Reactive layer functionalization of UV curable coatings

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Abstract

UV LED lamps are increasingly replacing mercury lamps. However, LED curable formulations for coatings often suffer from incomplete surface curing due to stronger oxygen inhibition. This intrinsic limitation is also a unique opportunity, since the incompletely cured top layer contains reactive groups, which can be the basis for surface functionalization.

Here, we present a new process called Reactive Layer Functionalization (ReLaFun). Compounds with a certain functionality are coated onto the reactive layer followed by UVC surface cure, resulting in tailored properties. The ReLaFun process requires minimal amounts of functional compounds, for which compatibility with the substrate is not necessary. As a proof of concept, surfaces were tailored to be hydrophilic and scratch resistant using ReLaFun.

1 Introduction

UV curable functional coatings are an interesting alternative to solvent-based lacquer coatings, because they can be cured within seconds requiring substantially less energy and time than the drying of solvents. Besides, they are free of volatile organic compounds and safer to work with. UV LED curing of functional coatings has recently become very attractive due to its even higher energy efficiency compared to conventional UV lamps, fast on-off times and long lifetime. While traditional mercury arc lamps emit around 70 % of the total power in the infrared and visible range and thus have relatively low output efficiencies, UV LEDs emit almost 100 % of their emission power in a tunable, very narrow wavelength range.

However, there is one major drawback associated with UV LED curing: powerful commercial UV LED lamps exist mainly in the UVA spectral range. Lower wavelength LEDs are extremely difficult to manufacture at reasonable power densities. Because of its long wavelength compared to other UV spectral ranges, UVA exhibits the highest penetration depth and is thus ideal for curing of thick coatings. For complete curing of the coating surface, a high dose of UV at the surface is necessary, though. This is especially important when curing in air, since oxygen atoms present abundantly in air readily quench radicals during UV curing[1]. While there are measures to mitigate oxygen inhibition such as adjusting the formulation[2] or increasing the irradiation dose, incomplete surface curing remains an unsolved issue in UV LED curing.

The incompletely cured layer still contains reactive groups, which can be used to generate a specific functionality on the surface in a second step. Importantly, it has been shown that a second curing step of an oxygen inhibited layer does not negatively affect its properties[3]. Instead of trying to prevent oxygen inhibition, such a layer can thus also be exploited for further surface functional modification. In oxygen inhibition lithography for instance, an incompletely cured inhibition layer is irradiated a second time through a mask to create patterned surfaces[4]. Others used the inhibited layer to swell the fully cured coating underneath and thus create a surface pattern[5]. Li et al produced superhydrophobic coatings without substrate pretreatment by taking advantage of the reactive group in the incompletely cured layer[6]. They spray-coated a superhydrophobic formulation onto an oxygen inhibited polyurethane acrylate. For the second curing step, they relied on UV initiated thiol-ene chemistry rather than (meth-)acrylate polymerization. None of these studies investigated the addition of a functional layer that is cured using UVC in a second step, though.

Here, we present a process termed “reactive layer functionalization (ReLaFun)” utilizing the reactive groups in the incompletely cured layer for surface functionalization. After applying and UV LED curing a base coat, a thin second layer with a desired functionality is added on top of the reactive layer and surface cured using a lamp with sufficient emission in the UVC range. The two layers are connected by covalent bonds leading to considerable benefits in terms of adhesion. Moreover, the choice of functional component is virtually unlimited as long as it contains UV curable groups. The functional group does not have to be compatible with the substrate. In addition, only very small amounts of functional component are required, which can be an economical benefit.

2 Experimental

For the base formulation, 47.5 wt% Genomer* 4297, 47.5 wt% PETiA and 5 wt% Genocure TPO-L (all Rahn, Switzerland) were mixed for 1 minute in a SpeedMixer^{TM} (Hauschild, Germany) at 1600 rpm. Substrates from cardboard (Carta Integra, Antalis, Switzerland), floatglass (Glas Trösch, Switzerland), polypropylene (BJ100 HP, Borealis, Austria) or polyvinylchloride (Amsler & Frey, Switzerland) were coated with base formulation at a thickness of 20 μm using a universal film applicator (ZUA2000, Zehntner, Switzerland) unless indicated otherwise. The samples were cured in either a UV LED nail lamp (Sun2C, SUNUV, China) for 60 seconds or in a laboratory scale UV curing setup with a 385 nm LED lamp (Hönle, Germany) at a UVA dose of 0.21 J/cm^2 in air resulting in a coating with an incompletely cured reactive layer.

