Appl Microbiol Biotechnol (1986) 23:407—409

Applied and Microbiology Biotechnology

Short contribution

A rapid technique for evaluating the biodeterioration potential of polyurethane elastomers

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Summary. The technique described provides a rapid method for screening thermoplastic polyurethanes against deteriogenic micro-organisms using thin films (0.4—0.5 mm thick) of plastic prepared in an electric platens press. The films are inoculated with a spore suspension of *Gliocladium roseum* and can be viewed directly under the light microscope for evaluation of surface effects; selective staining can be used to reveal fungal mycelium. Results can be obtained within a week which correlate with longer term tests using commercial samples. The technique can also be used to isolate potential polyurethane deteriorating micro-organisms from the environment and to confirm their biodeteriogenic activities.

Introduction

The biodeterioration of polyurethanes (PU) is well documented (Seal and Pathirana 1982) and it is established in general terms that polyester PU are more susceptible to microbial attack than polyether PU (Darby and Kaplan 1968). The evaluation of susceptibility at a quality assurance level involves the exposure of specimens to either a defined group of micro-organisms (usually fungi) in a petri dish test (American Society for Testing and Materials 1980; International Organisation for Standardisation 1978) or a natural soil flora (Deutsches Institut für Normung 1984). The nature of the specimens, i.e. their physical dimensions, is such that several months may be required to obtain an observable effect. In our experience even longer periods may be necessary for the biodeterioration mechanism to manifest itself as a change in the physical properties of the PU in such tests.

Our research on the biodeterioration of polyurethanes (Pathirana and Seal 1984a, 1984b, 1985) supports the suggestion that the polyester segment of the PU structure is the initial site of attack, and we have isolated fungi capable of induced esterase (lipase) activity in the presence of poly(caprolactone) diol. Most notable among these is *Gliocladium roseum* (Bainier) which is capable of causing extensive deterioration of polyester PU (Pathirana and Seal 1983) over short time periods (within 28 days). This has led us to develop a rapid method incorporating *G. roseum* and the use of thin films of PU so that direct microscopic viewing of the film using transmitted light is possible in order to detect surface deterioration within seven days.

Materials and methods

Fungal strain. Gliocladium roseum (IMI 260419) isolated by Pathirana (Pathirana and Seal 1983) from deteriorated polyurethane, routinely grown on malt extract agar slopes at 30° C, and maintained at room temperature and as freeze-dried cultures.

Media. Malt extract agar (MEA) containing malt extract, 30.0 g; mycological peptone (Oxoid Ltd), 5.0 g; aureomycin, 0.05 g; agar, 12.0 g; distilled water, to 1000 ml, pH 5.4.

Polyurethanes. A range of commercial formulations incorporating different polyol and diisocyanate compositions (see Table 1).

Preparation of polyurethane films: the PU were obtained as either extruded granules or injection moulded platens. Thin films were produced using a hydraulic electric platens machine. A small amount of the PU was placed centrally between silicon coated aluminium plates which were positioned between the platens preheated to 200° C. After sufficient time for the polymer to melt pressure was applied (10 tonnes, using a

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Table 1. Effect of *Gliocladium roseum* on a range of polyurethane compositions

Polyurethane composition	Magnitude of surface effect after 7 days at 30°C[e]
Poly(ethylene adipate)/MDI[a]	+
Poly(ethylene/butylene adipate)/MDI	+
Poly(hexanediol carbonate)/MDI	−
Poly(tetrahydrofuran)/MDI	−
Poly(caprolactonediol)/MDI	+[d]
Poly(caprolactonediol)/TDI[b]	++[d]
Commercial polyester PU (A)[c]	++[d]
Commercial polyester PU (B)[c]	+
Commercial poly(caprolactone) PU[c]	+[d]
Commercial polyether PU[c]	−

[a] 4,4 Diphenylmethane diisocyanate
[b] Tolylene diisocyanate
[c] Composition not known
[d] Surface effect observed after 4 days
[e] + = Moderate cracking, ++ = Extensive cracking, − = no surface deterioration

10.0 cm ram) and held for 10 min. The platens were water cooled rapidly to below 50°C before reducing the pressure and removing the thin film (now 0.4—0.5 mm thick).

