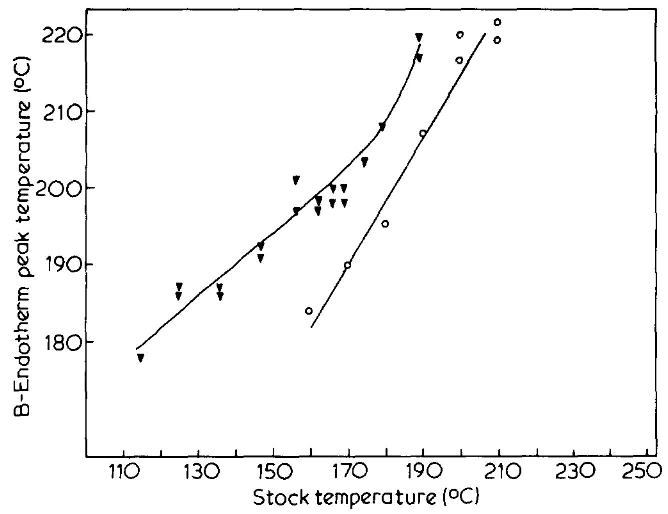

Figure 5 Temperature of peak B (°C) *versus* stock temperature (°C); symbols as *Figure 2*

universal applicability of the rheological method have already been expressed[2], since the standard curve depends on shear history, time and temperature. In order for the technique to be a useful one it must obviously be applicable to processed samples. *Figure 4* shows d.s.c. traces obtained for Compound 1 samples blended under different conditions and extruded using a Leistritz LS-30-34 twin screw extruder. It is noted that endotherms A and B are again discernible. (The peak near 100°C is one which develops on room temperature storage of rigid PVC, due to a slow reduction in free volume[7]). All samples were extruded using the same conditions and it is apparent that peak B is at a similar temperature in all cases, and about 20°C above the temperature at the die (183°C).

It appears therefore that the position of peak B provides information about the maximum temperature to which the polymer has been subjected. *Figure 5* shows how this temperature increases with processing temperature for the two compounds studied. The area of endotherm A appears to be related to the level of fusion. The nature of the endotherm is not yet fully understood, but it is possible that it is due to the formation of imperfect ordered regions which are produced as a continuous PVC network develops, and which subsequently melt on reheating. Further work is being carried out to investigate the changes occuring in the compounds, and the value of this thermal analysis technique in assessing fusion levels.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the Science Research Council for the provision of a grant to support the programme of which this work forms a part. Thanks are also due to B.P. Chemicals Ltd. who are supporting the programme and Akzo Chemie who provided the stabilizers.

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A procedure for rapid conditioning of hygroscopic test pieces by humidity cycling

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(*Received* 29 *September* 1980; *revised* 20 *March* 1981)

INTRODUCTION

Tests on hygroscopic polymers often have to be made at moisture contents that are in equilibrium with the air humidities that they will meet in service, such as, for example 60% r.h. Since the polymer has been moulded at a high temperature and therefore starts life very dry, it must be stored in the test humidity for enough time to allow it to reach the new equilibrium moisture content. If the moulding is small this conditioning time may be short but for large mouldings it may be very long. In fact dimensional analysis of the diffusion equation shows that the conditioning time is proportional to the square of the minimum characteristic dimension of a simple-shaped moulding. So, for example, a 1 mm thick nylon-66 sheet will take about 1580 h to reach 98% of equilibrium at 60% r.h. from 0% r.h. at 23°C, whilst a 3.17 mm (1/8 inch) sheet will take about 15 900 h (95 weeks).

0032-3861/81/081136-04$02.00

EXPERIMENTAL

Various methods have been used to accelerate the conditioning of specimens with elevated temperatures. One method, which has been incorporated in an ISO standard[1] in spite of disapproval on technical grounds by certain Member Bodies including that of the U.K., requires the storage of the samples in an aqueous solution of potassium acetate at a temperature between 95° and 100°C for periods up to 7 days. The Standard claims that no degradation has been experienced within this time limit provided that no additives can migrate into the solution and provided that the specimen's electrical properties are not being measured (since they might be affected by residual salt). The Standard also points out that the mechanical properties may be different from those obtained by normal room-temperature conditioning. Another method[2], aimed at 50% r.h., requires storage above a saturated sodium nitrite solution at 70°C for about three weeks followed by 3 months at 50% r.h. and at a temperature of 23°C. Although this second method avoids the problems associated with immersion in water, the use of high temperatures could affect the structure of the material and hence its properties[3].

