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Fungal Susceptibility of Polyurethanes

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One hundred laboratory-synthesized polyurethanes were tested by a mixed-culture petri dish method for susceptibility to fungus attack. Polyether polyurethanes were moderately to highly resistant to fungal attack, whereas all polyester polyurethanes tested were highly susceptible. The susceptibility of the polyethers was related to the number of adjacent methylene groups in the polymer chain. At least two such groups were required for appreciable attack to occur. The presence of side chains on the diol moiety of the polyurethane reduced susceptibility.

Polyurethanes, as a group, are being used increasingly for a wide variety of purposes. The various physical and chemical properties of these materials make them adaptable to products which have application in many industrial and commercial products, such as rigid and flexible foams, fabric coatings, adhesives, and rubbers. A survey of the microbiological aspects of polyurethanes, including a preliminary report of this work, has been presented (2).

Unlike most synthetic polymeric (plastic) materials, polyurethanes have frequently been found to be subject to attack by microorganisms, especially fungi. There is considerable presumptive evidence that the polyester type polyurethanes are commonly attacked by fungi, whereas the polyethers may be completely or almost completely resistant. This distinction has been derived from observations of commercially formulated polyurethane rubbers, textile-coating materials, adhesives, etc. Since the exact composition of such formulations is seldom known, it is difficult to determine whether the observed growth of fungi is on the polyurethane itself or is, at least in part, due to other ingredients in the formulation, for example, stearic acid.

This investigation was undertaken to determine the extent of growth of fungi on a series of selected, specially synthesized polyurethanes as contrasted to commercially formulated materials. It was hoped to find the relationship between chemical configuration and fungal susceptibility and to provide a basis for tailoring new polyurethanes which would be resistant to fungal attack while still retaining the desirable properties of related susceptible types. One hundred polymers prepared by reacting four diisocyanates with 25 diols were subjected to standard petri plate tests to determine their ability to support or inhibit fungal growth. The monomer diols, which were chosen to provide both polyether and polyester polyurethanes, included polyethylene glycols, polypropylene glycols, alkane diols, bisphenols, and adipic acid polyesters of alkane diols. The monomer diols and polyesters, unreacted with the diisocyanates, were also tested in the same manner.

MATERIALS AND METHODS

The polyurethanes were synthesized by condensation of the diisocyanates with the diols or polyesters as given in Tables 1 and 2. All materials were of the highest purity obtainable and were further purified if deemed necessary.

The diisocyanates (Table 1) included three with aromatic and one with linear aliphatic configuration.

The diols (Table 2) were selected to represent a variety of classes, and several representatives of each class were used. The polyether polyurethanes were made from three polyethylene glycols, four polypropylene glycols, 13 alkane diols (both straight-chain and branched) and two bisphenols. The polyester diols were made from three alkane diol esters of adipic acid.

The polyurethanes were made by reacting the monomer diols, the polyester diols, and the polyether diols with the diisocyanates under anhydrous conditions in the presence of 0.025% ferric acetylacetonate as catalyst based on the diol weight. A preliminary test of one diol (dipropylene glycol) with and without the catalyst indicated that there was no effect on the growth of the fungi due to the presence of the catalyst.

Table 3 gives the average molecular weights found for some of the synthesized polyurethanes.

The biological assay consisted of a standard petri dish test (1) with modifications as noted. The six organisms recommended by the American Society for Testing Materials (1) were used (*Aspergillus niger* QM386, *A. flavus* QM380, *A. versicolor* QM432, *Penicillium funiculosum* QM391, *Pullularia pullulans* QM279c, and *Trichoderma* sp. QM365) with the addition of *Chaetomium globosum* QM459. Observations on the amount of growth were made after 1, 2,

TABLE 1. *Diisocyanates used in the study*

Compound	Melting or boiling point (C)	Source[a]
Tolylene-2,4-diisocyanate	21	Na (Nacconate 100)
3,3′-Bitolylene-4,4′-diisocyanate	71	Na (Nacconate 200)
Diphenylmethane-4,4′-diisocyanate	37	Na (Nacconate 300)
1,6-Hexamethylene-diisocyanate	140–142/21 mm	Mo (Mondur HX)

[a] Na = National Aniline Div., Allied Chemical Corp.; Mo = Mobay Chemical Co.

