

Water Permeability of Poly(diallyl Isophthalate) Films

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Synopsis

The prepolymer of diallyl isophthalate is employed as a material for a moisture-protective coating which is applied in the solution form, free of radical initiator. The effect of the absence of radical initiator, temperature and time of cure, and thickness of coat is evaluated in terms of the permeability of water through the protective films of the polyphthalate. Temperature of the noncatalytic cure can be as low as 170°C, and the presence of an initiator in the coating formulation does not bring about any improvement in the moisture resistance of the films.

INTRODUCTION

Diallyl phthalate and isophthalate molding compounds are well known in the plastics industry for their remarkable performance with respect to the electrical, thermal, and moisture-resistant properties. They are widely used in the electronics and electrical industry as molding compounds cured by organic peroxides at elevated temperature and pressure. Protective coatings based on diallyl isophthalate are claimed to withstand temperatures as high as 240°C for long periods of time, even under extremely humid conditions. The preservation of excellent electrical properties at high temperature and humidity is another appreciated feature of the diallyl phthalates.

Despite their importance and large commercial use,¹⁻³ however, diallyl phthalate and isophthalate are described in the literature only scarcely, and it has usually been the ortho derivative that is of concern in theoretical and developmental studies. The polymerization of diallyl phthalate was described⁴ as a process leading to an insoluble gel, and the preparation of a prepolymer was suggested in order to avoid the problem. The prepolymer is a relatively linear, partially polymerized diallyl phthalate that softens and flows under heat and pressure.¹ It crosslinks to a three-dimensional, insoluble, thermosetting resin in the presence of appropriate catalyst or upon exposure to appropriate heat.

In many cases, it is a mixture of polydiallyl phthalate with another material, or a copolymer of diallyl phthalate, that has found practical use.⁵⁻¹²

The polymerization and copolymerization of diallyl phthalate and isophthalate can be initiated by heat,⁶ ionizing radiation,^{9-11,13} or by radical

initiators.^{4,6-8,12,14-17} Benzoyl peroxide^{4,6,8,12,16} and *tert*-butyl perbenzoate^{15,17} are the most common initiators used; however di-*tert* butyl peroxide,¹⁵ hydroxyperoxide,¹⁶ and azobisisobutyronitrile⁷ have also been reported.

Various techniques and applications could be found for the diallyl phthalate protective layers of crosslinked polymer.^{11,18,19} However, the widest use of diallyl phthalate prepolymer is probably in molding materials^{1-3,20} despite the fact that the prepolymer is soluble in many organic solvents, like aromatic hydrocarbons, ketones, acetates, some chlorinated aliphatic hydrocarbons, and others. Upon cure, the prepolymer is converted into a three-dimensional framework which is not affected by any of the foregoing solvents. This makes the prepolymer a suitable material for preparing coating solution that can be applied on the objects to be protected by dipping, rolling, and curtain techniques.

In searching the literature, we found no data on the moisture protection provided by poly(diallyl phthalate) and poly(diallyl isophthalate) when the prepolymer is applied in the form of solution. In the present work, we report on the water permeability of protective coats or films, prepared from a diallyl isophthalate prepolymer solution. The water permeation was followed as a function of temperature and time of cure, concentration of initiator, and thickness of coating applied.

EXPERIMENTAL

Performance of the diallyl isophthalate coatings in terms of the resistance to moisture penetration through the protective films was evaluated by a technique²¹ employing moisture-sensitive electrical resistors as substrates for coating, and measuring resistance of the resistors before and after the exposure of the coated resistors to water vapor. The performance of the coatings was indicated by a resistance change of the resistors. In the presence of a minute amount of water, the resistor increases its resistance value, and in the limit it may become an open circuit. The resistance change is proportional to the voltage applied, the time for which it is applied, and the amount of water which is present. In the ideal case of no penetration of water through the protective coating, there should be no resistance change.

