

- Liquid films and the plasma-enhanced deposition of solid coatings – new perspectives in-between polymer and plasma chemistry

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Abstract

Liquid films of e.g. HMDSO and MMA can be converted by a non-thermal plasma, thus forming solid polymer films upon various substrates. This versatile process offers the possibility to combine the benefits of classic polymerization and plasma chemistry.

Keywords: Dielectric barrier discharge, HMDSO, PDMS, PMMA

1 Introduction

The plasma-enhanced chemical vapour deposition (PECVD) of polymeric films using hexamethyldisiloxane (HMDSO) is a process well known and described in the literature.[1] Since the vapour pressure of HMDSO is only about 43 hPa at room temperature, the use of high monomer concentrations within the feed gas stream might well lead to HMDSO aerosol drops reaching the surface. However, Bour and coworkers did show that there is no major impact on the applicability of the resulting films as barrier coatings.[2] Nevertheless, the protective properties e.g. as corrosion resistant coating can well be improved via an additional plasma post-treatment step after turning off the monomer feed.[3]

In an earlier study, we demonstrated the possibility to deposit SiO₂ via a two-step process.[4] In the first step, a silicon-containing primer film is deposited from gas mixtures of SiH₄ and N₂. In the second step, an air plasma is employed to fully oxidize the primer film and yield stoichiometric SiO₂. The second process shows that deep modifications of films are well possible via oxidizing plasmas.

The use of plasma discharges for the initiation of a polymerisation reaction is discussed in the literature especially well for methyl methacrylate (MMA) e.g. by Johnson and coworkers.[5] However, all of these studies report on the generation of a substance from MMA monomer which then can serve as an initiator for polymerization later on, whereas no complete polymerization of the liquid was found. This might be explained by the generation of a high radical density region at the interface between gas and liquid phase, whereas the reaction velocities and the diffusion lengths of the radicals were found to be relatively small.[6]

2 Experimental

2.1 Plasma treatments

The plasma treatments were conducted using a vessel with a volume of approx. 10 l. A soda-lime glass petri dish (STERIPLAN®, 120 mm in diameter) included in the lid was used as dielectric, while an 80 mm high voltage (HV) electrode plate was fixed onto it using high temperature silicone (Soudal gasket seal). An alternating HV Fourier synthesis pulse generator (Ingenieurbüro Jürgen Klein, S/N 040-3) with a pulse duration of 0.6 µs at a peak voltage set to 13 kV and a repetition rate set to 1.6 kHz was connected to the HV electrode, while the substrate holder and the reaction vessel were linked to the ground potential.

The substrates were weighed before and after applying the monomer resin on top. Afterwards, they were placed inside the reaction vessel, leaving a gas gap of approx. 2 mm to the glass dielectric above.

2.2 Materials

The films were deposited using hexamethyldisiloxane (HMDSO, 98.5%, Sigma-Aldrich) and methyl methacrylate (MMA, >99%, Sigma-Aldrich) monomers. Composite filler particles (aluminium trihydroxide in a PMMA matrix) were obtained from Kolpa d.d., Slovenia.

As substrates sheets (all 80 mm in diameter) of aluminium (0.3 mm thick), polyethylene (0.3 mm thick) and polypropylene (0.7 mm thick) as well as shape memory effect plates (10 x 10 x 2 mm³) on the basis of a Cu-Al-Mn-Fe alloy were used.

2.3 Analytical methods

The deposited films were analysed by means of light microscopy (Leica EZ4 D stereo microscope), confocal laser scanning microscopy (CLSM, Keyence VK-X210 microscope with VK-X200K controller) and FTIR microscopy (Bruker IFS 66v).

3 Results and Discussion

Plasma treatments using an open reaction vessel led to a complete loss of monomer, while closed reactors without any gas buffer aside the plasma region did not lead to the formation of solid films. Using the device described above, however, clear solid coatings formed from HMDSO and MMA as well.

3.1 Plasma-polymerised HMDSO

The films deposited using liquid HMDSO are well transparent as shown by the CLSM image depicted in fig. 1. Depending on the deposition parameters, the films' surfaces exhibit wave-like patterns (see light shadows in fig. 1) and upright column structures (see darker spots in fig. 1).

