rubber–bitumen blend are rather insensitive to the sizes of the mandrels used. For each membrane recorded in *Table 1* the values of the elasticities are higher than the value for the polyester base: the elasticities fall in the order SBS blend, APP blend, LDPE blend. The yield points of the SBS and APP blend membranes are somewhat higher than the yield point of the polyester base membrane. However the yield point of the LDPE membrane is similar to that of the polyester base. In contrast to membranes formed from the SBS and APP blends the membrane prepared with a polyethylene blend is not significantly stronger than the polyester base.

In *Figure 3* we show measurements made on a series of samples of an APP membrane at different temperatures. It is apparent that there is at least a five-fold increase in the stiffness of the material when cooled to below 25°C and that there is a 10-fold increase in the yield point of bending. Both plots show a glass transition temperature of 22°C. The measurements have detected the embrittlement temperature of the polymer–bitumen component of the membrane.

STRESS RELAXATION

This was measured after three stages of the bending cycle by stopping the motor turning the driving cylinder: when the bending was in the elastic region, before the yield point; when the bending was at the yield point; and when the material had been bent beyond the yield point. Typical results are shown in *Figure 4*. The force decay curves with time, $F(t)$, have been analysed using a Williams–Watts stretched exponential function[6], where F_0 is the range of fall in $F(t)$, $F(\infty)$ is the value of $F(t)$ at infinite time, t_0 is a time constant characterizing the

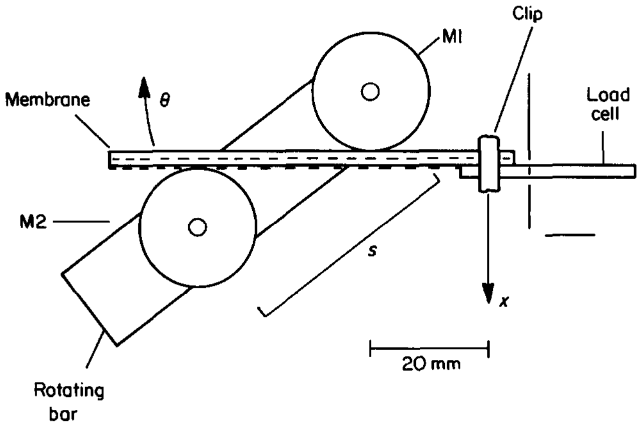

Figure 1 Diagram of the measurement system, showing the membrane clipped to the load cell and touching the mandrel M1 and the driving cylinder M2. The clip is centred 20 mm from the mandrel M1, and s is the distance between the centre of the two cylinders. For the measurement the metal bar rotates at 9° min^{-1} carrying the driving cylinder M2 so that the membrane is bent around the mandrel M1. The bending force is measured in the direction x by the load cell extension to which the clip attaches the end of the membrane

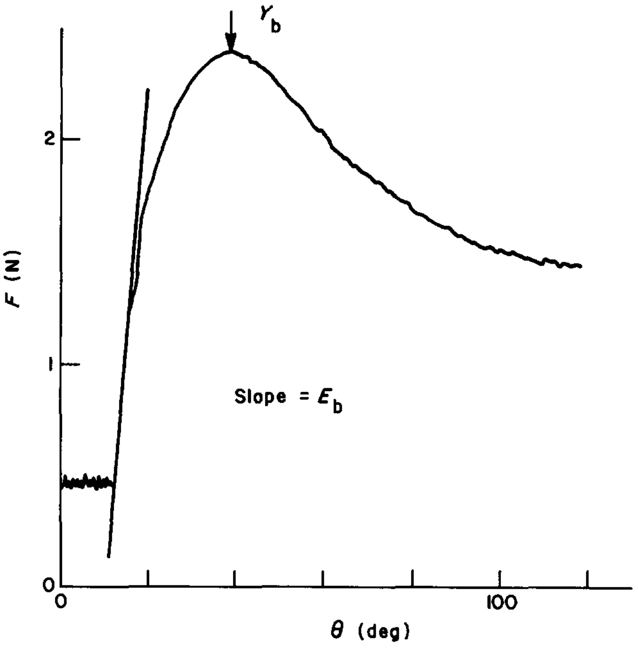

Figure 2 A bending measurement made on a membrane containing a SBS rubber, showing the elasticity, E_b (N deg^{-1}), at the initial bend, and the yield point, Y_b (N). For the first period of the measurement the membrane was not gripped tightly by the cylinders

