CONTACT ANGLES OF WATER ON LAMINATED PLASTICS AND THEIR RELATION TO RATE OF WATER ABSORPTION

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INTRODUCTION

Two important properties of any plastic material are the amount of water it absorbs and the rate of absorption since these will determine whether the material can be used where good dimensional stability or good electrical properties are required.

The standard water absorption tests are those of the American Society for Testing Materials (hereafter referred to as A.S.T.M.): test D–570–42 for 24 hour absorption, and test D–229–46 for total absorption. These involve the preparation of a special test piece and the weights of the piece before and after immersion in water. The water absorbed is expressed as percent by weight.

In this work, the contact angle of water on several plastic samples was measured to see whether there was any good relation between contact angle and the rate of water absorption or total water absorption. The point of interest is that contact angle measurements can be made quickly and easily with a minimum of equipment and do not require a standard sample. It might be noted that neither our tests nor the A.S.T.M. test measures ultimate water absorption. Our samples were still absorbing after 840 hours.

MATERIALS AND METHODS

The plastic samples used were commercial laminates prepared and donated by the Synthane Company.[2] Each sample was cleaned of mold lubricants and mold release agents by wet blasting and in our laboratories was washed with soap and then with alcohol and dried before use. The edges were sealed with lacquer so that absorption took place only through the surfaces. Water absorbed was measured by weighing. Five different compositions of laminates were used: 1. a melamine resin, with continuous filament woven glass; 2. a phenolic resin with fine weave cotton fabric; 3. phenolic resin with staple fiber nylon fabric; 4. phenolic resin plasticized with tung oil and laminated with paper; and 5. phenolic resin with paper.

Contact angles can be measured by a number of methods. The sessile drop method was not good for our purpose since the surface of a laminate is not completely homogeneous or smooth. A second method, which gives an average contact angle, is measuring the angle of a meniscus across the surface of a partly immersed plane sample. This second method was used in two modifications. In the first modification, called the tilting plate method, the sample is partly immersed in the water and then tilted until the surface of the water is perfectly flat at the line of contact. Thus, the angle of the sample is the contact angle. This measurement can be made precise, since a slit of light projected by a small slide projector can be reflected from the water surface onto a screen and the sample tilted until the slit image is straight.

The second modification, which was used most, was to immerse the plastic sample partly into the water, keeping the sample vertical. A shadowgraph is obtained by focusing a beam of light parallel to the water surface and by allowing the shadow image of the surface and the sample to strike a slow emulsion photo-

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[2] Synthane Corp., Oaks, Pennsylvania.

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graphic paper. This has the advantage of giving a permanent record. The angle of the meniscus is then measured with a protractor.

The angle measured by these methods was the advancing angle. The receding angle on these surfaces was less reproducible and very small, a hysteresis of 20 to 40 degrees not being unusual.

All water absorption tests were run on duplicate samples. They were in complete agreement. The contact angles were reproducible to about 3 or 4 degrees, and each reported angle is the average of 5 or more determinations on each sample.

RESULTS AND DISCUSSION

The main factor influencing the contact angle is the affinity of the surface for water. The factors influencing the rate of water absorption are the chemical nature of the plastic, the nature of the laminating filler, and the physical structure of the laminate, particularly with regard to the completeness of bonding between the plastic and the laminated material. One might expect the rate of water absorption to be related to the contact angle since both are determined by the affinity of the plastic for water. One might further expect that those samples which eventually absorb the most water would also be the fastest absorbers, but this is not always the case. The actual weight of the water absorbed, and the rates of absorption are listed in table 1.

TABLE 1

Rate of water absorption by laminated plastic samples

	Sample One*		Sample Two		Sample Three		Sample Four		Sample Five	
Hours	g./hr.	log+5	g./hr.	log+5	g./hr.	log+5	g./hr.	log+5	g./hr.	log+5
0.4	1.500	5.176	.096	3.982	.022	3.342	.0110	3.041	.0615	3.789
1.5	.155	4.190	.015	3.176	.002	2.301	.0027	2.431	.0200	3.301
3.5	.080	3.903	.001	3.041	.....	.....	.0030	2.477	.0170	3.230
6.5	.043	3.633	.....	.....	.0013	2.114	.0010	2.000	.0130	3.114
12.5	.020	3.301	.....	.....	.0010	2.000	.0009	1.954	.0095	2.978
25.5	.0093	2.968	.0017	2.230	.0013	2.114	.0010	2.000	.....	.....
50	.0024	2.380	.0023	2.362	.0010	2.000	.0003	1.477	.....	.....
97	.0011	2.041	.0018	2.255	.0006	1.778	.0006	1.778	.0049	2.690
167	.0004	1.602	.00093	1.968	.0003	1.477	.0003	1.477	.0040	2.602
286	.....	.....	.00065	1.813	.0002	1.255	.0001	1.114	.0030	2.477
575	.0002	1.230	.00065	1.813	.0002	1.230	.0001	1.176	.0020	2.279
840	.0001	1.041	.00040	1.602	.....	.....	.0001	0.875	.0011	2.041