The hydrophilic formulation was 90 wt% RCX 19-247, 5 wt% Genocure* TPO-L and 5 wt% Genocure* DMHA (all Rahn, Switzerland). The scratch resistant formulation was based on methacryl-POSS (MA0735, Hybrid Materials, US) with 5 wt% Genocure* TPO-L and 5 wt% Genocure* DMHA. 5 μm of either hydrophilic or scratch resistant formulation was coated onto the reactive layer using the same universal film applicator. Hydrophilic coatings were then cured for 60 s in the UV LED nail lamp followed by UVC (ET20-TS, sterilAir, Switzerland) curing at a UVC dose of 1.65 J/cm^2. Scratch resistant formulations were cured in an UVAcube2000 (Hönle, Germany) at a UVC dose of 3.1 J/cm^2.

Double bond conversion was measured by ATR Infrared Spectroscopy (Nicolet iS5 FTIR Spectrometer, Thermo Scientific, Switzerland) by following the unreacted acrylate specific C-H stretch peak at 809 cm^{-1} standardized to the carbonyl peak at 1723 cm^{-1}. The total amount of initially present unreacted acrylate groups were obtained from spectra of freshly prepared formulations.

Layer thicknesses were evaluated through weight measurements of samples with a defined size.

Hydrophilicity was assessed by static water contact angle measurements performed on a Krüss DSA100, Germany. To examine the antifogging behavior of hydrophilic coatings, they were placed over a beaker of boiling water and their fogging behavior recorded on video.

Scratch resistance was evaluated by scratching coated samples with steel wool (grade 0000) and 2 kg of weight 20 times and subsequent optical imaging.

