Preparation and investigation of unsupported multilayer coating composites concerning their in-plane stress-strain and bending characteristics

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ABSTRACT

In many converting processes, the material behaviour of coated paper and especially of its coating layers is responsible for paper quality performance. Quality imperfections of printed products addressed in this paper are coating cracking and fold cracking which can lead to expensive claims.

This study presents the results of a new methodology for preparation and testing of unsupported multilayer coating films concerning in-plane stress and bending behaviour. By applying the new methodology, multilayer coating composites were prepared and tested concerning material properties like e.g. E-modulus, in-plane stress-strain characteristics and bending characteristics. The influence of the synthetic binder (latex)-starch ratio and pigment type on the strength properties of unsupported single coating layers and multilayer coating composites was investigated.

The in-plane stress-strain and bending stress measurements showed the embrittling or “hardening” effect of starch application on stress-strain curves (yielding behaviour) and bending behaviour of single and multilayer composites. Variation in pigment type at the equal latex-starch ratio had a comparably lower influence on stress-strain behaviour than the starch application; finer pigments with a steep particle size distribution led to a more ductile “softer” material behaviour at a lower level of maximum strength. The combination of fine pigments, low starch and high synthetic binder (latex) amount resulted in “soft” in-plane stress-strain behaviour at sufficient strength level and good bending stress development.

The behaviour of multilayer coating composites is determined by the behaviour of the more rigid single coating layer leading to a coating composite with high E-modulus and low yielding behaviour .Low E-modulus and high yielding behaviour of multilayer coating composites lead to a lower bending stresses, which should lead to a less critical fold cracking behaviour (CaF).

INTRODUCTION

Pigment coatings, especially multilayered coatings at high coat weights, have a decisive influence on the properties of paper and paperboard. In order to provide optimal performance of papers during printing and converting, the single coating layers are quite different in their composition. These differences are also strongly influencing the mechanical behaviour of the coating layer and therefore fold cracking during the folding procedure too.

For coated papers the base paper dominates the stress-strain behaviour of these papers. Since it is difficult to evaluate the contribution of the material properties of the coating layer on the stress-strain behaviour of the coated paper from measurements of the final coated paper [1], it is preferable to examine the coating layer material behaviour isolated from the base paper.

On coated papers, investigations concerning the effect of each single coating layer on the multilayered composite are difficult to perform due to factors like, e.g. coating colour penetration. According to *Joyce et al* [2] coating penetration has an influence on the viscoelastic material behaviour of paper. Depending on the immobilization solids of coating colour, papers absorb more or less water from the coating. Additionally to the paper thickness increase, frozen stresses caused by drying strains are released if sufficient coating water is present. The relationship between the decrease in bending stiffness of paper and increased coating penetration (e.g. due to lower solid content of the coating) could be shown by dynamic mechanical measurements.

Therefore it is preferable to perform measurements of coating material properties on single coating films under consideration of anisotropy caused by pigment types (e.g. kaolin). A preparation methodology for such unsupported single layer coating films was developed by *Prall* [3] and used by *Husband et al.* [4, 5] for studies regarding pigment volume and pigment shape influence on in-plane viscoelastic and strength properties. The preparation method of Prall offers a good basis to investigate in-plane stress-strain and bending behaviour of thin single coating layers. Generally, coatings show strong viscoelastic in-plane tensile behaviour in static mechanical measurements. The elongation decreases with increasing pigment volume concentration while the tensile strength increases. The maximum strength is reached at the critical pigment volume concentration [3] and the E-modulus (Young) increases rapidly around the critical pigment volume concentration. The pigment shape and size distribution influences the in-plane tensile strength, with a higher shape factor and larger particle size the in-plane strength increases. [4, 5]. An increased binder level leads to in-plane tensile strength and elongation increase, whereas above a critical binder level the increase in elongation is faster than below. According *Kan et al.* [6] and *Alam et al.* [7], the viscoelastic behaviour of coatings depends on the viscoelastic properties of binder and pigment and the volume fractions. They showed that the E-modulus decreases with increasing binder volume (after film forming) and correlates with the stiffness of the coating layer.