TABLE 2. *Diols used in the study*

Diol	Purity	Physical form	Source[a]
Ethylene glycol	Chemically pure	Clear liquid	F
1,3-Propanediol	Used as received	White solid	E
1,4-Butanediol	Boiling point, 228–230 C	Clear liquid	Ma
1,5-Pentanediol	Used as received	Clear liquid	E
1,6-Hexanediol	Melting point, 42–47 C	Clear liquid	A
2,3-Butanediol	N_D^{20}, 1.4323	Clear liquid	A
2,5-Hexanediol	Used as received	Clear liquid	A
2-Methyl-1,4-butanediol	N_D^{20}, 1.4472	Clear liquid	A
2,2-Dimethyl-1,3-propanediol	Used as received	White solid	A
3-Methyl-2,4-pentanediol	N_D^{20}, 1.440	White solid	A
2-Methyl-2,4-pentanediol	N_D^{20}, 1.4250	Yellow liquid	A
2-Ethyl-2-methyl-1,3-propanediol	Used as received	White solid	A
2,3-Dimethyl-2,3-butanediol	Redistilled	White solid	E
Diethylene glycol	N_D^{20}, 1.4460	Clear liquid	A
Triethylene glycol	Used as received	Clear liquid	A
Pentaethylene glycol	N_D^{20}, 1.4606	Clear liquid	A
Dipropylene glycol	N_D^{20}, 1.4396	Clear liquid	A
Polypropylene glycol 400P	Molecular weight (found), 400	Clear liquid	O
Polypropylene glycol 1020P	Molecular weight (found), 990	Clear liquid	O
Polypropylene glycol 1320P	Molecular weight (found), 1,200	Clear liquid	O
2,2-Bis(4-hydroxyphenyl)propane	Used as received	White solid	N
Bis(4-hydroxyphenyl)dimethylsilane	Analytically pure	White solid	N
Prepolymer			
Polyethyleneglycol adipate	Molecular weight, 2,390; 14 prepolymer units	White solid	Mo (Multrathane R14)
Poly-1,3-propanediol adipate	Molecular weight, 5,240; 28 prepolymer units	White solid	Mo (Multron R16)
Poly-1,4-butanediol adipate	Molecular weight, 1,950; 10 prepolymer units	Clear liquid	Mo (Multrathane R144)

[a] A = Aldrich Chemical Co.; E = Eastman Organic; F = Fisher Scientific; Ma = Matheson, Coleman and Bell; Mo = Mobay Chemical Co.; N = Natick Laboratories; O = Olin Chemical Corp.

and 3 weeks of incubation at 30 C. Growth was rated visually on a scale of 0 to 4, as follows: 0 = no growth; 1 = trace of growth (visible under microscope but not visible to naked eye); 2 = light growth; 3 = moderate growth; 4 = heavy growth.

The salt-agar medium contained (per liter): $NaNO_3$, 3.0 g; K_2HPO_4, 1.0 g; $MgSO_4 \cdot 7H_2O$, 0.25 g; KCl, 0.25 g; yeast extract, 0.2 g; and agar, 10 g. The yeast extract was included to assure germination of fungus spores; it normally supported a very small amount of growth and fruiting and provided a basis for judging zones of inhibition around the material under test.

Aseptic methods were not used except for routine maintenance of fungus cultures. The spore suspensions were used without washing.

As a viability control, a small piece of polyvinyl-

TABLE 3. *Molecular weights found for synthesized polyurethanes*

Diol	Diisocyanate[a]			
	TDI	MDI	TODI	HDI
1,5-Pentanediol	1,180			
3-Methyl-2,4-pentanediol			2,740	
2-Methyl-2,4-pentanediol			1,620	2,570
Diethylene glycol				7,740
Pentaethylene glycol		3,500		3,740
Dipropylene glycol				6,740
Polypropylene glycol, molecular weight 400		3,990		
Polypropylene glycol, molecular weight 1,020			2,540	3,300
Polypropylene glycol, molecular weight 1,320				2,370
2,2-Bis(4-hydroxyphenyl) propane			1,130	
Bis(4-hydroxyphenyl) dimethylsilane			1,180	
Polyesters				
Polyethylene glycol adipate				1,640
Poly-1,3-propanediol adipate				2,410

[a] TDI, tolylene-2,4-diisocyanate; MDI, diphenylmethane-4,4′-diisocyanate; TODI, 3,3′-bitolylene-4,4′-diisocyanate; HDI, 1,6-hexamethylene-diisocyanate.