The test was performed at 100% humidity, 100°C, atmospheric pressure, and under an electrical potential applied to the resistor leads. The resistors employed a nickel-phosphorus thin film as their resistive element.²²

The prepolymer of diallyl isophthalate, DAPON M molding powder, was supplied by Canada Colors and Chemicals, and manufactured by FMC Corporation.

The protective film of poly(diallyl isophthalate) on a resistor was made as follows. DAPON M prepolymer was dissolved in solvent, and the solution was degassed by applying a slight vacuum. Concentration of the resin in the solution ranged between 28% and 40% for various solvents. The degassed coating solution was deposited on a resistor either by curtain

or dipping techniques, and after a 60-min drying period at 90°C, the coating was cured at a specified temperature for a specified time. The procedure was repeated if more than one coat was applied. The drying period at 90°C was omitted or classified as a cure time when a radical catalyst was used in the coating formulation.

RESULTS

Benzoyl peroxide (BP) and *tert*-butyl perbenzoate (TBPB) were used as radical initiators of the crosslinking process. The concentration of the initiators appeared to be a crucial factor in determining mechanical strength of, and temperature effect on, the cured coating. A concentration higher than 3% per resin by weight yielded brittle coatings that became severely cracked when heated above 160°C. The effect on the moisture permeation of the initiator concentration is shown in Table I. Using TBPB, we explored a higher range of the initiator concentration (expts. 1-10); and using BP, we worked in a lower range of the initiator concentration (expts. 13-19). Experiments 5, 6, and 12 compare the two radical initiators. Experiments 11 and 12 indicate necessity of cure at higher temperature than 110°C. Experiments 3-6 show the ineffectiveness of a low temperature (110°C) baking.

Table II and Figure 1 present moisture-resistant characteristics of diallyl isophthalate protective coatings when no radical initiator is employed in

TABLE I
Effect of Initiator Concentration on Moisture Permeability*

Expt. no.	Cure schedule, temp./time, °C/min	Concentration, % per resin		R_0 , ohms	$\Delta R/R_0$, %
		BP	TBPB		
1	60/50; 200/10	0	0	1167.6	0.07
2	60/50; 200/10	0	0	1172.9	0.06
3	60/50; 150/15	0	5	1169.3	0.08
4	60/50; 150/15	0	5	1170.1	0.09
5	60/50; 110/15; 150/15	0	5	1166.1	0.09
6	60/50; 110/15; 150/15	0	5	1172.1	0.09
7	60/50; 200/10	0	5	1174.3	0.11
8	60/50; 200/10	0	5	1168.9	0.09
9	60/50; 150/15	0	22	1170.1	0.13
10	60/50; 150/15	0	22	1172.4	0.11
11	60/45; 110/15	5	0	1170.4	0.48
12	60/45; 110/15; 150/5	5	0	1171.7	0.09
13	150/20; 210/10	0	0	2110 × 10 ³	0.57
14	150/20; 210/10	0	0	1910 × 10 ³	0.58
15	150/20; 210/10; 250/15	0	0	1815 × 10 ³	0.77
16	150/20; 210/10	0.04	0	1830 × 10 ³	0.93
17	150/20; 210/10	0.04	0	1892 × 10 ³	0.53
18	150/20; 210/10	0.16	0	1860 × 10 ³	0.86
19	150/20; 210/10	0.16	0	1823 × 10 ³	0.55

* Experiments 1-12 and 13-19 were run for 1 hr under load of 5 V and for 2 hr under load of 40 V, respectively. Thickness of the coats was about 0.13 mm.