An alternative method for thin single coating layer material characterisation is microindentation. Due to material behaviour characterisation in thickness direction of the coating, the accuracy of the microindentation tests result depends on the coating material behaviour (influence of plasticity) and type of indenter. According *Barbier et al.* [8] accurate indenter results can be only ensured by isotropic and uniform coating microstructure. Hence, a material behaviour characterisation of multilayered coatings by micro indention does not seem practicable.

Additionally to the material behaviour of each single coating layer, its location and interaction within the multilayer composite have to be considered concerning converting behaviour as presented by *Alam et al* [9]. They showed that for double or triple layer coatings different concepts in coating composite design are required in order to achieve a decrease in fold cracking propensity at a desired level of bending stiffness.

Multiple coating layer composite studies based on the results of the measurements on single coating layers alone are insufficient to describe the in-plane stress-strain and bending characteristic of multiple coated papers, since the interaction between the single coating layers and the stress development within the multilayer coating composite by shear and lateral forces are not considered.

This study investigates the relationship between in-plane elasticity and in-plane yielding behaviour of single and multiple coating layers regarding bending stress development. It was assumed that besides the elastic material behaviour the yielding behaviour has a substantial influence on the fold cracking (CaF) propensity.

MATERIAL AND METHODS

The single layer coatings were prepared following the method of *Prall* [3] and *Husband et* al. [4, 5].The substrate was a polyethylene terephthalate film (Look, Roosting film, Terinex Ltd) as used by *Husband et* al. [4, 5]. After coating, the single coating layers were oven dried at 105°C for 5 min. The single coating, layers were produced by using of a 100µm wet film thickness wire-wound bar resulting in with a dry film thickness of 45-50µm

For multilayer preparation the first single coating layer was prepared in the same manner as described above. Before application of the second coating layer, the first coating layer had to be climatized for at least

6 hours. Typically, multilayer composite calipers of 100 µm were achieved based on two single coating layers with a thickness of 50 µm.

Coating formulations with varied latex-starch ratios (latex: PE 1831, T_g = 16, CIBA; starch: Dextrin A = Dextrin 7333, Cargill; pigment: HC 60, Omya) were prepared to obtain a sufficient range in coating layer material properties. The latex-starch ratios were varied by exchanging latex by starch (1:2) with constant pigment type. Additionally, one latex-starch ratio with different pigment sizes (HC 60 and CC 60) was tested (*Table 1)*. Two multilayer composites were produced; the first with varying latex-starch ratio, the second with different pigment types (*Table 2*).

Single layer based on Binder/starch ratio			
Sample	Binder [%]	Starch [%]	Pigment type
	Tg 16	*Dextrin A*	*Omya*
9,5 / 0,0	9,5	0,0	HC60
9,0 / 1,0	9	1,0	HC60
8,5 / 2,0	8,5	2,0	HC60
7,5 / 4,0	7,5	4,0	HC60
5,0 / 7,0	5	7,0	HC60
Single layer based on Pigment type			
	Tg 16	*Dextrin B*	*Omya*
8,5 / 2,0 HC60	8,5	2,0	HC60
8,5 / 2,0 CC60	8,5	2,0	CC60

Table 1. Coating formulations of single layer based on different latex - starch ratios and pigment types

Multilayer composite based on Binder/starch ratio of		
	Single layer A	*Single layer B*
(9,5/0,0 & 5,0/7,0)	9,5/0,0 HC60	5,0/7,0 HC60
Multilayer composite based on Pigment type of		
	Single layer A	*Single layer B*
(HC60 &CC60)	8,5/2,0 HC60	8,5/2,0 CC60

Table 2. Coating formulations of multilayer coating composites

For the variations of both influential parameters - latex-starch ratio and pigment type system – also commercial coatings were investigated. Three commercial coatings were chosen regarding pigment type and latex-starch ratio (*Table 3)*. Whereas coating C1 contained a pigment type mixture with more coarse than fine pigments, high starch and low latex amount, coating C2 contained more fine pigment with a steep particle size distribution than coarse pigment, low starch and high latex amount. Coating C3 contained 100% of a fine pigment with steep particle size distribution, high latex amount and contained no starch. The multilayer composites were produced of two commercial coating layers C1 + C3 and C2 + C3 (*Table 4*).