TABLE 4. *Maximal growth rating obtained with fungus mixture on (pure) polyurethanes and on constituent monomers*

Diol	Monomer	Polymer[a]			
		TDI	MDI	TODI	HDI
Polyethers					
Ethylene glycol	2	0	1	1	0
1,3-Propanediol	2	1	2	1	1
1,4-Butanediol	4	2	2	3	2
1,5-Pentanediol	3	3	3	2	1
1,6-Hexanediol	2	2	3	3	1
2,3-Butanediol	4	2	0	1	1
2,5-Hexanediol	2	2	1	1	1
2-Methyl-1,4-butanediol	4	2	1	1	1
2,2-Dimethyl-1,3-propanediol	3	2	0	1	1
3-Methyl-2,4-pentanediol	1	2	1	1	1
2-Methyl-2,4-pentanediol	2	2	1	1	1
2-Ethyl-2-methyl-1,3-propanediol	3	2	1	1	1
2,3-Dimethyl-2,3-butanediol	2	0	1	1	0
Diethylene glycol	2	1	1	1	0
Triethylene glycol	2	1	1	2	0
Pentaethylene glycol	2	2	2	1	0
Dipropylene glycol	2	0	0	0	0
Polypropylene glycol (molecular weight, 400)	2	2	2	2	2
Polypropylene glycol (molecular weight, 1,020)	2	3	3	3	3
Polypropylene glycol (molecular weight, 1,320)	2	3	2	3	2
2,2-Bis(4-hydroxyphenyl)propane	1	0	0	0	0
Bis(4-hydroxyphenyl)dimethylsilane	1	0	0	0	—
Polyesters					
Polyethylene glycol adipate	4	4	4	4	3
Poly-1,3-propanediol adipate	4	4	4	4	3
Poly-1,4-butanediol adipate	4	4	4	4	3

[a] For abbreviations, see footnote to Table 3.

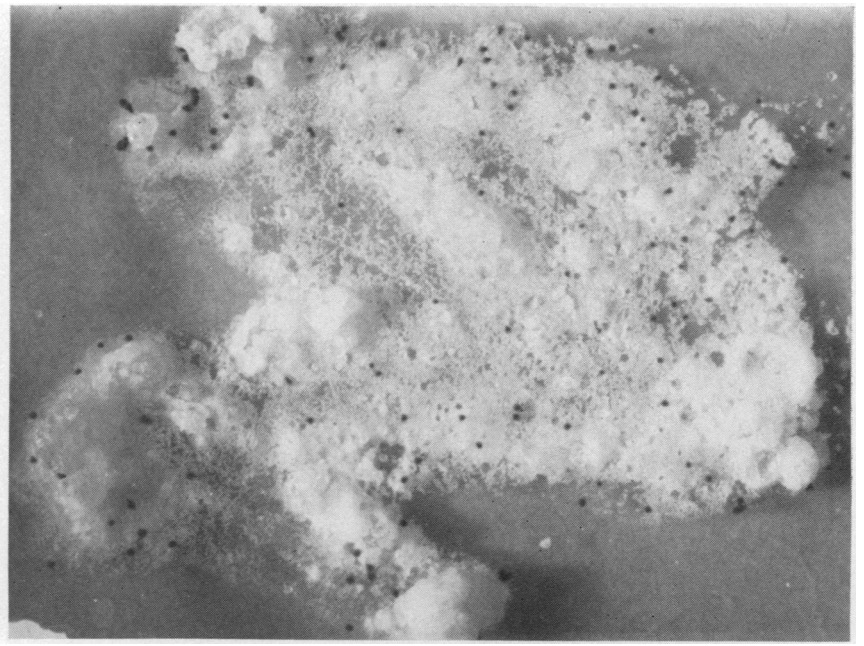

FIG. 1. *Growth on polymer of 3-methyl-2,4-pentanediol × TDI showing perithecia of Chaetomium globosum. Original photo magnification = 10×. Three weeks of incubation.*

butyral tape was substituted for the test material. In every case, this material supported good growth when inoculated with the spore suspension.

Each monomer and each polymer was tested individually. All tests were repeated at least three times. The results of the replicate tests agreed closely with each other, but only the highest rating is reported.

