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Clearcoats Based on Maleimide/Vinyl Ether Combinations - Investigations into Their Properties and Curing Behaviour

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Summary: UV curable maleimide/vinyl ether blends were discussed in literature during the last years. Results of basic research were published which mainly contained RTIR spectroscopy, differential photocalorimetry, and the mechanism of radical formation. Partially, these results indicated high reactivity and low sensitivity to oxygen inhibition. Therefore, UV curable clearcoats containing maleimides and vinyl ethers were formulated and UV cured in air atmosphere.In principle, it was possible to use equimolar maleimide/vinyl ether blends as photoinitiators for acrylates. However, their efficiency was inferior compared to commercial α cleavage photoinitiators. On the other hand, formulations based on certain maleimides and vinyl ether functional resins or/and reactive thinners could be cured without additional photoinitiators. The possibilities and limitations found are discussed.

1 Introduction

During the last years UV curable maleimide/vinyl ether blends (MI/VE) were an interesting new topic in the field of radiation curing. Possible mechanisms of radical formation based on H atom abstraction or electron transfer were discussed. Experimental investigations were presented which, e.g., presented results of RTIR spectroscopy and differential photocalorimetry. Partially, the results indicated high reactivity and low sensitivity to oxygen inhibition [1-10].

Two different pathways were proposed for the technical use of MI/VE systems:

i) The formulation of self-crosslinking coating vehicles containing MI and VE functionality which would not require external photoinitiators [2-4, 8, 10] and

ii) the use of MI/VE or other MI combinations as photoinitiators in acrylate formulations [3-5, 11, 12].

The goal of the study presented here was to check both possibilities with respect to curing behaviour and film properties. Thus, model formulations were prepared, applied on glass substrate, UV irradiated and tested.

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2 Experimental

Various MI derivatives were tested in the coating formulations. In this paper, the following compounds are mentioned:

- ADMI = bis-maleimide of versamin; liquid resin
- BMI = N-n-butyl maleinimide (Sigma-Aldrich)
- EMI = N-ethyl maleinimide (Sigma-Aldrich)
- tBMI = N-tert.-butyl maleinimide (Sigma-Aldrich)

Some other maleimides gave poor solubility in the coating formulations or other problems.

The maleimides were combined with vinyl ethers or VE blends, resp., in stoichiometric ratio (1:1). The general name “vinyl ether” is used here in spite of the fact that some of the compounds tested were other vinyl (or allyl) derivatives. The resins and reactive thinners considered in this paper were abbreviated as follows:

- BEDVE = butanedioic acid bis-4-[(ethenyloxy) butyl] ester
- BETVE = 1,2,4-benzentricarboxylic acid tris-[4-(ethenyloxy) butyl] ester
- CHVE = cyclohexane dimethanol divinyl ether
- DVE-2 = diethylene glycol divinyl ether
- DVE-3 = triethylene glycol divinyl ether
- HDDVE = hexane diol divinyl ether
- NVP = N-vinyl pyrrolidone
- PDVE = aromatic polyester divinyl ether resin
- PPVE = polyfunctional polyester vinyl ether resin
- UDVE = aliphatic urethane divinyl ether resin

The stoichiometric MI/VE mixtures were used either as self-crosslinking vehicles or as photoinitiators in acrylate formulations. The coating materials were hand-applied on glass (ca. 50 µm film thickness) and UV cured in air atmosphere. The following UV curing devices were used:

1. Beltron BE 20/III, two 80 W/cm electrode-powered radiators, first Ga-doped, second non-doped
2. Fusion LC 6/2, two 120 W/cm microwave-powered F300S units, first bulb Fe-doped (D bulb), second non-doped (H bulb).

The irradiation conditions considered in this paper are:

- one non-doped 80 W/cm Hg bulb, 5 m/min belt speed (abbreviation: 80/5)
- one non-doped 120 W/cm Hg bulb, 20 m/min belt speed (abbreviation: 120/20)

- all four radiators arranged in a series using both curing devices, belt speed 4 or 5 m/min in both curing units (abbreviation: all/4 or all/5)

The curing results were estimated by means of pendulum hardness (KÖNIG method) and scratch resistance (finger nail test). Furthermore, selected films were investigated by IR spectroscopy (ATR technique) and ERA (a radiometric method [13, 14]).