It was considered that it might be possible to reduce these extended times by storing at a higher relative humidity such as 90% for a short time before conditioning at 60% r.h. Alternative methods might be to cycle: 90%–0%–60% r.h. or 90%–0%–90%–60% r.h. for suitable periods.

However, in view of the long times involved it was felt that laboratory trials of this method would be relatively unproductive, especially if the experiments had to be repeated. It was therefore thought best to simulate the experiments on the computer and then to do some spot checks in the laboratory. The simulation was done by the Crank–Nicholson finite-difference method[4]. Unidirectional diffusion was assumed; the thickness of the sheet was divided into 40 elements, and the diffusion coefficient for nylon-66 was taken as the measured value[5] of $D = 0.147 \exp(0.2696\ c) \times 10^{-3}\text{mm}^2/\text{h}$, where c is the percentage moisture content. The equilibrium moisture contents were measured as 1.52% at 30% r.h., 2.10% at 40% r.h., 2.70% at 50% r.h., 3.53% at 60% r.h., 4.45% at 70% r.h. and 6.75% at 90% r.h., all at 23°C.

The main exploratory simulations took 1 mm thick test pieces at 0% moisture content and conditioned them to a final equilibrium at 60% r.h. and 23°C, for an uniform 3.53% moisture content. The two criteria for completion of conditioning were (a) the mean moisture content must be $3.53 \pm 0.03\%$ and (b) the maximum divergence from 3.53% at any point must not exceed 0.2%. It will be noticed that each of these two criteria resulted in separate limit lines on the graphs of *Figures 1* and *2*. *Figure 1* shows the effect of a half cycle: x h at 90% r.h. followed by storing until equilibrium at final humidities of 30, 40, 50, 60 and 70% r.h. respectively. *Figure 2* shows the effect of a full cycle: 180, 190 or 200 h at 90% r.h., then x h at 0% r.h. followed by storing until equilibrium at 60% r.h.

With either procedure it is evidently important to condition the test pieces to within quite close time limits, otherwise the time to equilibrium increases greatly. This was found to apply to the half-, full-, and one-and-a-half cycle conditioning procedures. However, if accurate timing can be achieved, a considerable saving in conditioning time is possible: shortening the time for a 1 mm thick piece that is being conditioned to 60% r.h. from 1580 h to about 250 h, a saving of 83% (or for a 3.17 mm (1/8 inch) test piece from 95 weeks to 16 weeks).

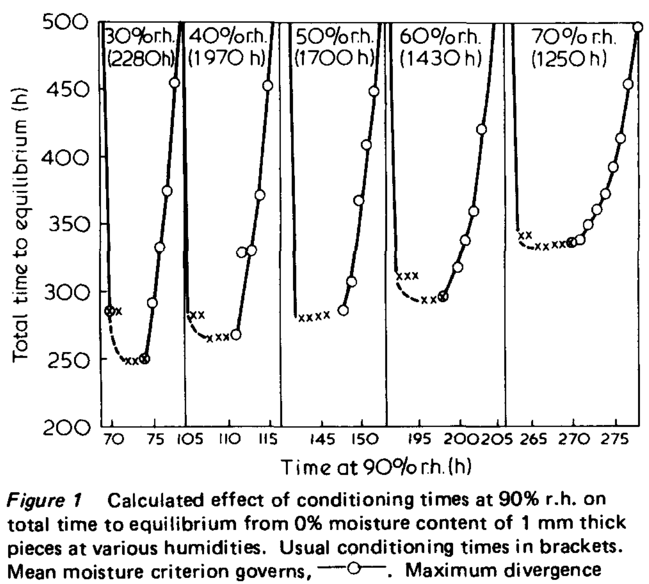

Figure 1 Calculated effect of conditioning times at 90% r.h. on total time to equilibrium from 0% moisture content of 1 mm thick pieces at various humidities. Usual conditioning times in brackets. Mean moisture criterion governs, —○—. Maximum divergence criterion govens, —X—. Both criteria govern, —⊗—

