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Free Radical UV-Curable Release Coatings Without Silicon Monomers Using Poly(methylhydrosiloxane) Co-Initiator

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To ensure easier removal of adhesive, backing materials can be coated with a release film. UV-curable release coatings based on acrylate or epoxy silicone oligomers represent an increasing proportion of release liners available on the market. In order to alleviate their current problems of recycling, metal contamination and initiator insolubility, we have developed a synthetic methodology able to reduce silicone content below 1 wt\%. Silicon monomer-free, our approach relies on a type II radical photoinitiator consisting of benzophenone and poly(methylhydrosiloxane) (PMHS, 1600 g/mol), a silicone derivative with the general structure O-Si(H)(CH\textsubscript{3}). The ability for PMHS to act as co-initiator in radical photopolymerization is revealed by real-time Fourier transform IR spectroscopy. Release properties are evaluated through a probe tack experiment using a commercial pressure sensitive adhesive. Using 1,6-hexanediol diacrylate as resin, release properties are achieved at 1 wt\% PMHS, and can be also maintained with poly(ethylene glycol) diacrylate, or tripropylene glycol diacrylate monomers. A ten times decrease in adhesion energy is observed when PMHS is used against a non-reactive silicone thanks to chemical bonding between co-initiator and polymer network.

Keywords: Coating, Pressure sensitive adhesive, Photopolymerization, UV irradiation

1. Introduction

The role of a release coating is to form a weak boundary layer between two substrates. The objective may be either a removal of interactions to impart non-fouling or non-adhesive properties, or more generally, a sufficient reduction of interactions to maintain adhesive strength at very low level [1]. This second property is sought after in release liners, which are a class of commercial products manufactured on a large scale. In a release liner, the release coating forms the topcoat, and acts as vehicle for an adhesive. Its function is to maintain the adhesive substrate until the point of application when it must peel away cleanly with little application of force. Pressure sensitive adhesives (PSA), adhesive tapes, diapers and feminine hygiene products are by far the most common examples of products containing release coatings [2]. Because release coatings are usually applied onto the surface of a thermally-sensitive substrate (i.e. paper or plastic), an increasing proportion of release surfaces are now produced by radiation curing [3]. Indeed, UV/EB curable coatings can be prepared at ambient temperature from solvent-free formulations, making them compliant with sensitive substrates but also with current and upcoming environmental legislations [4].

In industry, the vast majority of UV-curable release coatings are based on acrylate or epoxy silicone oligomers, i.e. exhibiting a poly(dimethylsiloxane) backbone (PDMS, [-O-Si(CH\textsubscript{3})\textsubscript{2}-]\textsubscript{n}, where \(n\) is the degree of polymerization) [5]. Although silicone technology has achieved today the desired level of release, mechanical and thermal properties, it raises a number of issues. Firstly, separating the release coating from the rest of the liner is challenging, making recycling expensive and currently unsustainable. Secondly, silicon oligomers pose problem of metal contamination, because they are
usually synthesized via Pt, Rh or Cr-catalyzed hydrosilylation reactions between SiH-functionalized PDMS and epoxide/acylate derivatives bearing vinyl groups [6]. The catalytic residues (between 100 - 300 ppm) can affect the appearance of the release liner or, even worse, cause migration problems when it comes to substrates for plastic packaging or fabrics. Thirdly, it is often difficult to find a suitable photoinitiator because of poor solubility in silicone monomers.

Despite these limitations, very few non-silicone release coatings were reported in both the academic and patent literature. Some recent examples include fluorinated polyurethane [7] or alkoxyallene resins [8,9], without knowing whether or not they gave rise to an industrial application or were marketed. This very limited number of results highlights the key role of silicone in the release properties, mainly for two reasons. Firstly, PDMS chains display a dimethyl surface to the air, leading to very low surface energies, thereby decreasing the reversible work of adhesion ($W_{ad}$). Secondly, the flexibility of PDMS chains enable to reduce the energy dissipation during the debonding process.