*Under each sample number, the first column is the number of grams of water absorbed per hour; the second column is the log of the first column plus five.

The logarithm of the rate of water absorption plotted against time yields some important information (fig. 1). It is immediately obvious that there is a real relationship between the contact angle and the rate of absorption. The relation is not precise, but a more exact relation should be obtained for samples which are solid plastic with no filler.

The shape of these curves provides some information about the structure of the laminate. In general, each curve consists of three parts. The first part is the rapid drop in rate from a high value to one of about one-tenth the initial rate in the first hour or two. The samples with the highest initial rate drop the fastest. We attribute this to the physical structure of the laminate since it is most marked for the samples in which there is the poorest bonding between plastic and laminated material. Thus, we would expect a higher percentage of voids at the surfaces, and cracks at the surface between plastic and filler, which would take in water by capillary action. These voids would be filled in a short time.

The third portion of the curve is a virtually straight line, of much the same slope for samples of the same plastic, independent of filler. In this part of the curve we feel that the absorption is that of the plastic material itself. The fact that the rate is still highest for those samples which were initially highest merely means that the effective surface of the plastic material is larger, since it would include more surface about the voids.

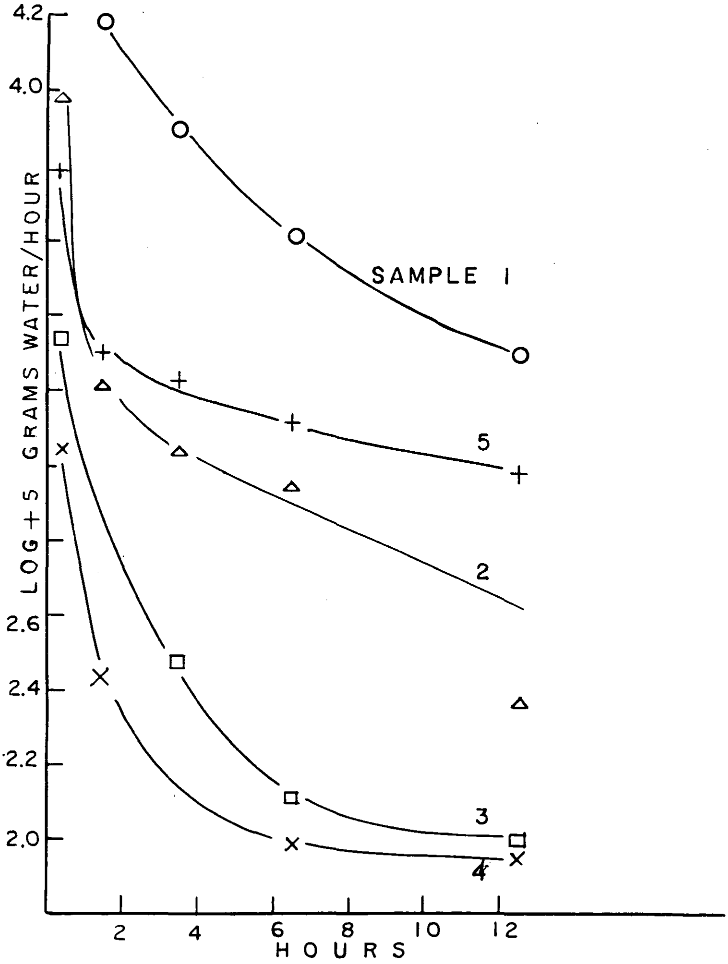

FIGURE 1. The log of the rate of water absorption in grams per hour, plotted as a function of time. 1. melamine resin with continuous filament woven glass. 2. phenolic resin with fine weave cotton fabric. 3. phenolic resin with staple fiber nylon fabric. 4. phenolic resin laminated with paper and plasticized with tung oil. 5. phenolic resin with paper.