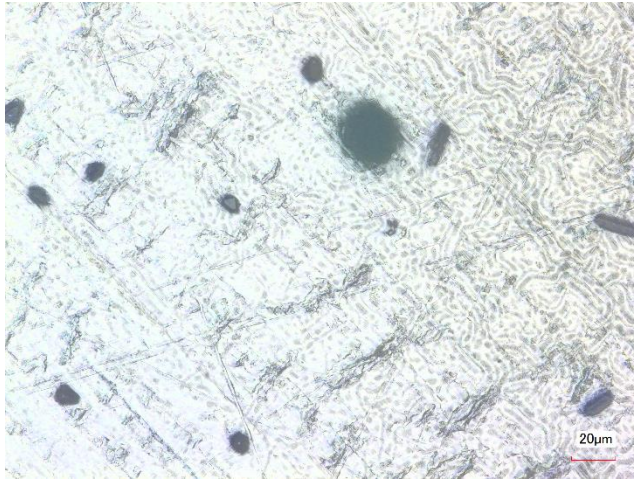


Fig. 1. CLSM image of plasma-polymerized HMDSO on an aluminium substrate.

The chemical structure of these films is exemplarily given by the ATR-FTIR spectrum of a coated PE substrate shown in fig. 2. Some of the bands of the PE substrate are still remaining (denominated in black, c.f. [7]), whereas the bands from the coating are similar to PDMS-like polymers, i.e. typical HMDSO-based PECVD films (c.f. [8]).

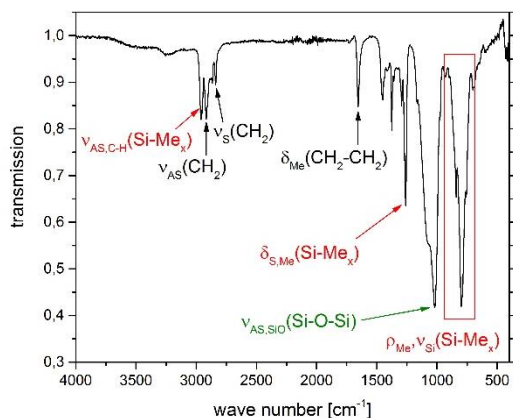


Fig. 2. ATR-FTIR spectra of plasma-polymerized HMDSO on a rough PE foil substrate.

However, in contrast to typical plasma-polymerized HMDSO and PECVD coatings, these films are not entirely cross-linked. Therefore, large parts of the film can be dissolved, e.g. in tetrahydrofuran.

3.2 Plasma-polymerised MMA

The liquid MMA films led to clear, stable PMMA films as verified by ATR-FTIR (not shown). This process even works well including different fillers. As an example, fig. 3 shows a CLSM image of a coating including composite particles (white colour) with large particle diameters ($D_{0.5} = 75.66 \mu\text{m}$) and a broad size distribution. The composite particles are still well recognizable, but completely incorporated into the plasma-polymerized PMMA matrix.

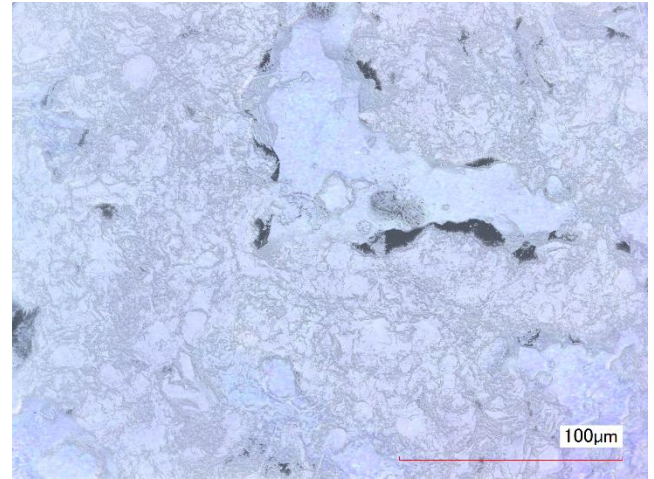


Fig. 3. CLSM image of plasma-polymerized, particle-filled MMA on a polypropylene substrate.

4 Conclusion

Liquid monomer films can be employed in plasma discharges to yielding up to $10 \mu\text{m}$ thick, clear, solid polymer coatings in only 15 min curing time. This is deposition rate is higher than for most PECVD processes and by far higher than for classic radical polymerization. Pure monomers get partially cross-linked, but can include fillers such as large particles which would not be possible via PECVD. This way, the benefits of PECVD and classic polymer chemistry can be easily combined into one single, versatile process.

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