3 Results and Discussion

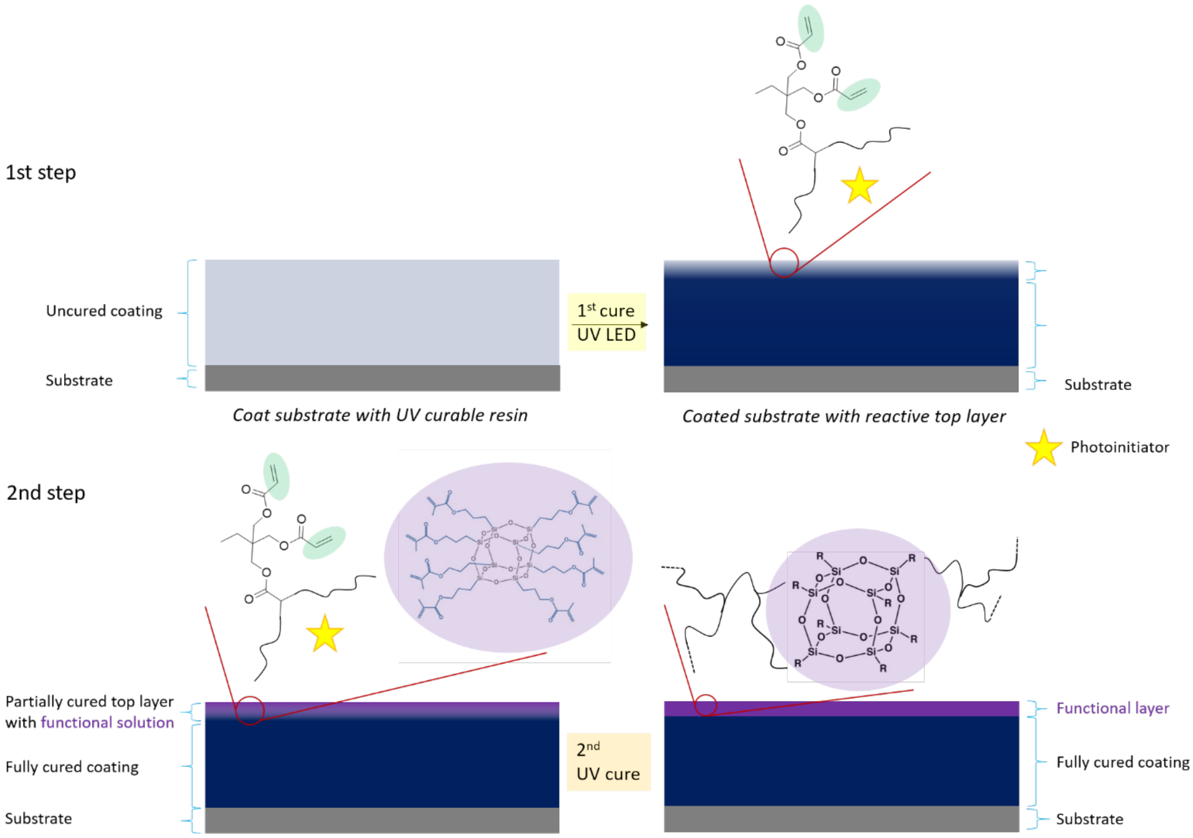

Figure 1: Schematic showing the ReLaFun process: In a first step, a substrate is coated with a base formulation, which is then cured under UV LED resulting in an incompletely cured top layer due to oxygen inhibition. In a second step, a functional ink is coated onto this reactive layer and fully cured under a UVC lamp leading to a surface with tailored properties.

In this work, a process termed reactive layer functionalization (ReLaFun) was developed (Figure 1). A substrate is coated with a base formulation, which adheres well to the chosen substrate. This base formulation is then UV LED cured under ambient conditions resulting in a tacky layer, which is not completely cured due to oxygen inhibition at the surface. In a second step, the tacky base layer is coated with a small amount of a functional formulation with the aim to deliberately modify the coating's surface properties. This functional layer is then fully cured using a lamp with sufficient intensity in the UVC range to allow for complete surface cure. This can be either a standard mercury lamp or a dedicated UVC lamp. Provided the right choice of base layer, ReLaFun coatings generally show good adhesion to a wide variety of substrates due to the spatial separation of functional surface coating and substrate and the covalent bonding between the base and the functional layer. Combinations of substrates and coating formulations that have so far been incompatible can finally be combined using ReLaFun. Also, the amount of functional formulation required to achieve the desired functionality is minimal. Finally, the coatings can be tailored to exhibit a wide range of functionalities with the only real limitation being that they are (meth-)acrylated.

Layers of base formulation cured in air under a UV LED lamp emitting in the UVA region often show incompletely cured surface layers due to oxygen inhibition. Here, curing conditions were chosen in order to promote the formation of such a layer.