Table 1 Bending characteristics of membranes tested at ambient temperatures

Membrane system	Mandrel size (mm)[a]	Temperature (°C)	E_b (N deg^{-1})	Y_b (N)
V (14% LDPE)	30/30/40	21	0.070 (±0.03)	0.65 (±0.21)
T (27% APP)	30/30/40	20	0.22 (±0.04)	2.0 (±0.2)
R (10% SBS)	30/30/40	19	0.30 (±0.04)	3.5 (±0.3)
R (10% SBS)	40/20/40	16	0.32 (±0.03)	3.6 (±0.6)
Polyester base	40/20/40	17	0.017 (±0.006)	0.65 (0.26)

[a] See text

Table 2 Stress relaxation time constants, t_0, for membranes; $m = 0.27$ in equation (1)

Material sample no.	Temperature (°C)	Start[a]	Period of decay (s)	t_0 (s) $n = 40$[b]	t_0 (s) $n = 32$[b]
LDPE blend					
V1/B/41	7	Y	1600	0.49 ($\pm$0.08)	2.0 ($\pm$0.3)
V1/B/53	18	Y	3000	1.0 ($\pm$0.1)	9.1 ($\pm$1)
V1/B/63	17	Y	43200	1.5 ($\pm$0.2)	9.2 ($\pm$0.6)
V1/B/54	17.5	BY	3000	2.4 ($\pm$0.3)	9.9 ($\pm$1.5)
V1/B/55	17	AY	3000	0.73 ($\pm$0.09)	8.4 ($\pm$0.6)
V1/B/5678	−21	Y	3000	0.16 ($\pm$0.04)	0.2 ($\pm$0.1)
SBS blend					
DB/B/423	17	BY	1400	1.0 ($\pm$0.2)	25 ($\pm$5)
DB/B/40	15	Y	1400	0.32 ($\pm$0.05)	0.80 ($\pm$0.08)
DB/B/456	18	AY	1400	0.16 ($\pm$0.02)	0.39 ($\pm$0.04)

[a] Y, BY and AY indicate at yield point, before yield point and after yield point, respectively

[b] For $n = 40$ the points are recorded at equal intervals over the full decay curve. For $n = 32$, only the *last* 32 of the 40 points are used in the non-linear least squares fit

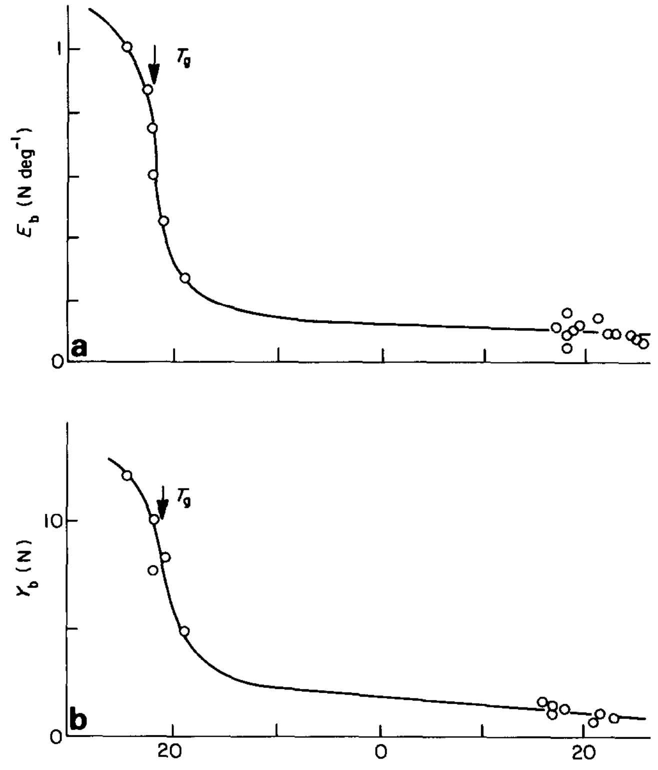

Figure 3 For an APP membrane covered with talc: (a) a plot of bending elasticity, E_b, against temperature, and (b) a plot of yield point force, Y_b, against temperature. Both measurements show a glass transition temperature (T_g) at −22°C

decay, and m is a small number (<1) that causes the relaxation to spread over a time-scale longer than that of a simple exponential function.