TABLE II
Effect of Time of Cure on Moisture Permeability*

Expt. no.	Temperature, °C	Time, min	$R_0 \times 10^{-4}$, ohms	$\Delta R/R_0$, %
1	200	5	397	1.0
2	200	10	397	1.0
3	200	10	398	1.5
4	200	15	397	1.3
5	200	15	400	1.5
6	200	20	393	1.3
7	200	20	394	2.0
8	200	30	404	2.2
9	200	30	398	1.8
10	215	10	398	1.0
11	215	10	396	1.0
12	215	15	397	2.0
13	215	20	393	1.5
14	215	20	397	1.5
15	230	5	393	2.5
16	230	5	399	1.5
17	230	10	397	1.0
18	230	10	393	0.8
19	230	15	394	1.3
20	230	15	400	1.3
21	230	20	391	1.8
22	230	30	396	1.0
23	230	30	400	2.0

* Tests were run for 1 hr under load of 40 V. Thickness of the coats was about 0.13 mm.

TABLE III
Effect of Thickness of Coating on Moisture Permeability*

Expt. no.	Thickness $\times 10$, mm	$R_0 \times 10^{-4}$, ohms	$\Delta R/R_0$, %
1	1.3 \pm 0.1	448	1.6
2	1.3 \pm 0.1	446	1.3
3	1.3 \pm 0.1	443	1.8
4	1.3 \pm 0.1	448	0.9
5	1.3 \pm 0.1	446	2.5
6	2.0 \pm 0.2	456	0.9
7	2.0 \pm 0.2	444	0.9
8	2.0 \pm 0.2	436	1.1
9	2.0 \pm 0.2	446	1.1
10	2.0 \pm 0.2	441	0.9

* Condition of cure: 170°C for 10 min. Tests were run for 1 hr under load of 40 V.

the formulation of the coating solution. The temperature range explored is from 140° to 230°C. The effect of time of cure on the moisture permeability of the coating was followed at 200°, 215°, and 230°C. Table II clearly indicates no effect of time at the range of 5 to 30 min.

In Figure 1, we find no effect of temperature of cure on the moisture performance of the protective coating when the cure is carried out at a constant temperature between 140° and 230°C. The experiments at

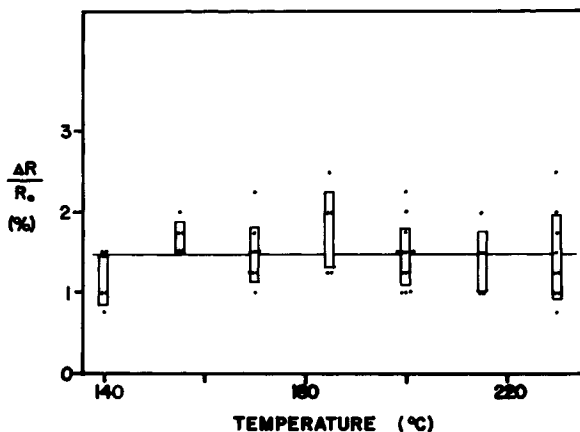


Fig. 1. Moisture performance of poly(diallyl isophthalate) coating as function of temperature of cure. $\Delta R/R_0$ indicates change of resistance of nickel-phosphorus film coated with poly(diallyl isophthalate) after exposure to the moisture test for 1 hr under a load of 40 V. Points represent individual measurements, and bars are standard deviation.

140°, 155°, 170°, and 185°C represent coatings cured for 10 min. The experiments at 200°, 215°, and 230°C represent coatings cured for various times between 5 and 30 min and are similar to the experiments shown in Table II. The rectangles mark out the mean value \pm standard deviation. The solid line was constructed by the graphic least-squares method. In Table III, protections against moisture imparted by different thicknesses of coating are compared.

DISCUSSION

The presence of a radical initiator of polymerization in the diallyl isophthalate coating appeared to introduce to the cured coating the tendency to crack at elevated temperatures. This, of course, detracts from the inherent high-temperature stability advantage of diallyl isophthalate protective coatings. The tendency to crack lessened and diminished as the concentration of initiator in the formulation was decreased, and the decrease of the concentration of initiator had no effect on the permeability of cured coating to moisture.