Single layer_Binder/starch ratio				
Sample	**Binder [%]**	**Starch [%]**	**Pigment type A**	**Pigment type B**
	Tg 16	*Dextrin A*	*coarse*	*fine*
C1	5	8,0	65%	35%
C2	8,5	2,0	15%	85%
C3	7,5	0	0	100%

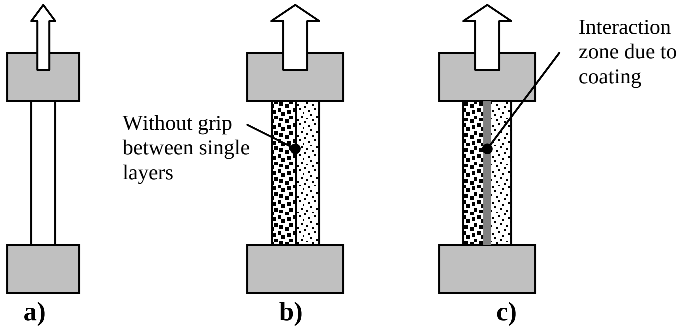
Table 3. Formulations of commercial single coatings

Multilayer composite based on commercial coatings		
	Single layer A	*Single layer B*
(C1 + C3)	C1	C3
(C2 + C3)	C2	C3

Table 4. Multilayer coatings of commercial single layers

The in-plane tensile and bending characteristic measurements were performed on a Zwick-Roell, ProLine TC-FR2.5N TN.009 testing machine to determine elastic modulus, bending force, maximum stress and elongation at break. The samples were cut into parallel strips of 25mm length and 15mm width and conditioned at 23°C and 50%RH for 12 hours. The results of in-plane stress-strain and bending measurements were based on mean values of 15 test samples.

In-plane tensile tests were done on unsupported single coating layers, two single coating layers together (without surface grip) and multilayer composites (*Figure 1 a, b, c*) with 10mm measurement length and 10 mm/min constant movement speed. The bending behaviour evaluation was performed on single coating layers and on multilayer coating composites where the composite layers are defined as shown in *Figure 2*.



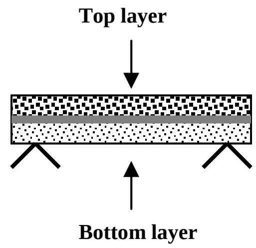


Figure 1. Types of in-plane tensile test samples
a) single coating layer
b) two single coating layers together
c) multilayer composite

Figure 2. Layer definition of multilayer composite at bending measurements

The bending characteristic determination was performed with a novel 3 point measurement methodology with 8 mm contact faces distance (l = 8mm). In contrast to the commonly used 2 point standard bending stiffness determination methodology, the caliper was considered in bending characteristic calculation.

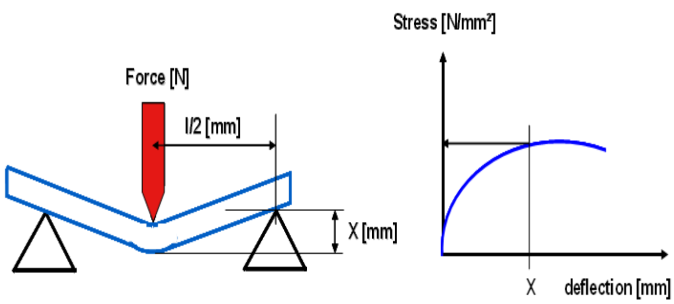


Figure 3. 3 point bending methodology and stress characteristic

Based on deflection force and coating caliper, the bending stress characteristic of outer fibre was calculated by *equation1*,

$$\sigma_b = \frac{M_b}{W_b};\qquad \text{(Eq 1)}$$

where σ_b = Bending stress [N/m²], M_b = Bending moment [Nm] and W_b = resisting torque[m³]