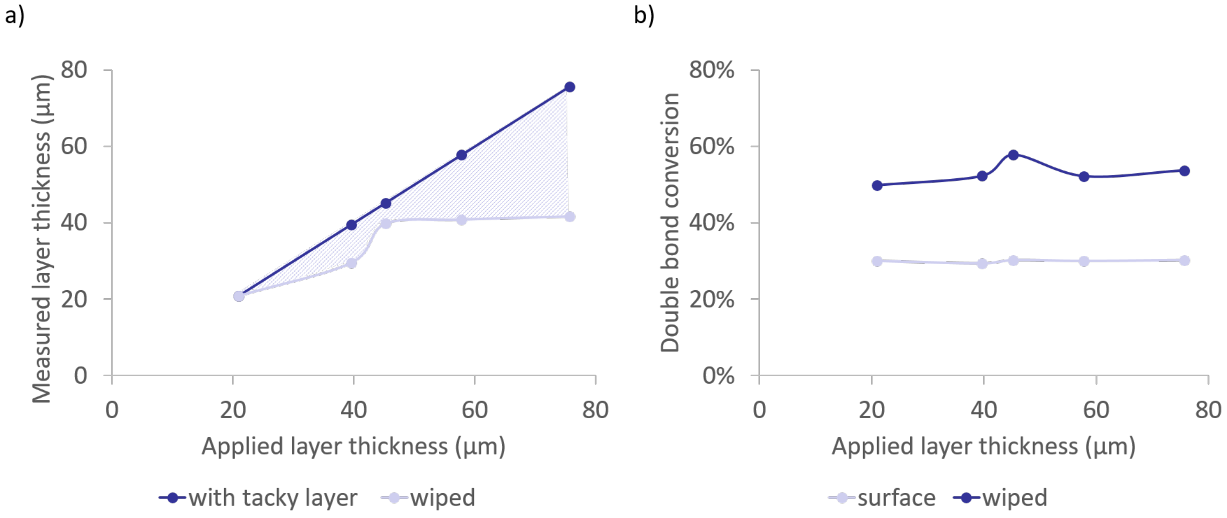

Figure 2: UV LED curing of base formulation. a) Measured layer thicknesses for UV LED (385 nm) cured layers applied at thicknesses of 20, 40, 60 and 80 µm including the tacky layer and when wiped with isopropanol to remove the tacky layer. The height of the shaded region between the curves corresponds to the tacky layer thickness at a given applied thickness. b) Double bond conversion measured by ATR IR spectroscopy of the incompletely cured surface layer and after wiping the sample with isopropanol to remove the incompletely cured layer.

Irradiation with both a laboratory scale 385 nm UV LED lamp run at belt speeds as high as 100 m/min or with a low-price UV LED nail lamp (365 and 395 nm) produces similar reactive layers. The thickness of the reactive, tacky layer depends on the applied layer thickness

(Figure 2a). While at a relatively low thickness of 20 µm the tacky layer is thinner than 1 µm, its thickness increases with applied layer thickness up to more than 30 µm for 80 µm total applied coating thickness. On the contrary, the methacrylate double bond conversion as a measure for degree of cure is not affected by the applied layer thickness under the given curing conditions (Figure 2b). The surface double bond conversion lies around 30 % regardless of coating thickness. Coatings that have been wiped with isopropanol to remove the incompletely cured layer show a bulk double bond conversion of approximately 50 % after UV LED curing. Having established how to reproducibly produce reactive layers with specific thicknesses, the second coating step involving the application of the functional layer was investigated.

To demonstrate the potential of the ReLaFun process, various substrates, including very hydrophobic polypropylene foils, were tailored to be hydrophilic using ReLaFun. In Figure 3a, the water contact angle of cardboard coated with hydrophilic ReLaFun is shown as a function of hydrophilic component concentration.