In this study, we propose a novel generation of UV-curable silicone-based release coatings in which the release properties are provided, no longer by silicone oligomers, but by a silicone co-initiator. The main advantage is a drastic reduction of silicone concentration from generally 50 - 90 wt% to 0.2 - 1 wt%. As a result, the above-mentioned problems of recycling, metal contamination and initiator insolubility can be mitigated or eliminated. Remarkably, we demonstrate that release properties can be preserved despite the substantial decrease of silicone content. As illustrated in Fig. 1, we used a type II radical photoinitiator containing a mixture of benzophenone as hydrogen acceptor, and PMHS or poly(methylhydrosiloxane) with the repeating unit -O-Si(H)(CH$_3$)- as hydrogen donor (DH). Like other aromatic ketones, benzophenone reacts from its first triplet state ($^3\pi$ , $^3\pi^*$ -state) with high quantum yield by abstracting hydrogen from the SiH groups of PMHS. The term “Type II” refers to the bimolecular reaction involving an electronically excited oxidant (‘BP$^3$), and a reductant (PMHS), called co-initiator. PMHS is a not a conventional co-initiator in contrast to tertiary amines such as ethyl aminobenzoate (EDB) used as reference in this study [10,11]. However, Lalevée et al. proved in 2009 that a number of hydridosilane species (containing SiH groups), including PMHS, could act as efficient co-initiator in the radical photopolymerization of acrylate monomers in combination with BP or thioxanthone derivatives [12]. Hydrophobicity of the resulting coating was assessed by water contact angle measurements, but the release properties were not investigated [13]. Currently, PMHS is widely used in organic chemistry as a mild and stable reducing agent easily transferring hydrides to metal centers, but its use as co-initiator was poorly exploited [14]. PMHS is inexpensive, easy to handle, and more environmentally friendly than silicone monomers because its synthesis does not require any hydrosilylation step.

![Initiation mechanism of type II radical photoinitiator including a hydrogen donor (PMHS = DH, oxidant) and acceptor (BP, reductant). PMHS was proposed as reductant instead of conventional tertiary amines or thiols. Generally, it is assumed that the radicals generated from the co-initiator (D* = Si*) trigger the polymerization, while ketyl radicals (-C(=O)(OH))- resulting from the oxidant react by disproportionation.](image)

**Fig. 1.** Initiation mechanism of type II radical photoinitiator including a hydrogen donor (PMHS = DH, oxidant) and acceptor (BP, reductant). PMHS was proposed as reductant instead of conventional tertiary amines or thiols. Generally, it is assumed that the radicals generated from the co-initiator (D* = Si*) trigger the polymerization, while ketyl radicals (-C(=O)(OH))- resulting from the oxidant react by disproportionation.

We report herein the synthesis and characterization of release coatings prepared with the type II radical photoinitiator BP/PMHS (1/1 wt%). 1,6-Hexanediol diacrylate (HDDA) was employed as a model non-silicone monomer for the preparation of the cross-linked release surface. The release properties were evaluated through a probe tack test using a commercial PSA. To emphasize the effect of PMHS, the adhesion properties were systematically compared with those of an analogous film prepared with the conventional photoinitiating mixture BP/EDB (1/1 wt%). The ability for PMHS to act as co-initiator was revealed by real-time Fourier transform IR spectroscopy (RT-FTIR). The last part discusses in detail the effects of different experimental parameters on adhesive properties, including monomer type, PMHS concentration, and the difference between PMHS and a non-reactive silicone.

**2. Experimental**

**2.1. Materials**

Poly(methylhydrosiloxane) trimethyl silylated (PMHS, 1400-1800 g/mol, 15-25 cps) and poly(dimethylsiloxane) trimethyl silylated (PDMS,
15-25 cps) were purchased from Gelest. Ethyl aminobenzoate (EDB), 1,6-hexanediol diacrylate (HDDA), poly(ethylene glycol) diacrylate (PEG200 diacrylate), tripropylene glycol diacrylate (TPGDA) were obtained from Sigma-Aldrich. The PSA film was prepared from a commercial acrylic latex (Encor® 4106, Arkema).