W_b is defined by equation 2 and M_b by equation 3

$$W_b = \frac{I}{e}\qquad \text{(Eq 2)}$$

$$M_b = F \times \frac{l}{2}\qquad \text{(Eq 3)}$$

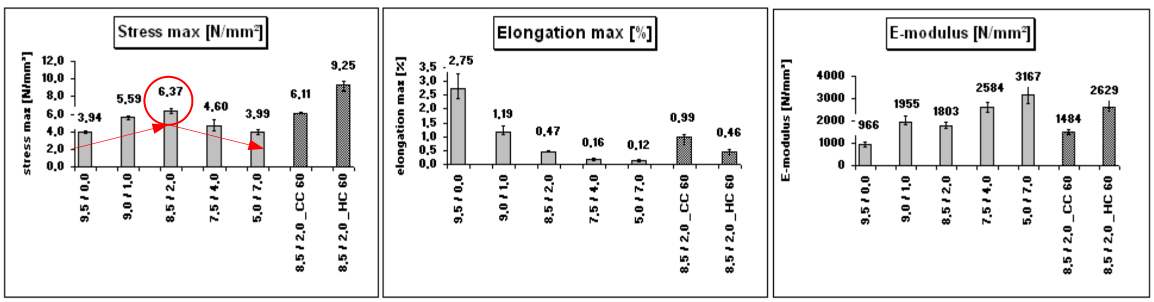
where I = geometrical moment of inertia [m*m³], e = distance of outer fibre from neutral line [m], F = bending force [N] and l/2 = distance of force contact [m]

RESULTS

The investigation was divided in three evaluation parts:

a) In-plane tensile and bending material behaviour determination of unsupported single coating layers
b) In-plane tensile stress-strain behaviour determination of unsupported multilayer coating composites
c) Bending characteristic determination of unsupported multilayer coating composites

<u>a) In-plane tensile and bending material behaviour determination of unsupported single coating layers</u>:
The single coating layer investigation showed the expected large effect of starch content on the material properties of the coating layers (*Figure 4a*). Replacing latex by starch resulted in an increase of strength up to 2% starch addition (+42% at 1% starch and +65% at 2% starch). It could be observed that below a specific binder amount optimum (8.5/2.0 latex/starch ratio), the decreases in strength due to latex reduction can not be compensated by higher starch amounts (*Figure 4 a*). The starch addition decreased the elongation potential dramatically (-55% at 1% starch and -80% at 2% starch, *Figure 4b*).

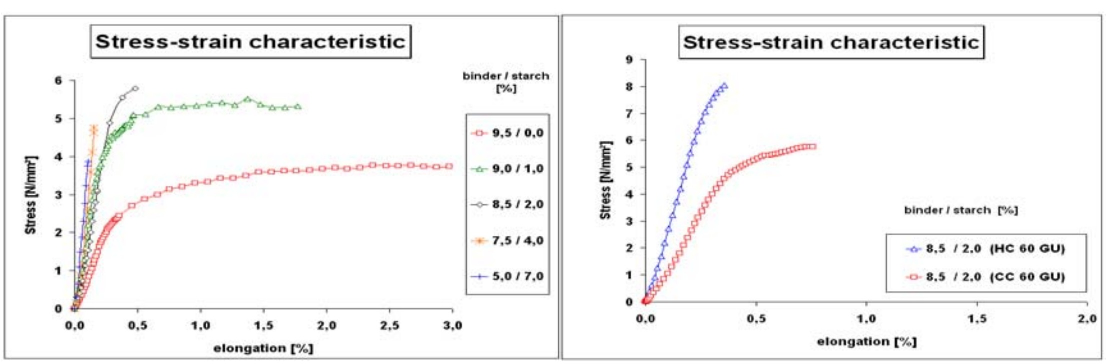


a) b) c)

Figure 4. a) Stress maximum, b) elongation at stress max and c) E-modulus of single coating layers based on latex-starch (Dextrin A) and pigment particle size (Dextrin B)

Finer pigments (CC 60) with steep particle size distribution (psd) showed a decrease in stress maximum (-28%), but an increase in maximum elongation (twice higher) compared to coarse pigments. Similar tendencies were presented by Husband et al [4, 5].
Based on the results of the latex-starch ratio and pigment size investigation, no correlation concerning elongation and stress maximum could be found. In contrast to that, a relationship of the E-modulus value with the elongation potential could be observed (*Figure 4 b, c*).

As shown in *Figures 4c and 5a,* latex replacement by starch made the coating layer more rigid and led to an increase in E-modulus and substantial change in stress-strain behaviour. While less deformation resistance and strong distinct yielding were obtained for the sample without or very low starch content, the exchange of latex by starch caused a substantial steeper slope of the stress-strain curve (*Figure 5 a*).