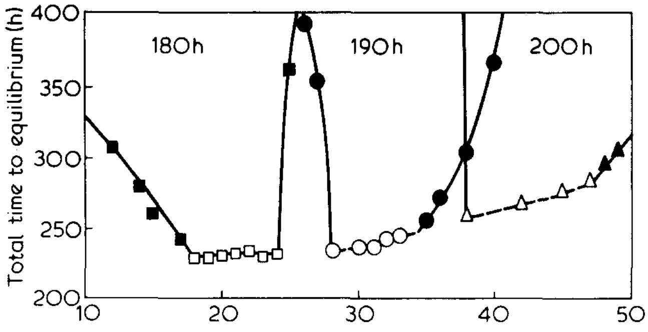

Figure 2 Calculated effect of conditioning times at 0% r.h. following 180, 190 or 200 h at 90% r.h. on total time to equilibrium at 60% r.h. of 1 mm thick pieces. Mean moisture criterion governs: 180 h, —■—; 190 h, —●—; 200 h, —▲—; maximum divergence criterion governs: 180 h, —□—; 190 h, —○—; 200 h, —△—

If the test pieces in the laboratories were to behave exactly as the computer predicts, there would be no problem. Unfortunately, serious errors are likely to arise in (a) the diffusion coefficient, (b) the initial moisture condition of the test piece and (c) the equilibrium moisture content at a given relative humidity; all three of which are assumed and included in the computer programme. A further difficulty is that monitoring of the test piece moisture distribution is not feasible, since the critical moisture content occurs in the core and unless this reaches the equilibrium value quickly, the conditioning time is greatly prolonged. The other consideration is that the full cycle and the one-and-a-half cycle procedures appear to have little advantage over the half-cycle conditioning; regarding either completion time or tolerances.

The recommended procedure given below is based on the following decisions:

(i) A single half-cycle at an extreme humidity should be used prior to storing at the final desired relative humidity.

(ii) The only monitoring equipment required should be a chemical balance.

(iii) Since it is not possible to allow for an unknown starting condition, the test piece should start at or near 0% moisture content, in other words it should be stored in a desiccant between the time of moulding and the start of conditioning.

By taking the optimum times for the half cycle at 90% r.h. from *Figure 1* and considering the calculated moisture contents at these times and the final equilibrium moisture contents and those at 90% r.h.; the following relationship was found:

$$(U_c - U_f) = K(U_{\max} - U_f) \qquad (1)$$

where U_c is the percentage moisture content at which the final conditioning must begin; U_f is the final equilibrium moisture content in percent; $U_{\max}$ is the percentage moisture content at 90% r.h.; K is almost constant, drifting slowly from 0.219 for a final r.h. of 30%, to 0.199

Table 1 Results of rapid conditioning method at 23°C

Final conditioning humidity (%)		30	50	60	70
At 90% rh to changeover	Predicted time (h)	705	1400	1890	2590
	Actual time (h)	670	1510	2374	2950
At changeover	Increase in moisture content (%)	2.24	3.48	4.18	4.76
At final conditioning humidity	Increase in moisture content (%) at total times of:				
	1510 h	1.24	–	–	–
	2374 h	1.23	2.65	–	–
	3550 h	1.23	2.58	3.40	4.22
	4510 h	1.27	2.61	3.42	4.27
Total equilibrium time (h)	Estimated from results	1500	2500	3500	3500
	Computer prediction	2400	2700	2820	3230
Predicted time by simple conditioning method (h)		22000	16350	13750	12150

for one of 70%. A suitable value of K is given by $K = 0.1926 + 0.02324\ U_f - 0.00502\ U_f^2$.

Determination of the value of U_c therefore gives a criterion for deciding when a test piece should be transferred to the final conditioning environment.

The ability of the criterion of equation (1) to prevent the three most serious errors described above, was investigated with the computer:

(a) Errors in diffusion coefficient, thickness or time all include errors in the dimensionless parameter Dt/L^2 (where D is the diffusion coefficient, t is the time and L is the thickness), which could be investigated by altering any one of the individual variables. Doubling the thickness was found to increase fourfold the time to 60% r.h., indicating that the minimum time for this thickness was still obtained. However, large variations of thickness within a test piece could still cause serious errors, since thick areas would take longer to condition than thin ones.

The effect of different diffusion coefficient-moisture relationships was also tested. With a linear relationship passing through two extreme values of the exponential curve quoted above, the criterion of equation (1) gave a minimum conditioning time. With a constant diffusion coefficient of $0.509(10^{-3})$ mm^2/h, however, the criterion of equation (1) missed the correct changeover time by 7 h at 50% r.h., thus causing the total conditioning time to be 2.5 times as long as the minimum value. This could be corrected by a small adjustment in the value of K.