Cultural conditions. Small squares (2.0 cm × 2.0 cm) of the PU film were rinsed in ethanol (70% v/v) to remove surface contamination; for example, grease from the pressing process. Some films were sterilized by fumigation in ethylene oxide (20% in water) overnight. A spore suspension of *Gliocladium roseum* (100 µl, 10^6 ml^{-1}) was spread onto pre-poured MEA plates. The films were placed aseptically on the agar surface and the plates incubated at 30°C for up to 28 days. Sterile controls were carried out in parallel to investigate the effects of chemical hydrolysis. Films were removed at regular intervals, cleaned in ethanol (70% v/v), and placed directly onto microscope slides for viewing. Fungal hyphae were stained using cotton blue (0.05 g in 100 ml lactophenol).

Results and discussion

All of the susceptible polyester PU showed easily recognisable cracks or perforations of the film after 7 days incubation with *G. roseum* (Table 1). Damage to the poly(caprolactone) PU films was observed after only 4 days whereas the polyether PU did not exhibit any surface effects during the 28 day incubation period. The effects of chemical hydrolysis were examined using non-inoculated controls but no damage was detected. Two types of damage were observed: crazing and stellate (Figs. 1 and 2). The stellate effect caused complete perforation of the PU films whilst the crazing effect was closely associated with the fungal hyphae (Fig. 1) and eventually resulted in the breakdown of the film. The effects were not confined to any particular PU composition. Although ethanol (70%) may not be regarded as a complete sterilizing agent it was found to be effective in preventing contaminating growth during the incubation periods used in the test. Ethylene oxide was found to be completely effective as a sporicidal agent and is recommended for use with this technique where possible.

The results obtained are consistent with longer term testing we have carried out on thicker specimens, and with in-service failures we have experienced. The technique has been employed in two other areas: the isolation of PU deteriorating fungi from the environment using a screened substrate technique (films placed on microscope slides and covered with nylon filtration cloth, mesh size (5 µm), and to screen both environmental isolates and standard plastic test fungi for their

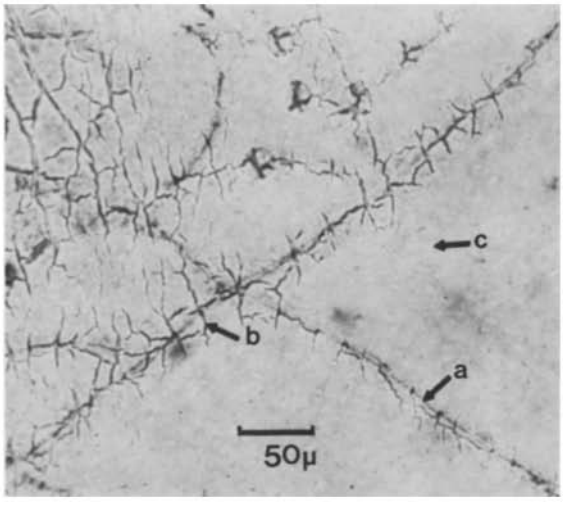

Fig. 1. Crazing in *PU* film. **a** stained hypha; **b** fine cruk; **c** intact film

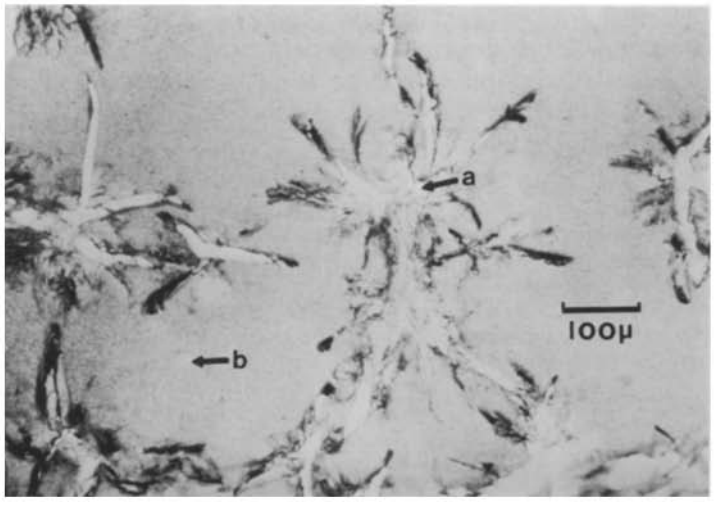

Fig. 2. Stellate cracking in *PU* film. **a** complete perforation of film; **b** intact film

ability to deteriorate a known susceptible PU. Although we have found our strain of *G. roseum* to be the most active of our collection of PU deteriogens, other fungi belonging to the genera *Alternaria, Fusarium, Penicillium* and *Ulocladium* are also able to produce similar effects. As with all rapid screening methods caution should be exercised in the interpretation of negative results.

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Received July 20, 1985/Revised September 23, 1985