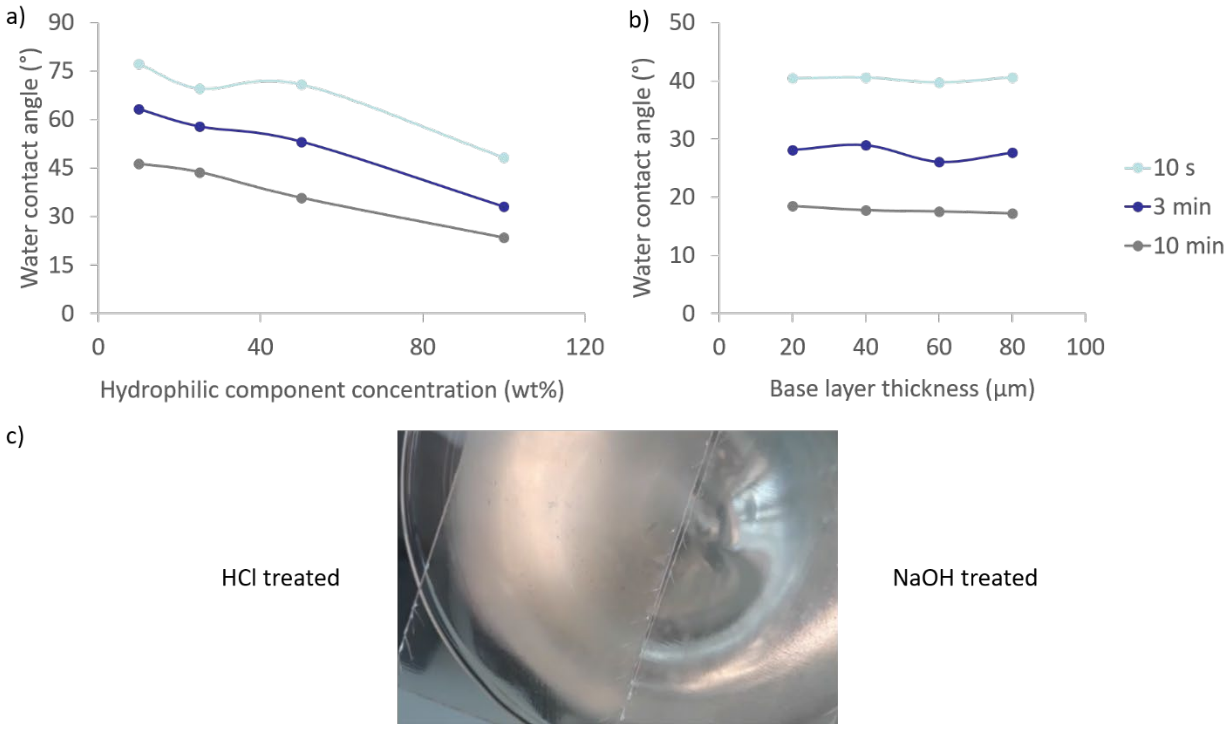

Figure 3: Hydrophilic ReLaFun. a) Time dependent water contact angle of hydrophilic ReLaFun coating at different functional ink concentrations in the functional layer. b) Time dependent water contact angle of hydrophilic ReLaFun coating with varying base layer thickness. c) Hydrophilic ReLaFun coated samples treated with HCl or NaOH placed over boiling water to observe antifogging behavior.

The chosen hydrophilic formulation, RCX 19-247, clearly shows time dependent water contact angles. To be able to compare the different formulations, water contact angles were measured 10 seconds, 3 and 10 minutes after deposition for all samples. While this decrease in contact angle with time was also observed when the hydrophilic formulation was mixed with base formulation at low concentrations, very hydrophilic coatings with contact angles below 30 ° were only achieved using a formulation containing exclusively hydrophilic components. In contrast to the concentration of hydrophilic components, the base layer thickness had no influence on the hydrophilicity of the ReLaFun coatings (Figure 3b). Since the hydrophilicity of a coating is determined by its outermost few nanometers, this was expected. Apart from offering the possibility to tune the coating's surface properties, the ReLaFun process also exhibits considerable advantages in terms of adhesion. Hydrophilic formulation directly coated onto PVC, a medium surface energy polymer substrate, tends to delaminate in humid conditions, whereas no delamination was observed for hydrophilic ReLaFun coatings on the same substrate. On even more hydrophobic substrates such as polypropylene, the hydrophilic formulation de-wets before curing. With ReLaFun, even such difficult substrates can be coated without pretreatment. Hydrophilic surfaces on hydrophobic parts are interesting in optical components because they can prevent fogging. To demonstrate antifogging behavior of our ReLaFun coatings, coated samples were placed over boiling water (Figure 3c). Freshly coated samples did not show good antifogging behavior, possibly due to the time dependence in water contact angle. However, after immersing the samples in 0.1 M NaOH, they became truly antifogging. The same samples immersed in acidic solution did not show the same effect. This indicates that the hydrophilicity of the studied hydrophilic formulation could be enhanced through pH adjustment of the formulation.