The coatings cured noncatalytically were exposed to the action of solvents for several days. Little or no effect of the solvents on the coating was observed. Compared to the easy solubility of the prepolymer, the resistance to solvents of the cured coating must be a result of polymerization taking place in the protective film during the cure.

The temperature at which the polymerization process yields the maximum performance of the material with respect to moisture permeability is as low as 140°C if the duration of cure is 10 min or more. Cure at higher temperature does not improve the resistance of the poly(diallyl isophthalate) film to permeation of water. However, the film itself is affected visually.

While the protective coatings cured at 170°C and higher temperature preserve their original glassy appearance for the whole duration of the moisture test, the coatings cured at 140° and 155°C become rough on the surface. Exposure to 170°C for 10 min seems to be the optimum cure schedule for the prepolymer of diallyl isophthalate when it is applied in the form of solution, free of radical initiator. An additional supply of heat does not improve performance of the coating.

An improvement in the resistance to moisture penetration can be achieved by forming a thicker coat on the substrate to be protected. The increased thickness of the protective layer is not necessarily the factor that brings about the improvement. It is generally accepted that there are imperfections in the protective films, and these are the easiest paths for foreign agents to penetrate through the coating. If two or more layers of a coating are formed independently on the surface, the probability that the regions of imperfection in neighboring deposits would overlap each other is less than one, i.e., the number of throughchannels is decreased, and the moisture characteristics improve.

This work was supported in part by The National Research Council of Canada.

References

1. FMC Corporation, *DAPON Diallyl Phthalate Resin*, Product Specification Bulletin.
2. Allied Chemical, Plastics Div., *PLASKON DIALL, DAP Molding Compounds*, Product Specification Bulletin.
3. Messa Plastics Co., *DIALL Plastic Molding Materials*, Product Specification Bulletin.
4. C. A. Heilberger and J. L. Thomas, U.S. Pat. 2,832,758 (1958).
5. J. Hiroshima and T. Ishizuka, Jap. Pat. 17,102 (1964).
6. Solvay and Cie., Brit. Pat. 793,481 (1968).
7. Solvay and Cie., Belg. Pat. 545,030 (1956).
8. G. Takahashi, *Kobunshi Kagaku*, **14**, 151 (1957).
9. P. G. Garnett, *Pigment Resin Technol.*, **1**, 4 (1972).
10. K. Yokoyama, M. Gotoda, T. Kodama, and Y. Kono, *Nippon Genshiryoku Kenkyusho Nempo, JAERI*, **5026**, 101 (1970).
11. M. Gotoda, K. Yokoyama, K. Kinuhara, and M. Okta, *Nippon Genshiryoku Kenkyusho Nempo, JAERI*, **5027**, 100 (1971).
12. T. Ono and T. Wakayoshi, Jap. Pat. 43,310 (1971).
13. D. Porret and P. G. Garrett, Germ. Pat. 1,961,978 (1970).
14. S. Kohn and G. Taguet, Fr. Pat. 1,133,032 (1957).
15. F. Lalau-Keraly, *Compt. Rend.*, **250**, 2697 (1960).
16. C. A. Heilberger and J. L. Thomas, Brit. Pat. 861,817 (1961).
17. Ciba Ltd., Fr. Pat. 1,564,365 (1969).
18. M. E. Hall, Fr. Pat. 2,000,183 (1969).
19. Y. Ninomiya, *Nippon Secchaku Kyokai Shi*, **3**(4), 291 (1967).
20. J. Kumanotami, H. Kamada, K. Yoshida, and T. Wakayashi (to Sumitomo Chemical Co. Ltd.), Germ. Pat. 1,940,531 (1970).
21. J. Rybicky and J. P. Marton, *J. Appl. Polym. Sci.*, **18**, 2611 (1974).
22. ASTM Special Publication No. 265, Symposium on Electroless Nickel Plating, published by American Society for Testing Materials, 1959.

Received November 19, 1973

Revised February 20, 1974