The intermediate portion of the curve shows a transition period in which both mechanisms of absorption are taking place and the filler is being soaked. Thus, the transition for the melamine-glass laminate is sharp with little or no intermediate portion. This is explained by the fact that glass does not absorb. The transition is also relatively abrupt for the sample filled with nylon since the nylon and phenolic resin would absorb at about the same rate and total extent. The intermediate portion is most prolonged for the cellulose and paper filled samples, meaning that these fillers are soaking faster than the plastic and finally becoming saturated, at which time we enter the third portion of the curve for these samples.

The sharp first portion of the curve lasts for less than an hour for the sample of contact angle 28 degrees, for one and a half hours for angles 41 to 46, and for about 5 or 6 hours for angles 53 to 58.

The melamine-glass laminate starts at the highest rate and drops off most rapidly. Probably there are more capillary voids, due to lack of complete bonding between glass and resin. This high initial rate drops off more rapidly than the initial rates for the other materials, but the actual rate for the melamine-glass laminate remains above the rates for the other samples, since the effective absorbing surface is greater due to the voids. For this same reason the rate drops more rapidly due to faster saturation of the resin.

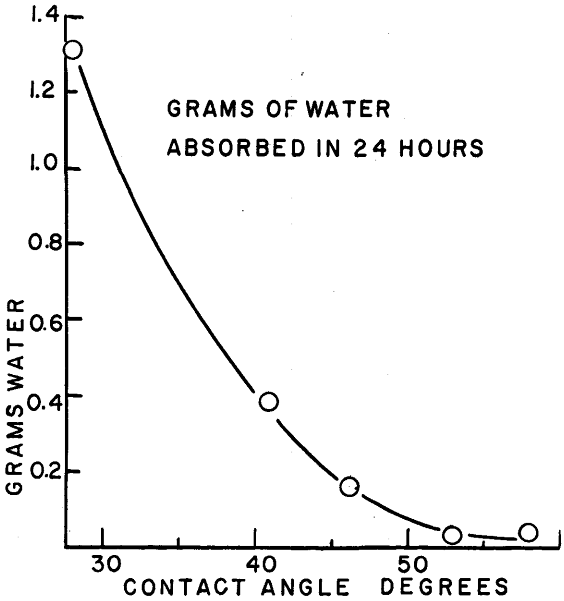

FIGURE 2. Grams of water absorbed in 24 hours plotted as a function of the contact angle of water on the plastic surfaces.

The phenolic-paper laminate and the phenolic-cotton sample yield curves which are similar in shape and slope, except that the phenolic-cotton curve drops off more rapidly in the period from two to 25 hours, but has the same slope thereafter. The difference must be due to the filler. Possibly the more continuous structure of the paper keeps the rate higher, but at 25 hours the decrease in the rate of the two is about equal, meaning we are dealing with diffusion into the resin in both cases.

The phenolic-nylon rate starts at a lower value and the slope of the rate changes more slowly, there being a less abrupt transition from capillary absorption to absorption by the material. This curve is probably more like that of a pure plastic since in this case the filler, nylon, is itself a plastic with roughly the same affinity for water as the phenolic resin.

The tung oil plasticized phenolic-paper sample is a separate case, but we might expect a less voided structure, and a plasticized paper, which would give a case most nearly like that of the phenolic-nylon sample.

Since the amount of water absorbed in a given time interval varies in a complex way with the thickness of the piece, similar data should be obtained for each thickness and a thickness versus rate curve found. The contact angles we measured and compared with the results of the 24 hour A.S.T.M. immersion test in figure 2. The correlation is evident. However, for the contact angle test to be used for the prediction of the water absorption rate, these data must be collected for a much larger number of samples. This paper can be considered only as indicating such a possibility.

Ultimate water absorption data from the manufacturer are compared with our data for 840 hours immersion in table 2.

TABLE 2

Ultimate water absorption expressed as percent by weight

Sample	Our data, 840 hours	Manufacturer's data
1	6.54	6.5
2	4.60	8.0
3	1.22	1.0
4	1.44	2.0
5	13.6	12.0

CONCLUSIONS

The logarithm of the rate of water absorption of five laminated plastic samples is a function which varies, within the limits of uncertainty of the contact angle measurement, with the contact angle of water on their surfaces, despite a considerable difference in the fillers used in the samples. The nature of the fillers probably contributes to absorption in four ways: (1) the number of capillary voids in the sample due to the type of filler, (2) the rate of wicking action of the filler, (3) the greater effective plastic absorbing surface due to the voids, and (4) the total absorption capacity of the filler itself.

REFERENCES

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