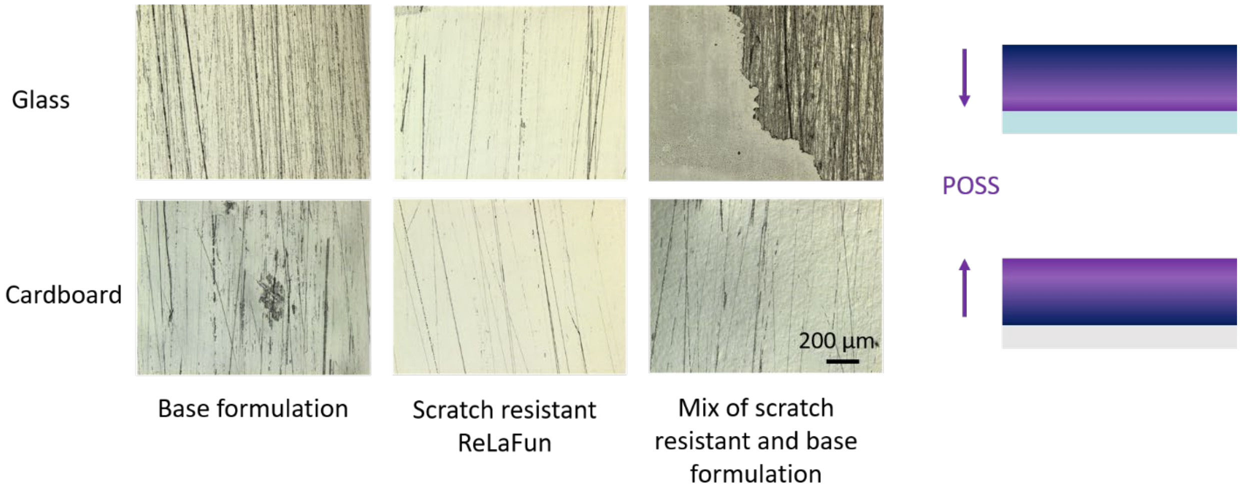

Figure 4: Scratch resistant ReLaFun on glass and cardboard substrates. Scratch tests performed on base formulation coatings, scratch resistant ReLaFun coatings and mixtures of base formulation and scratch resistant formulation coated on glass and cardboard. In the mixtures, POSS behaves differently on glass and cardboard, as explained in the cartoons.

As a second industrially relevant example, we demonstrate that highly scratch resistant coatings can be produced by ReLaFun. A methacrylated polyhedral oligomeric silsequioxane (POSS) was chosen as the scratch resistant functional component. Both on glass and on cardboard, POSS containing ReLaFun coatings are a lot more scratch resistant than the base formulation (Figure 4). Because POSS is hydrophobic in nature, it is expected to segregate to the surface when mixed into a coating resulting in similar surface chemistry to what is obtained by ReLaFun. Thus, another series of samples, where 50 wt% of POSS was mixed into the base formulation was produced and tested in 20 µm thick coatings for its scratch resistance. The substrate proved to influence the segregation behavior of POSS and therefore the scratch resistance of substrates coated with mixed formulations. On glass, POSS clearly impairs the adhesion of the base formulation to the substrate. Furthermore, the coating is heavily damaged by the scratching, indicating that POSS does not segregate to the surface. On paper, however, the addition of POSS improves the scratch resistance compared to the base formulation, which is assumed to be caused by the surface segregation of the POSS. Thus, whether ReLaFun offers benefits over just mixing a functional component into an existing formulation also depends on the substrate. Because POSS surface-segregates so strongly on cardboard, the minimum necessary POSS concentration for optimum scratch resistance was evaluated.

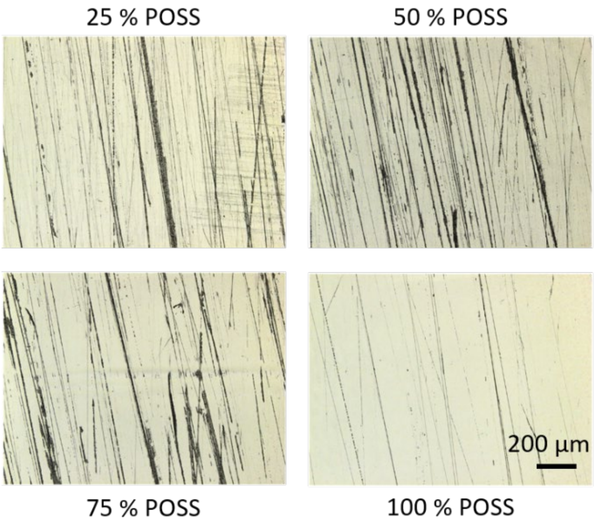

Figure 5: Influence of POSS concentration on scratch resistance of ReLaFun. POSS concentration was varied. Only coatings consisting of 100 % POSS methacrylate show good scratch resistance.

The POSS concentration in the functional formulation was varied between 25 and 100 % and the scratch resistance of the obtained coatings assessed (Figure 5). Similar to what was observed for the hydrophilic ReLaFun, a pure layer of the functional component (100%) is also required for optimal scratch resistance. Since only 5 µm thin layers were used for the functional layer coatings, the total amount of POSS in lower concentration mixes apparently was insufficient to reach high scratch resistance. The following ReLaFun experiments were hence all conducted with 100 % POSS methacrylate concentration.