3 MI/VE photoinitiators in acrylate systems

Different commercial acrylate binder systems were used to investigate the photoinitiator efficiency of equimolar MI/VE blends. The example discussed here consisted of 70 % polyester acrylate oligomer and 30 % of an polyether acrylate reactive thinner with higher functionality (PPTTA). 97.5 weight parts of this mixture were completed with 2.5 parts of MI/VE to obtain UV curable clearcoats. Commercial α cleavage standard photoinitiators (i.e., HMPP, HCPK, and BDK) were used as reference.

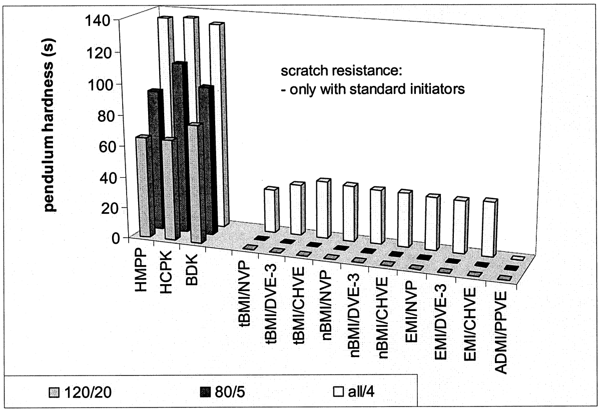


Figure 1. Curing results of polyester acrylate/polyether acrylate clearcoats (70:30) with 2.5 weight % of photoinitiator or MI/VE

As demonstrated in fig. 1 the MI/VE blends led to acrylate polymerization at very intense UV irradiation but they were not able to compete with the three standard initiators. Certain improvements were found after addition of tertiary amines, i.e. 3 % DMB (see fig. 2) or 5 % of a polyfunctional amine but the main conclusion was the same. This was also valid for higher photoinitiator or MI/VE concentrations (5 weight % photoinitiator, without and with 3-5 % amine).

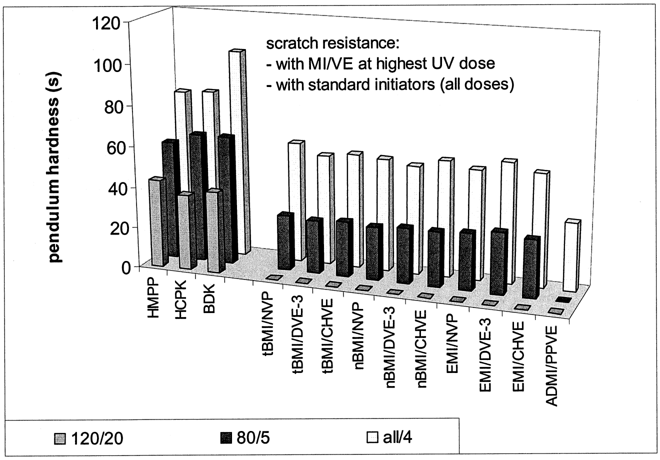


Figure 2. Curing results of polyester acrylate/polyether acrylate clearcoats (70:30) with 2.5 weight % of photoinitiator or MI/VE + 3 weight % DMB

Furthermore, other acrylate formulations containing an aromatic epoxy acrylate gave similar results.

4 MI/VE as binders and reactive thinners

4.1 Formulations with monofunctional maleimides

The following facts became clear during preliminary investigations on stoichiometric mixtures containing monofunctional MI components:

- EMI and BMI gave the highest curing efficiency.
- Many maleimides are solids and, hence, not all of them could be incorporated. Moreover, low-melting solids like EMI were incorporated at increased temperature but in some formulations they re-crystallized on storage.
- Neither a sole low-molecular mass vinyl ether (i.e., reactive thinner) nor an undiluted VE functional resin (PDVE, PPVE, or UDVE) gave optimum film properties in the combination with monofunctional MI.

  The achievement of lower viscosities and the incorporation of solid maleimides were additional reasons to blend the VE resins with VE reactive thinners.

Thus, the VE compounds were mixed in a weight ratio of 70 parts resin and 30 parts reactive thinner. The VE groups (sum of both vinyl ethers) and the MI amount gave a molar (stoichiometric) ratio 1:1. Fig. 3 shows that the curing results on glass, for a large part, were still in-sufficient. PDVE and PPVE (with varied reactive thinners) gave better results with respect to pendulum hardness compared to UDVE. PPVE, however, showed better scratch resistance than PDVE.