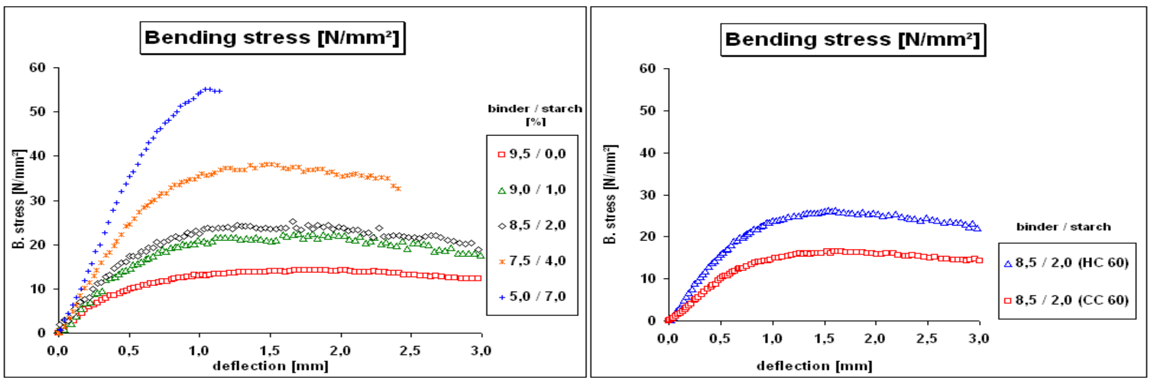


a) **b)**

Figure 5. Stress-strain characteristic caused by a) latex exchange and b) pigment type exchange of single coating layers basing on latex-starch ratio (Dextrin A) and pigment particle size (Dextrin B)

A similar effect was observed by exchanging of CC 60 by HC 60 (*Figure 5 b*). The coarser pigment with wide particle size distribution caused stiffer material behaviour and less yielding behaviour at equal latex-starch ratio than the finer steep pigment (CC 60).

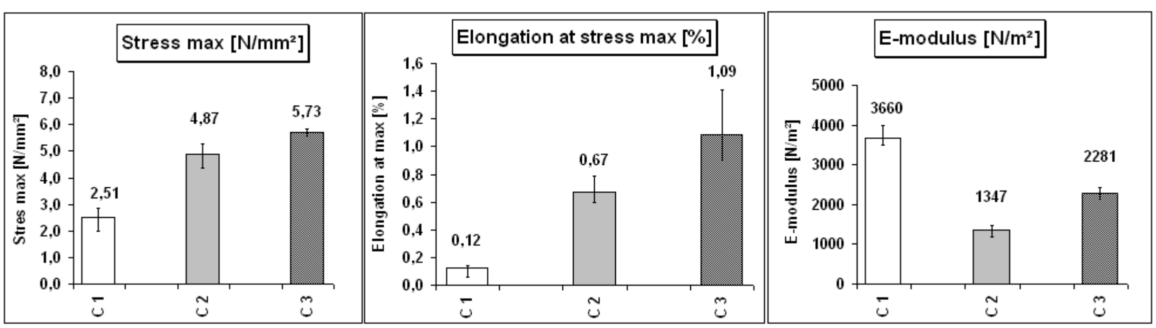
The effect of hardening by starch application and the influence of the pigment type could also be observed in the bending stress behaviour. Samples with low E-modulus and larger in-plane tensile yielding characteristic developed a significantly lower bending stress level (*Figure 6 a, b*). The rigid samples with latex-starch ratios of 7.5/4.0 and 5.0/7.0 developed very high bending stress level at small deflection and cracked before maximum deflection. The decrease in bending stress after the stress peak is an artefact caused by sliding of the samples due to exceeding of friction force balance.



a) **b)**

Figure 6. Stress-strain characteristic of single lab coating layers depending on a) latex-starch ratios and b) pigment type