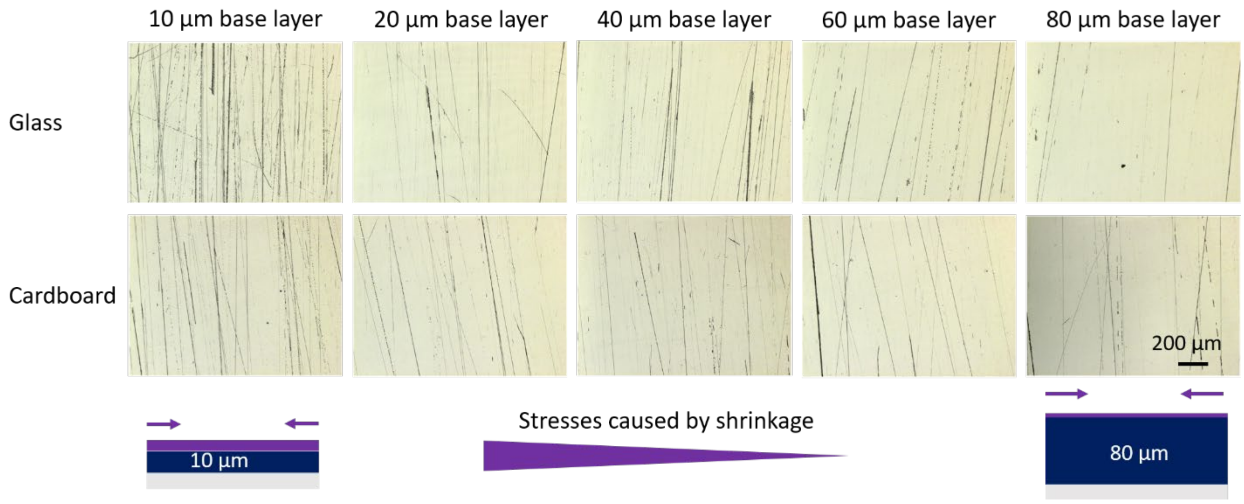

Figure 6: Influence of base layer thickness on scratch resistance of ReLaFun. Base layer thickness was varied while keeping the functional layer thickness constant. The increase in scratch resistance with higher base layer thickness can be explained by the stresses caused by the high curing shrinkage of the scratch resistant formulation leading to higher stresses in thinner base layers.

Scratch resistance not only depends on POSS concentration, but also on the base layer thickness (Figure 6). Lower base layer thicknesses are less scratch resistant than higher base layer thicknesses at the same functional layer thickness. This is true for both cardboard and glass, but more pronounced on glass. The reason for this decrease in scratch resistance is probably the high shrinkage of POSS methacrylate, the scratch resistant component, during curing leading to stresses within the top layer, which make it more prone to damage. Because cardboard is more flexible than glass, this decrease in scratch resistance is more pronounced on glass.

4 Conclusions

A process exploiting the oxygen inhibited layer of UV LED cured coatings was developed. Since this incompletely cured layer still contains reactive groups, a second layer coated on top can covalently bond to the base layer. While the base layer was tailored to achieve maximal adhesion to the substrate, the second layer was used to impart a specific functionality, such as scratch resistance or hydrophilicity, to the coating. Base layer thickness was observed to affect the thickness of the oxygen inhibited layer, but not its double bond conversion. Hydrophilic functionalization and even antifogging properties could be achieved by a 100 % concentrated hydrophilic formulation regardless of base layer thickness, because hydrophilicity is determined by the outermost few molecules of a coating only. On the contrary, when the functional layer was made from a 100 % scratch resistant formulation, the base layer thickness had a strong influence on the scratch resistance performance. The reasons are probably differences in cure shrinkage between the base layer and scratch resistant functional layer leading to pre-stresses, which vary in magnitude depending on base layer thickness. Similarly, the substrate material played a role in scratch resistance, but less so in hydrophilic functionalization, because the scratch resistant component showed a tendency to surface segregate. In summary, a versatile process with advantages in terms of adhesion, substrate compatibility and almost unlimited choice of functionality was developed.

Acknowledgement

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