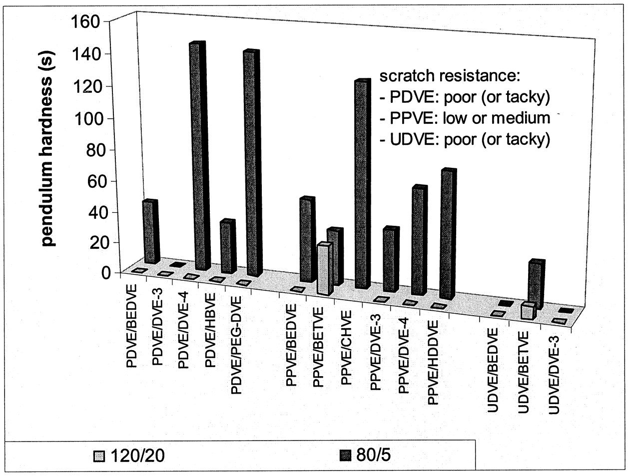


Figure 3. Curing results of stoichiometric mixtures of EMI with different blends of VE functional resins (70 parts by weight) and VE reactive thinners (30 parts by weight)

Fig. 4 demonstrates that improved hardness values (and good scratch resistance, too) could be obtained at an optimum content of the reactive thinner HDDVE. Similar results were also found using CHVE or DVE-3.

The addition of 5 % of a polyfunctional amine gave no significant improvement. In contrast, up to 5 % of additional liquid α cleavage initiator (HMPP) led to better hardness and scratch resistance (fig. 5). This was also supported by the crosslinking density investigated by ERA (fig. 6. Note: Lower M values indicate a higher crosslinking density [13, 14].).

Furthermore, within certain limits it was also possible to maintain sufficient curing properties at reduced MI amounts (fig. 7. The formulations considered here do not contain additional photoinitiators.).

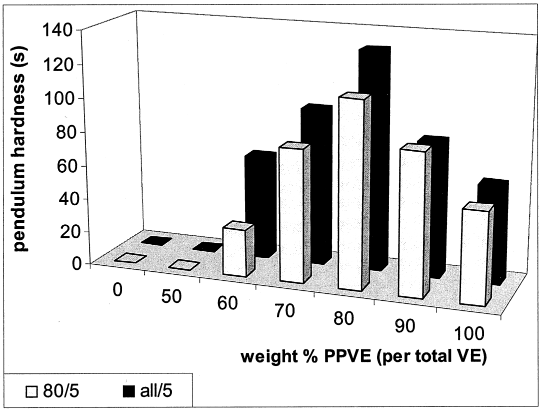
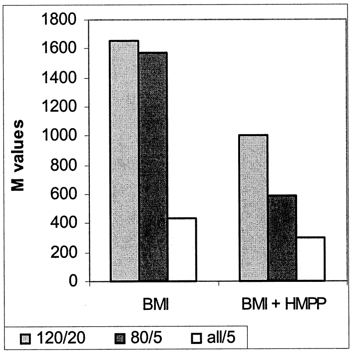


Figure 4. Pendulum hardness values of stoichiometric mixtures of EMI with varying blends of PPVE and HDDVE. The formulations do not contain additional photoinitiators.



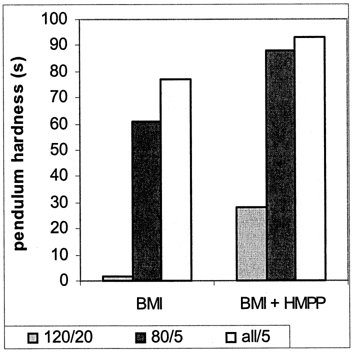


Figure 5. Figure 6.

Pendulum hardness (fig. 5) and M values (from ERA; fig. 6) obtained from a stoichiometric mixture of BMI with a VE blend (70 parts PPVE + 30 parts CHVE).
Formulation without and with 5 percent additional α cleavage initiator (HMPP).

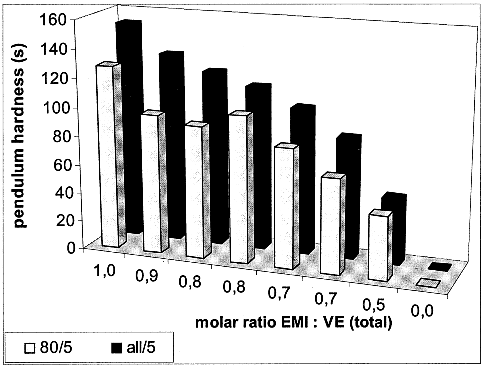


Figure 7. Pendulum hardness values of varying mixtures of EMI with a blend of PPVE (80 parts by weight) and HDDVE (20 parts by weight).