(b) An initial uniform moisture content of 0.5% was tried. This was found to actually reduce the conditioning time to 60% r.h. from about 243 h to 223 h, and again showed that the minimum time was obtained.

(c) The difficulty of accurately measuring high values of relative humidity together with the large effects on the moisture content of even a 1% error in the r.h. at this level, means that there may be a considerable error in the value of the equilibrium moisture content at the high humidity. Accordingly, the high moisture content $U_{\max}$ was reduced from 6.75% to 6.45% (equivalent to a reduction of 2% r.h.); thereby increasing the total conditioning time from 243 h to 249 h. This higher value is still near the minimum.

The recommended procedure for rapid conditioning is therefore as follows:

(i) On removal from the mould, store the test pieces at 0% r.h. until the conditioning procedure is to begin.

(ii) Establish the moisture contents at 90% r.h. and at the final conditioning r.h. as follows: take some thin shavings from a spare test piece, quickly weight them, condition them at the two relative humidities stated, and re-weigh. For example, shavings of about 0.25 mm thick, taken manually with a carpenter's plane, should reach equilibrium in less than three days. For maximum accuracy of the initial weighing, readings can be taken at a few intervals of a few minutes and a graph of weight *versus* the square root of time extrapolated back to get the weight at the time of cutting.

(iii) Weigh the remaining test pieces, store them at 90% r.h., and occasionally check the weight increase until it reaches the value given by equation (1) above. If the weight-change results are plotted *versus* the square root of time they fall approximately on a straight line, thus simplifying the estimation of the conditioning time.

(iv) Store test pieces at the relative humidity for final conditioning until equilibrium is reached.

Having established the rapid-conditioning method by computer simulation, some laboratory trials were made, all at 23°C. Nylon-66 discs, 3.10 mm thick by about 100 mm diameter were specially supplied for this experiment by I.C.I. Limited (Plastics Division), freshly moulded and then sealed in polythene bags with a desiccant until tested. The moisture contents at 90% r.h. and at the final relative humidities of 29%, 50%, 60% and 71% were established by the method described above from one of the discs, while the other discs were weighed and placed in a desiccator at 90% r.h. and 23°C. Duplicate discs were used for each final humidity. As the moisture increases reached the appropriate values of U_c as obtained in equation (1) and given in *Table 1*, the discs were placed in desiccators to reach equilibrium at the final relative humidities. The full results are given in *Table 1*, which includes predicted values obtained by computer simulation, i.e. from graphs similar to those of *Figure 1*, but scaled up to allow for the thickness of the test pieces. The predicted time by simple conditioning was obtained with a standard Crank–Nicholson finite-difference calculation. It may be noted that the slight moisture increase at 4510 h during the final conditioning represented a change in the ambient storage conditions, the change covering the approximate limits of control of the relative humidity.

RESULTS AND CONCLUSIONS

In this study a large number of very lengthy laboratory experiments, involving several years of work, have been simulated on the computer. Enough simulations were made to develop a 'rule-of-thumb' method of obtaining the final uniform moisture content in about one fifth of the usual conditioning time.

Besides the reduction in conditioning time, the method has the advantage of being relatively insensitive to accuracy of the starting moisture content, to accuracy of relative humidity levels, and to variations in the level of the diffusion coefficient. Large divergences from the present exponential form of the diffusion coefficient *versus* moisture content relationship, however, could affect the values of the coefficient K, which should then be recalculated.

However, there are two possible disadvantages. Firstly the method requires quite accurate timing. Secondly there may, in practice, be the need for ageing to remove the softening effects of conditioning at 90% r.h. However, in thicker pieces such as 3.17 mm, the saving in conditioning time is so great that there is time to age the test pieces and still show a big saving of time. In addition, since this rapid conditioning procedure should follow soon after moulding, the test pieces may also need to be aged to remove the long-term softening effects of the moulding temperatures: the two ageing procedures may then run concurrently.

Although these trials were made at a temperature of 23°C, it is expected that trials at moderately elevated temperatures should perform in a similar way since the computer simulation showed the method to be relatively insensitive to the level of the diffusion coefficient, which would be raised by an increase in the temperature.

ACKNOWLEDGEMENT

The author wishes to thank I.C.I. Limited (Plastics Division) for supplying the material for this study.

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