$$F(t) = F_0 \exp(-t/t_0)^m + F(\infty) \qquad (1)$$

Struik gives this equation for the physical ageing of amorphous polymers[7] with $m = 1/3$, and for bitumens Kubat[8] has found that $m = 0.27$. An Algol program for fitting this equation to the data provided by the microcomputer, using a non-linear least squares NAG routine[9], was run on the main frame computer to obtain values of the following parameters: F_0, $F(\infty)$ and t_0, and a second (FORTRAN) program was used for calculating the standard deviations of the values of these parameters from the hessian matrix[10]. It was not possible to recover values of the m parameter from the data, if they were similarly adjusted, but it was clear that if the value was 1.00, so that a simple exponential function was tested, the fit was less good than if values close to 1/3 were chosen. A constant value of 0.27 was assumed for m. Broadly similar conclusions to those reached here would be obtained if other values of m close to 0.27 had been used instead.

Stress relaxation parameters are recorded in *Table 2* for measurements made close to 17°C on two membranes, and at a low temperature on one membrane. There are two sets of values of t_0 presented for each measurement: in the first set 40 data points are fitted to obtain a t_0 representative of the decay curve recorded over the full period; the second set gives the t_0 value when only the last 32 of these points are used in the fit. It can be seen that the t_0 values differ by a factor of at least 4 for the LDPE blend, and by a factor of at least 2 for the rubber blend. Inspection of the residuals generally showed that there was a systematic deviation from the fitted curve by the points recorded during the first period. In general the early points indicate a more rapid adjustment to the distortion, and do not conform to the function in the same manner as do the latter points. If the standard deviations of the fits are compared, there is generally an improvement by a reduction of up to 50% in that parameter when the first section of points is ignored. It appears that the Williams–Watts function can represent the data, but that the distribution of relaxation times implicit in the function is not quite appropriate to these decay curves. Inspection of the second and third entries in the table suggest that the period of initial response may be of the order of 600 s for the LDPE membrane. The exception to this is the measurements made at −21°C on the LDPE blend. At this temperature the material is considerably springier, and the response to the distortion takes place over a shorter time and is less influenced by viscosity factors.

A further point of interest is the relationship of the t_0 values to whether the yield point has been reached or

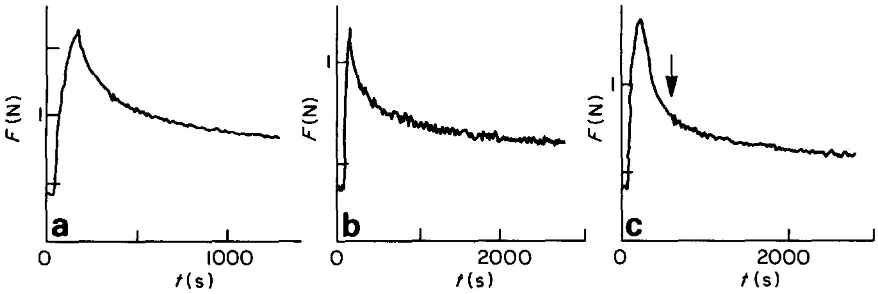

Figure 4 Stress relaxation studies on samples of a LDPE membrane: (a) relaxation started at the yield point, (b) relaxation started before the yield point and (c) relaxation measured after the yield point

passed. Once the membrane has yielded to the bending force, the response curve has a t_0 value that is smaller – the relaxation is more rapid. If the two types of membrane are to be compared, the rather limited set of data reproduced here allows a comparison only of the results obtained for decay periods of 1400 or 1600 s from the yield point; it seems that the rubber blend has perhaps the faster response. The measurement system might be used for a more systematic study of these membrane systems.

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