2.2. Film preparation

For probe tack test, two distinct surfaces were prepared: a UV-curable release coating and a PSA film. The release coating was deposited on the surface of a cylindrical aluminum probe with a diameter of 25 mm. For this, HDDA was mixed with 1 wt% of PMHS and 1 wt% of BP. In control experiments, PMHS was replaced by EDB. The films were deposited by spin coating to reach a thickness of approximately 10 µm, then cross-linked upon exposure to 5 passes under a UV conveyor system from Qurtech containing a H-bulb lamp (Fusion UV system). The belt speed of the conveyor was set at 10 m/min and the lamp intensity at 100 %. In these conditions, for each pass, the emitted light dose was 1.46 J/cm² [UVC (250–260 nm): 0.09 J/cm², UVB (280–320 nm): 0.42 J/cm², UVA (320–390 nm): 0.45 J/cm², and UVV (395–445 nm): 0.5 J/cm²]. The PSA film was prepared by depositing a small amount of waterborne dispersion (Encor® 4106) on a glass microscope slide and then doctor-blading it to form a film of uniform thickness. The thickness of the film was kept at approximately 70 µm. The sample was dried, first in air at room temperature, and then for 4 h at 70 °C.

2.3. Characterization

The probe tack tests were performed with a MCR302 rheometer (Anton Paar). In a typical measurement, a 25 mm diameter flat-ended cylindrical probe (D-PP25/AL/S07, Anton Paar) covered by the release coating (see previous section for details) came into contact with an adhesive film at a speed rate of 30 µm/s. The probe stayed in contact during 1 s at a pressure of 1 MPa. Then, it was slowly withdrawn at steady rate of 30 µm/s. During this second stage, the withdrawal force and the displacement were measured as function of time. More details about the measured data and exploitation are provided in the next section.

Acrylate conversion-time curves were obtained by RT-FTIR performed in transmission. For these measurements, the released surfaces were formed on an IR transparent BaF₂ pellet. In this case, the polymerizable formulation (see film preparation section for details) was exposed at room temperature to UV irradiation and also to an IR analytical beam. The films were irradiated by the polychromatic light of a mercury-xenon lamp (Hamamatsu, L8251, 200 W) coupled with a flexible light-guide, providing an irradiance of 580 mW/cm². The IR spectra were recorded throughout irradiation by a Bruker Vertex 70 spectrophotometer equipped with a MCT detector. The resolution of the infrared spectra was 4 cm⁻¹.

Contact angle measurements were carried out with a drop shape analyzer –Krus DSA 100 with the software Drop Shape Analysis. The drop volume was 0.2 µL, and it was deposited with a 0.50 mm diameter syringe.