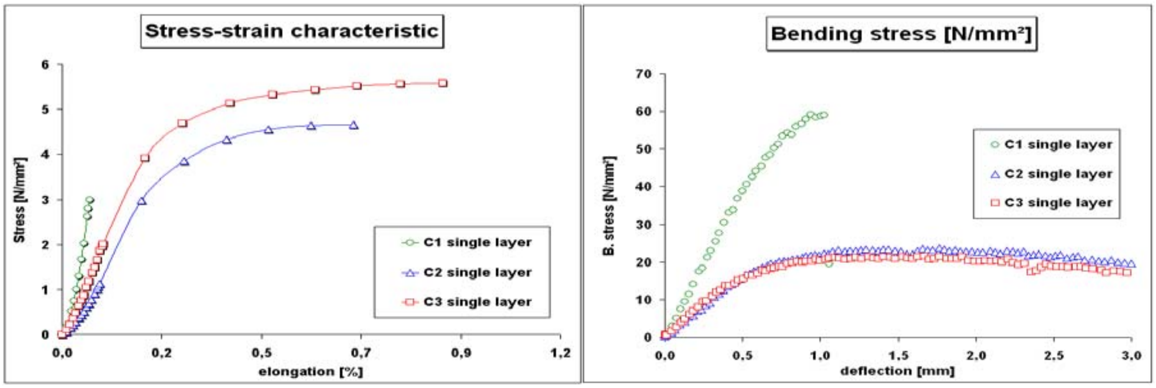
The commercial Coating C3 without starch, highest latex amount and finest pigment types exhibited the highest stress maximum and elongation at stress maximum level. Coating C1 and C2 showed equal tendency in strength and elongation properties as the lab coating films shown before. Low starch amount, high latex amount and fine, steeply distributed pigments (C2) caused higher stress maximum, larger elongation at stress maximum and lower E-modulus (*Figure 7 a, b, c*).



a) **b)** **c)**

Figure 7. a) Stress maximum b) elongation at stress maximum and c) E-modulus of single coating layers of commercial coatings

In *Figures 8 a) and b)* the relationship between stress-strain characteristic and bending stress characteristic of commercial coatings can be observed. Commercial coating C1 with lowest stress maximum, largest stiffness (highest E-modulus) and without yielding behavior in high strain regions developed highest bending stress level at small deflections (cracking before maximum deflection). Coating C2 and C3 showed less bending stress development (*Figure 8 b*) due to low E-modules and strong yielding behaviors in high strain regions.



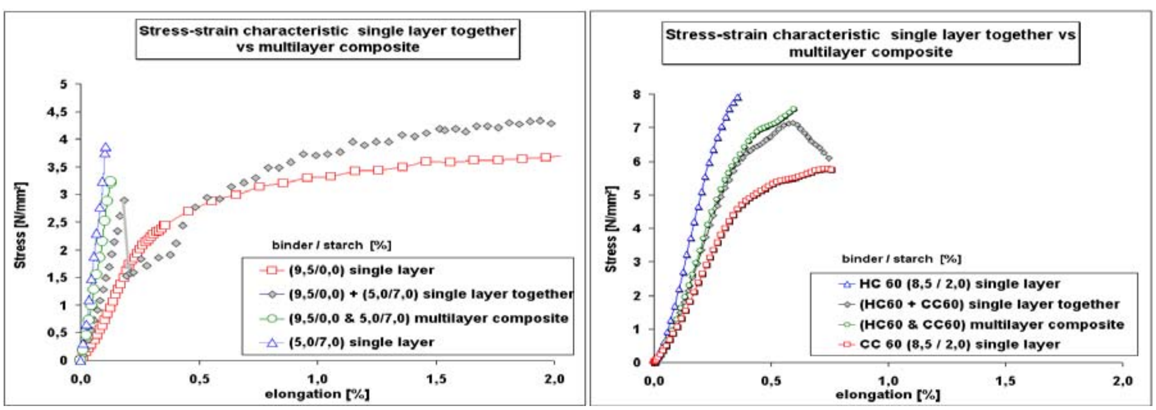
a) b)

Figure 8. a) Stress-strain characteristic and b) Bending stress of commercial single coating layers

Standard in-plane tensile measurements such as maximum stress, maximum elongation at break and E-modulus enable a sufficient analysis of coating layer material behaviour only in combination with in-plane stress–strain characteristic and bending characteristic evaluation. Especially the E-modulus and yielding behaviour give important informations concerning bending behaviour and CaF propensity.

b) <u>In-plane tensile stress-strain behaviour determination of unsupported multilayer coating composites</u>

The behaviour of multilayer composites was strongly determined by the stress-strain characteristics of the rigid layer (*Figure 9 a)*. Measured as single layer the rigid coating composite part (latex-starch ratio 5,0/7,0) showed a steep stress-strain characteristic without any yielding behaviour. Whereas the single layer of the soft (ductile) composite part (9,0/0,0) showed less deformation resistance and a strong yielding behaviour. Both composite parts exhibited similar maximum strengths.



