POLYMERIZATION AND SURFACE TREATMENT
IN A LARGE VOLUME MICROWAVE PLASMA GENERATOR

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ABSTRACT
Curing or cross-linking of polymer films was studied in order to evaluate
the Large Volume Microwave Plasma Generator technology for polymerization.
Polyurethane films were effectively and quickly cross-linked when exposed
to an argon microwave plasma. Plasmopolymerized coatings were also formed
from styrene or methylmethacrylate vapours; the plasmopolymer structures
were varied, especially with respect to the aromatic rings in styrene.

1. INTRODUCTION

The Large Volume Microwave Plasma Generator (LMPR)* was introduced a number
of years ago (1), and it is now being developed in a number of industrial
processes using both continuous and batch processing.

Some experimental works were also done on depositing plasma-polymer coatings
on metallic surface samples of steel or other metals, using for instance
to vour of thiofene, perfluorobutane, aniline or trichloroethylene (2). In
other experiments, some "plasmasilicones" were deposited on glass and alu
minium base surfaces heated at elevated temperatures (2,3). The results
showed that the coatings were not true polymers (and this was to be expected
since the compounds used cannot be polymerized in the normal sense of
classical polymer chemistry), but were convenient anticorrosive coatings (5).

In summary, in previous experiments, the microwave plasma process has pro
duced thin "polymeric" coatings of apparent good quality on various surfa
ces. This paper reports on studies made with coatings obtained with mate
rials normally used in macromolecular chemistry. It gives an evaluation of
the potential usefulness of the LMP process in various applications:

i. the treatment in the plasma generator of sample surfaces previously
coated with a thermosetting prepolymer;

ii. the production of coatings on a given surface from vapours of liquid
monomers injected into the reactor.

* LMPR : a Trade Name of Ecole Polytechnique de Montréal.
2. EXPERIMENTAL

A schematic diagram of the set-up is shown in Fig. 1. Microwave energy (freq. 2.45GHz) is directed to an open slow-wave structure 4. The field coupling between the slow-wave structure and the reactor 10 can be adjusted in such a way that the microwave density is uniformly dissipated. The gas (argon) pressure is measured by means of a precision vacuum gauge. A needle valve injector for liquid monomer 14 can be added to the set-up.

When a sample to be treated is introduced into the reactor, the first step is to obtain a good vacuum (0.01 Torr). Then a flow of argon is introduced, increasing the pressure to an appropriate value (ca. 1 Torr), and the microwave power is switched on to the desired power level. The time of treatment is also plotted as a parameter in the experiment.

3. MATERIAL AND METHODS

Compound mixtures and treatment of coated surfaces.

The compounds in this case were prepolymer used for polyurethane coatings: commercial either aliphatic (Desmodur N Bayer) or aromatic (Desmodur L) or phenol-blocked aromatic (Desmodur AP) polyisocyanates, stoichiometrically mixed with polyalcohols (respectively Desmophen 650, 1100 and 800); model molecules were also tested like tolylene diisocyanate and hexamethylene diisocyanate mixed with 1,4-butanediol.

The test samples deposited on quartz plates were placed inside the reactor, and the argon plasma applied for short time intervals to avoid over-heating. Treated coatings were submitted to solubility tests, organic microanalysis and IR spectroscopy.

Formation of polymer coatings from monomer vapours.

Polystyrene, polyethylenacrylate and polymethylmethacrylate films were formed on sample surfaces of brass, aluminium or steel. The gaseous mixture pressure was established either with a total pressure of 1.5 Torr and introducing a partial pressure of monomer up to 0.75 Torr (the partial pressure of argon decreasing from 1.5 to 0.75 Torr), or with a constant argon pressure of 1.5 Torr with an added partial pressure of monomer (0.0-0.75 Torr). In both cases, the microwave incident power necessary to ignite the plasma was found to vary linearly as a function of the monomer partial pressure. The obtained plasma polymer samples were submitted to organic microanalysis and IR spectroscopy.  

4. RESULTS AND DISCUSSION

Treatment of coated surfaces.