3. Results and discussion

3.1. Release coatings prepared with type II BP/PMHS radical photoinitiator

3.1.1. Probe tack experiment

Using 1,6-hexanediol diacrylate (HDDA) as model monomer, two films were prepared by radical photopolymerization using a type II photoinitiator BP/co-initiator (1/1 wt% with respect to the monomer). The first one included PMHS as co-initiator, while EDB was used for control experiments. It clearly appears that both formulations were soluble, even that containing PMHS, thanks to the low amount of co-initiator used. Additionally, they yield tack-free films after UV irradiation under air (see experimental section for details), suggesting the efficiency of the BP/silane initiating system. The adhesion properties of a PSA on the two UV cross-linked coatings were assessed through probe tack experiments following the methodology established by Creton et al [15]. Probe tack tests are intended to be simulations of thumb or finger tack tests. Zosel showed that the probe tack test could be used to gain some information on quantitative evaluation of the performance of the adhesive [16]. Creton et al. showed subsequently that information about the mechanisms of debonding of the adhesive could be also obtained when coupling with a camera [15]. In a typical experiment depicted in Fig. 2, the release coating was prepared on a steel probe – a flat cylindrical punch giving a uniform stress field and strain rate – while a PSA film (derived from commercial acrylic latex) was deposited onto a glass slide. Firstly, the test involved bringing the probe into contact with the adhesive. Subsequently, the probe was withdrawn at a fixed displacement rate (v = 30 µm/s). During each experiment, the
force ($F$), the displacement of the probe and the time ($t$) were acquired simultaneously. Figure 2 also shows a conventional stress ($\sigma$) – strain ($\varepsilon$) curve with $\sigma = F/A$ (MPa) for tensile stress and $\varepsilon = \frac{\nu \times t}{e}$ for strain ($e$ is the film thickness of the PSA, and the contact area of the probe is assumed to be the cross-sectional area called $A$). For PSA, the stress–strain curve is usually characterized by an initial peak, and possibly an extended tail, the latter being caused by the formation of fibrils. The first part of the curve is the linear elastic domain [17]. The deformation then becomes non-linear, inhomogeneous and non-reversible, and the curve decreases slightly [15]. Figure 3 compares the stress-strain curves of films prepared with PMHS/BP (trace a) and EDB/BP (trace b) at similar concentration (1/1 wt%) as well as an experiment where the steel probe was not covered (trace c). Clearly, the traces were very different in the three cases, illustrating distinct debonding mechanisms. The film including PMHS (a) was characterized by a low maximum stress ($< 0.05$ MPa), a sharp linear decrease of the stress to zero after the maximum and a small maximum extension ($< 0.3\%$). Such profile is typical of release coatings. Replacing PMHS by EDB led to a dramatic change of profile. Typical of a fibrillar failure, the curve displayed a significant stress increase, then decrease to a plateau value, which then remained nearly constant until the stress decreased to zero. The extension was high driving a maximum deformation (at the break) $\varepsilon_{max}$ of $17\%$, this suggests very limited release properties. The adhesion energy this coating was $2.5$ higher than that of coating containing PMHS. For the experiment on rough aluminum (c), the maximum stress was high (0.2 MPa) but the extension remained low ($< 1\%$). In this last case, the stress decreased almost instantaneously to zero after the maximum, and no plateau was observed in contrast to trace b. Because no cross-linked polymer was in contact with the PSA film, the adhesive could be stretched with much lower resistance [17]. One can deduce from this first series of results that PMHS, even at relatively small concentration (1 wt% with respect to the resin), is able to impart some release properties to a UV-cured polyacrylate coating initially devoid of any hydrophobicity. To understand these results and evaluate the impact of the surface properties of the cross-linked polymer sample, the values of water contact angle of the different coatings were compared. For the sample prepared with 1 wt% EDB (b), a water contact angle of $73^\circ \pm 2^\circ$ was obtained while the aluminum surface exhibits a value of $47^\circ \pm 2^\circ$ (c). By contrast, the water contact was increased to $95^\circ \pm 2^\circ$ in presence of PMHS (a), which was ascribed to its ability chains to migrate at the air/film interface. Interestingly, similar profiles were obtained for probe tack tests performed with other PSA films (data not given).
3.1.2. Photopolymerization kinetics
The progress of acrylate polymerization throughout irradiation was monitored using RT-FTIR for the two previous photoinitiating systems: BP/EDB and BP/PMHS. As shown in the series of conversion-time curves of Fig. 4, we note the higher reactivity of PMHS compared to EDB under air conditions, leading in both instances to a complete conversion of reactive functions in less than 5 s. The difference was attributed to a lower sensitivity of PMHS-based system to atmospheric oxygen inhibition [12]. In a control experiment involving no co-initiator, a slow polymerization took place. Such result was ascribed to self-initiation of acrylate upon irradiation by the portion of short wavelengths (<300 nm) emitted by the medium-pressure Hg arc. Indeed, use of a filter to block this irradiation completely inhibited the polymerization (results not shown). Therefore, conclusive proof was provided that PMHS can act as an efficient co-initiator.