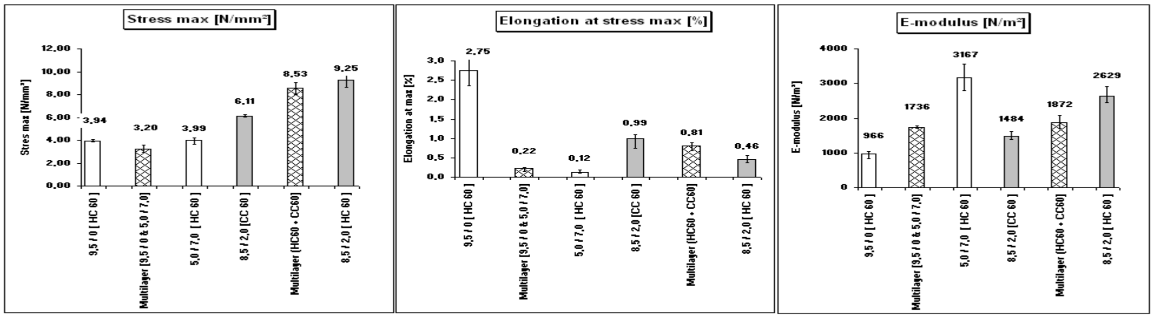
a) b)

Figure 9. In-plane stress-strain characteristics of single layer, single layer together and multilayer coating films based on a) latex-starch ratios and b) pigment type

Figure 9a and 9b show the insufficiency of the multilayer composite stress-strain characterisation by measurements of single layer coating and two single coating layers measured together.
When single coating layers with similar stress maximum (*Figure 9a*) were measured together, the high rigid coating layer cracked at low elongation (drop in the stress-strain curve), whereas the soft (ductile) single layer further developed the stress-strain characteristic.

The interaction of both stress-strain characteristics based on a multiple coating composite with force and strain transfer in the interface between the two layers caused a stress-strain behaviour and total cracking, determined mainly by the rigid composite part (9,0/0,0 & 5,0/7,0 multilayer).

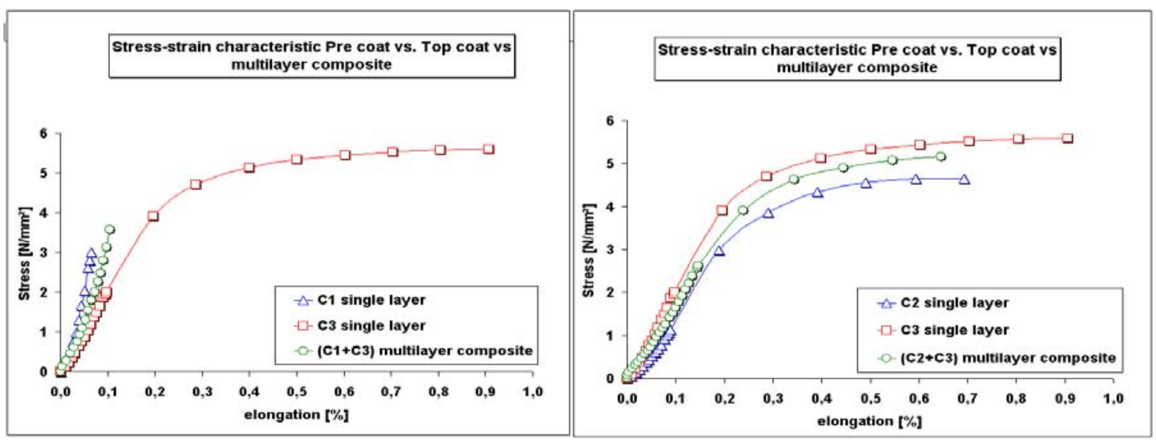
Figure 9b shows similar tendency of two single coating layers measured together by drop of stress-strain characteristic after cracking of the more rigid layer. The multilayer composite and single coating layers together showed an increase of total stress maximum due to higher stress maximum of one coating part.