Solid, syrupy, and gummy materials were transferred directly to the agar surface (Fig. 1 and 3); liquid materials of low viscosity were placed on fiberglass filter paper which was then placed on the agar (Fig. 2).

RESULTS

The results are presented in Table 4. Figures 1, 2, and 3 are presented to show representative fungal growth on selected substrates. Figure 1 shows the light growth obtained on the polyether polymer of 3-methyl-2,4-pentanediol × tolylene-2,4-diisocyanate (TDI). The dark spots are perithecia of *C. globosum*, the only fungus which appeared on this polymer. It is rated 2 (light growth). Figure 2 shows the growth obtained on the monomers 2,5-hexanediol (rated 2) and 2,3-butanediol (rated 4). The third piece in the plate is the cottonseed oil control (rated 4). Figure 3 shows the profuse growth obtained on the polyester polyurethane polymer of TDI reacted with the polyester diol of adipic acid and 1,3-propanediol. It is rated 4 and shows a mixture of all the fungi in the original inoculum.

DISCUSSION

The striking fact revealed by this study is that the polyether-linked polyurethanes are, as a group, significantly less available as nutrients for fungi than are the polyester-linked polyurethanes. Although there is considerable variability in the availability of specific polyethers, most of the polymers tested were highly resistant to attack. Those that were slightly or moderately attacked were limited to polymers of several low molecular weight unbranched alkane diols (1,4-butanediol, 1,5-pentanediol, and 1,6-hexanediol) and the higher molecular weight polypropylene glycols (molecular weight, 1,020 and 1,320). The availability of these as substrates for the fungi suggests that the enzymatic attack can occur only if there is a sufficiently long unbranched carbon chain length between the urethane linkages of the polymer. It also suggests that three adjacent methylene groups are required for appreciable attack to occur. The attack is weaker if only two such groups are present. Proximity of urethane linkages may interfere with enzyme accessibility to susceptible groups in the molecule. The shorter alkane diols (ethylene glycol and 1,3-propanediol) and the branched diols were, in general, relatively resistant to attack. Polymers made from the two bisphenols were completely resistant.

In contrast to the behavior in the polyethers, the polyesters were excellent substrates for fungal

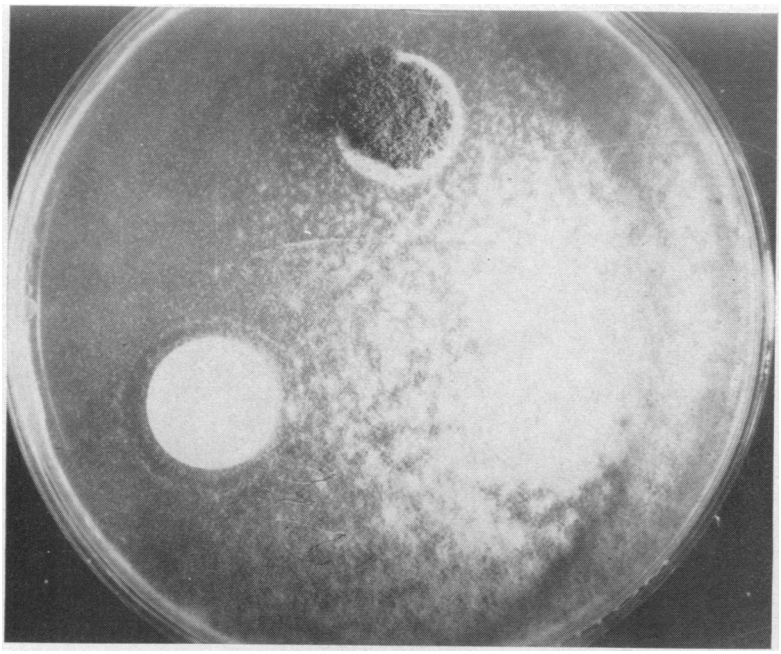

FIG. 2. *Growth of mixed fungi on 2,5-hexanediol (lower left) and 2,3-butanediol (lower right). The upper sample is cottonseed oil used as a control. Note stimulation of growth on agar around 2,3-butanediol. Three weeks of incubation.*