4.2 Formulations with ADMI

The higher-molecular bis-maleimide ADMI was combined with PPVE, PDVE and UDVE in stoichiometric ratio. Again, PPVE gave the best results with respect to scratch resistance after UV curing.

Fig. 8 shows that some combinations of PPVE with reactive thinners can give further improvements with respect to hardness. This is also supported by the results of IR/ATR spectroscopy (fig. 9) and ERA (fig. 10). Figs. 8-10 also demonstrate that the highest irradiation dose gives the most intense curing. However, the content of non-converted vinyl groups in the coating film could remain relatively high especially at the bottom side (fig. 9).

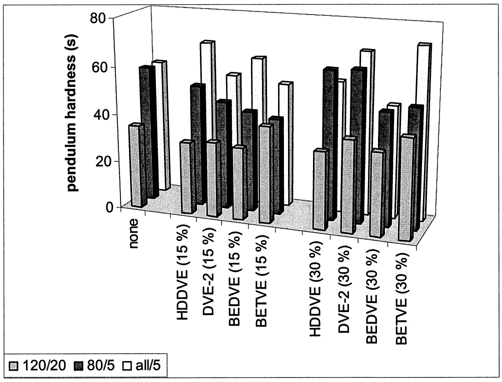


Figure 8. Pendulum hardness values of stoichiometric mixtures of ADMI with PPVE or with PPVE blends containing 15 % or 30 % of different VE reactive thinners.

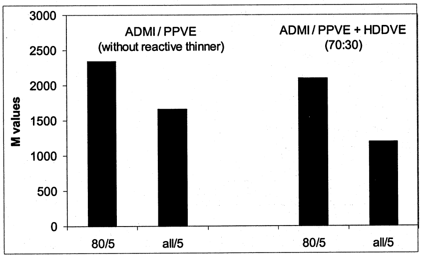


Figure 9.

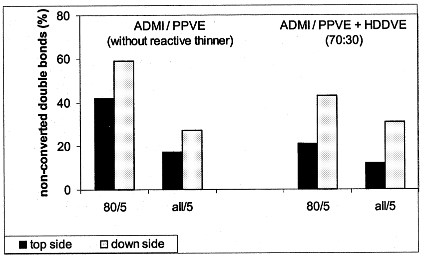


Figure 10.

Non-converted vinyl groups at the top and down sides (fig. 9, from IR absorbance at 1616 cm^{-1} related to 1710 cm^{-1}) and M values (from ERA; fig. 10) obtained from stoichiometric mixtures of ADMI with pure PPVE or with a blend of 70 % PPVE and 30 % HDDVE.

5 Summary

Maleimide/vinyl ether (MI/VE) combinations were tested with respect to their UV curing properties in air atmosphere. Their use as photoinitiators for acrylate systems was possible. Compared with commercial Norrish type I initiators, however, the reactivity proved to be poor.

In contrast, MI/VE binder systems could be cured without additional photoinitiators. For that purpose EMI, BMI, or the bifunctional ADMI could be used. Useful results were obtained especially in combinations with a polyfunctional vinyl ether modified polyester resin. Further improvements were found when this resin had been diluted with VE reactive thinners.

Furthermore, within certain limits it was also possible to use a VE excess instead of the stoichiometric ratio.

However, during the experiments some limitations became visible:

- After several days or weeks changes in the properties of MI/VE combinations (and sometimes gelation) can occur. Therefore, the curing tests had to be carried out within 24 hours after mixing MI and VE. But on the other hand, no inhibitor (like MEHQ etc. which is common for acrylate binders) was added here.
- The reactivity in air atmosphere seems to be limited. After curing with a belt speed of 10-20 m/min (one UV lamp) this became visible both from the mechanical properties (empirical check of scratch resistance and through curing) and from the conversion of vinyl double bonds at the film top and bottom sides (compare fig. 9).

- Sometimes, irritation effects were observed which, probably, were due to the MI components. This could be caused by liquid formulations as well as by incompletely cured films on the substrate.

  Such problems were more pronounced for low-molecular types like EMI or BMI.

Thus, an improvement of the properties of MI/VE binder systems would require aliphatic MI types with further increased reactivity, higher functionality or/and molecular mass and, thus, lower irritation.

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