Fig. 4. Conversion-time curves for HDDA photopolymerization depending on the photoinitiating system: square (■, BP/PMHS 1/1 wt%), circle (●, BP/EDB 1/1 wt%), triangle (▲, BP 1 wt% and no co-initiator).

3.2. Influence of different parameters on release properties
3.2.1. Effect of PMHS concentration
Figure 5 shows the evolution of the stress-strain curves during a probe tack test depending on the PMHS concentration: 0.2, 0.5 and 1 wt%. In all instances, the measured maximum stress was almost constant (0.03 – 0.05 MPa) whatever PMHS content. Conversely, the maximum deformation increased slightly upon increasing resin content from 0.2 wt% to 0.6 wt%. Clearly, in this range of concentration, there was a change of surface properties which decreased the slope at which the decrease of the stress to zero occurred, leading to higher adhesion energy $W_{adh}$. However, no plateau stress was observed, suggesting that significant release properties can be achieved even at very low concentration in PMHS (0.2 wt%).

Fig. 5. Influence of PMHS concentration on stress-strain curves of HDDA-based released coating preparation with type II photoinitiator BP/PMHS (1/x wt% with x = 0.2, 0.5 and 1 wt%).

3.2.2. Effect of acrylate resin
Previous experiments employing HDDA as monomer showed PMHS as a key component to impart release properties. The next issue was to assess whether PMHS could confer similar properties when using other monomers and oligomers. To answer this question, a range of cross-linked films were prepared using the same BP/PMHS photoinitiating system (1/1 wt%) but from poly(ethylene glycol) (200) diacrylate (PEG200 diacrylate) and tripropylene glycol diacylate (TPGDA) instead of HDDA. Figure 6 shows again the results of strain-stress curves together with control experiments carried out using BP/EDB. For the hydrophilic PEG200 diacrylate resins, there were striking differences between PMHS- and EDB-based films. TPGDA being much less hydrophilic,

Fig. 6. Results of probe tack experiments of an acrylic PSA on UV-cured coatings prepared with PEG$_{200}$ diacrylate (circle) and TPGDA (square) using BP/co-initiator mixture (1/1 wt%). Full symbols when PMHS co-initiator was used vs empty symbols for EDB.
the difference of release properties between the two samples was less marked. PMHS contributed to reduce the deformation extension and the adhesion energy. We also confirmed that all acrylate resins could achieve complete conversions regardless of the resin used.

3.2.3. Comparison of PMHS with a non-reactive silicon resin

One advantage of PMHS is that H abstraction from SiH creates silyl radical able to add upon monomers, driving the formation of covalent bond between PMHS and polymer network (see Fig. 1). The interest of having a reactive silicone was assessed in Fig. 7 where the adhesive properties of a PMHS-based coating was compared with an equivalent film prepared with BP/EDB and a non-reactive PDMS. To ensure a meaningful comparison with PMHS, similar PDMS molecular weight (1600 g/mol) and end groups (trimethyl silylated) were chosen, and two concentrations were investigated (1 and 5 wt% with respect to HDDA). Remarkably, in all cases, PMHS showed better release properties even when PDMS had a concentration 5 times smaller. At 1 wt% in silicone, the adhesion energy of PMHS-coating was 10 times smaller than that including PDMS. Increasing the concentration of PMDS proved to be inadequate as insolubility problems arose for concentrations higher than 5 wt%.

4. Conclusion

UV-cured release coating without silicone monomers were reported by employing the type II radical photoinitiator benzophenone/poly(methylhydrosiloxane) where the hydridosilane oligomer behaves as hydrogen donor or co-initiator. Release properties were evidenced using probe tack tests for coatings prepared from a range of multifunctional acrylate monomer and oligomers, originally not possessing such properties. This method offers practical and promising solutions to industrial issues in the field of release coatings by decreasing the content in silicone to 1 wt%. However, these results remain preliminary, further investigations are required as regards other technical aspects such as thermal resistance, mechanical properties, and debonding mechanism.

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