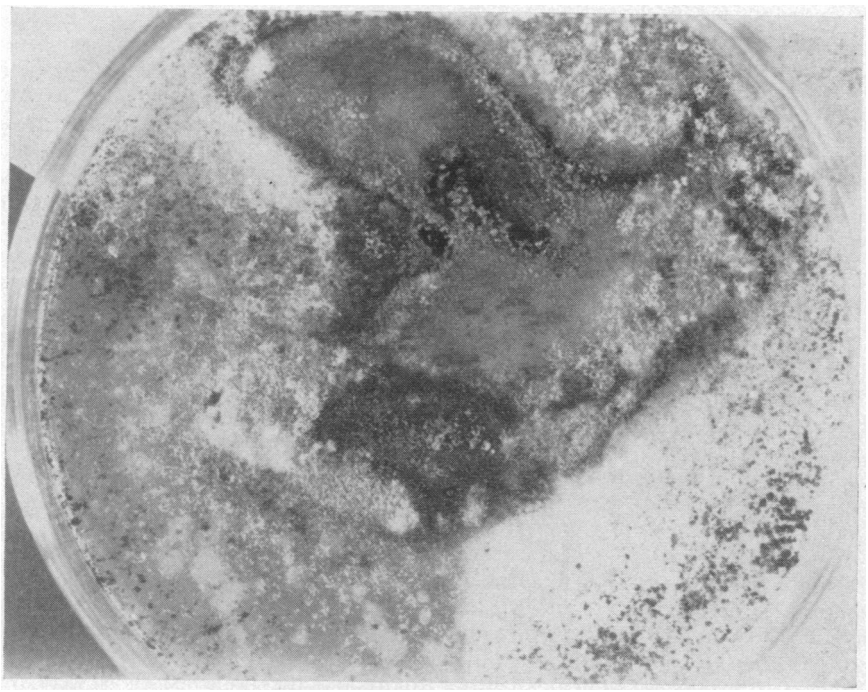

FIG. 3. *Growth of mixed fungi on the polymer of 1,3-propane adipate × TDI. Growth rating = 4. Photo after 2 weeks of incubation.*

growth. All polyester polymers were rated 4 except those made with 1,6-hexamethylene-diisocyanate (HDI) which were rated 3. The kind of profuse growth obtained on these polymers is shown in Fig. 3. Since the polyesters constitute a significant group of polyurethanes and include some of the least expensive (castor-oil based) types, the importance of microbiological susceptibility is apparent.

Comparison of the four diisocyanate series shows that polymers made with the linear diisocyanate (HDI) are appreciably less susceptible than those made with the three cyclical diisocyanates. This shows up especially in the polyester group where growth did not exceed a rating of 3. Of the cyclical diisocyanates, TDI resulted in more susceptible polymers than did diphenylmethane-4,4'-diisocyanate (MDI) or 3,3'-bitolylene-4,4'-diisocyanate, considering each series as a whole.

In general, the monomers were more susceptible to attack than their respective polymers. In only a few cases did monomers receive lesser ratings than corresponding polymers made from them. These were 1,6-hexanediol, 3-methyl-2,4-pentanediol, and the two higher molecular weight polypropylene glycols.

In almost all polyethers, at least traces of growth could occasionally be observed microscopically on the material, indicating that although it is not a good substrate for the fungi it is at least not fungistatic or fungicidal.

The fact that the polyester polymers of ethylene glycol and 1,3-propanediol are highly susceptible as contrasted to polyether polymers of these compounds which are highly resistant indicates that the polyester linkage is important in the breakdown and metabolism of the former. The weight of the empirical evidence found with commercially prepared formulations supports this conclusion. Adipic acid is well known to be used by fungi for growth, and most of the diols mentioned are also used to a limited extent.

Considering the variability in susceptibility that appeared with a given diol when reacted with different diisocyanates, it is evident that generalities should be drawn with care and that each polymer should be judged on its own merits. For instance, 2,3-butanediol by itself was a good substrate for growth, but polymers derived from it varied in susceptibility from zero (MDI) to 2 (TDI); with 1,5-pentanediol, the growth was rated 3, but polymers derived from it were rated 3, 2, and 1, according to the diisocyanate used.

Although polyester polyurethanes are, as a class, highly susceptible to fungal attack, the polyethers, depending on the diol and diisocyanate used, are also variously susceptible to attack, but to a considerably lesser extent. The presence of at least two, preferably three, unbranched linked methylene groups seem to be necessary for fungal attack to occur on polyether polyurethanes.

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