Generally, "plasmapolymerized" polyurethane samples were of poor quality as coatings, due to residual solvent which caused blistering. However, they were found to be insoluble in ethyl acetate and in dimethylformamide (DMF), indicating the cross-linking process was strongly accelerated in the plasma, related to treatment time (1 to 5 minutes) and temperature (80°C). Such a cross-linkage normally requires a heat-treatment of 120 to 160°C for 20 to 30 minutes. Moreover, diisocyanate-based compounds which normally are not thermosetting became insoluble in hot DMF, and thus highly cross-linked, after 5 minutes in the plasma.

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When compared with oven cured samples, the LMP treated samples showed a
decrease of the carbon and hydrogen contents, and an increase of the nitro-
gen content, especially in molecules having methyl groups, more readily
removable. Generally, this result indicates a removal of hydrocarbon chains
in molecules, and this was confirmed by IR spectra, even showing a decrease
of the aromatic substitution bands. Moreover, no free isocyanate was found,
but amide groups appeared, due to the rupture and rearrangement of isocyana-
te or urethane functions, inducing different possibilities of cross-linking
in the "plasmapolyurethanes". (Table 1).

Formation of polymer coatings from monomer vapours.

Insoluble "plasmapolymethylmethacrylate" samples showed an increase of the
carbon content and a decrease of the oxygen content, with a definite lack of
reproducibility. Infrared analysis revealed double bonds related to the
loss of hydrogen content, and the formation of hydroxyl groups (probably
acid), while the significant decrease of ester bonds confirmed the decrease
of the oxygen content. (Table 2).

The analysis of "plasmapolystyrene" samples showed lower carbon and hydro-
gen contents and the unexplained presence of oxygen. The deposits were se-
parated into two parts: soluble or insoluble in benzene. The IR spectra of
the non-soluble part revealed an almost complete removal of the aromatic
rings, and therefore the production of an almost pure aliphatic material,
with some acid groups probably produced by air leaks into the plasma, while
the soluble portions showed a slight substitution on the aromatic rings.
Thus it was shown that the out-of-chain aromatic rings are especially sensi-
tive to the argon plasma, and a privileged site for breaking the covalent
bonds and for recombination and cross-linking reactions.

5. CONCLUSION

The treatment of macromolecular films of polyurethane inside an LMP\textsuperscript{R} plasma
allows it to harden and cross-link the coatings in a very short time and
probably at a lower average temperature than presently used in standard
oven treatments of such coatings. However, the necessity to place the coa-
tings under vacuum produces an evaporation of the solvents and brings about the
porosity of the film, thus limiting the use of this process to coatings
which do not require solvents (powder coatings) and to plasmapolymers for-
med from monomer vapours.

The systematic tests on the formation of coatings in a plasma containing
methylmethacrylate vapours allowed us to derive the optimum deposition
conditions of the films, and showed that the microwave required to initiate
a discharge in the vapour, an argon gas mixture, was proportional to the
ratio of the partial vapour pressure of the monomer to the total pressure
of the gas mixture. However, a quick evaluation of the deposits showed that
teh coatings were non-uniform and the process is in general not repeatable
from onetrial to the next. These results are not really surprising if one
considers the complexity of the mixture and the large number of reactions
which can take place.

At last, the chemical and infrared analysis of the plasmapolymers showed
the great sensitivity of some functionnal groups to plasma: isocyanates
in polyurethane prepolymers, out-of-chain methyl groups in methylmethacry-
late, and especially aromatic rings in styrene.
REFERENCES

### TABLE 1
Microanalysis of polyurethanes and "plasmapolyurethanes"

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### TABLE 2
Microanalysis of "plasmapolymethylmethacrylate" and "plasmapolystyrene"

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Figure 1. Block diagram of apparatus:

1: variable 2.45GHz microwave power supply, 0-2.5kW
2: triple stub tuner
3: transition from rectangular waveguide to slow-wave structure
4: slow-wave structure
5: transition from slow-wave structure to rectangular waveguide
6: high power microwave dry load
7: cooling air blower
8: microwave field coupling between 4 and 10
9: transparent radiation shield
10: plasma reactor
11: argon storage cylinder
12: pressure regulator and gauge
13: needle valve
14: needle injector for monomers
15: precision vacuum gauge
16: liquid nitrogen trap
17: vacuum pump