a) **b)** **c)**

Figure 10. a) Stress maximum b) a) elongation at stress maximum and c) E-modulus of single coating layers and their multilayer composite of lab coatings

The E-modulus of the multilayer coating composites lay between the values of the single coating layers (*Figure 10 c*). The stress maximum of the multilayer coating composite of very rigid (latex-starch = 5.0/7.0) and very soft (latex-starch = 9.5/0.0) coating layers also showed - due to low single layer stress maxima - low stress maximum at a similar level for the multilayer composite (*Figure 10 a*). The elongation at stress maximum of this multilayer composite was substantially influenced by the very small elongation of the rigid, less deformable coating layer. This caused a small elongation at stress maximum, similar to the rigid single coating layer (*Figure 10 b*).
The coating composite based on different single coating film pigment types (HC60 versus CC60) showed less influence of the weaker/rigid coating layer part on elongation at stress maximum.



a) **b)**

Figure 11. In-plane stress-strain characteristics of single layers and multilayer coating films based on commercial coatings a) C1 and C3 and b) C2 and C3

The stress-strain characteristic results for the commercial multilayer coating composites (*Figure 11 a, b*) confirmed the observation of the multilayer lab coatings. The total in-plane stress-strain characteristic of the composites was determined by the rigid coating composite part. Less stress maximum without yielding behavior of one composite part could not be compensated by a composite part which exhibited high stress maximum and strong yielding behavior.
The strong dependence of stress maximum and elongations at stress maximum of the multilayer composite on the weaker/rigid coating layer (C1) part is also shown in *Figure 12 a*. Therefore, the disadvantage of a weaker/rigid coating layer on composite material strength can not be compensated by high strength and soft (ductile) material behaviour of the other composite layer.

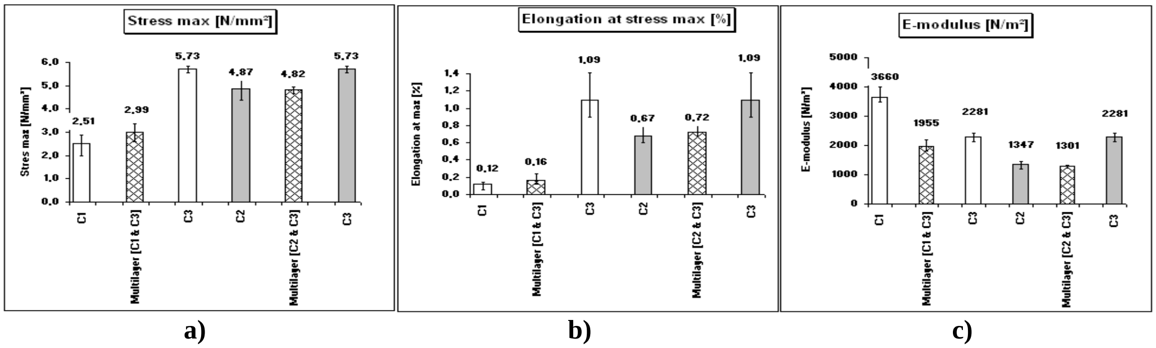


Figure 12. a) Stress maximum b) elongation at stress maximum and c) E-modulus of single coating layers and their multilayer composite of commercial coatings

c) __Bending characteristic determination of unsupported multilayer composites__

In spite of lower E-modulus compared to more rigid single composite component (*Figure 10 c and 12 c*), the bending characteristic of the multilayer composites showed a larger initial bending stress development than the single coating layers (*Figure 13 and 14*). The bending stress characteristic and cracking behaviour was also determined by the rigid composite part as the in-plane tensile characteristic. The decrease in elasticity and substantial decrease in yielding behaviour caused a cracking before maximum deflection (*Figure 13 a).*

Figure 13 b shows the influence of single coating layer location on the bending cracking behaviour. Due to top layer location of the less rigid and more deformable CC60 coating layer - refer to Figure 2 - a cracking of the composite layer before maximum deflection was caused. From mechanics it is known that the elongation on bending outside is always higher than on bending inside. The less deformable coating part achieves higher bending strain due to its location at bending outside, and less elongation at equal deflection causes cracking.

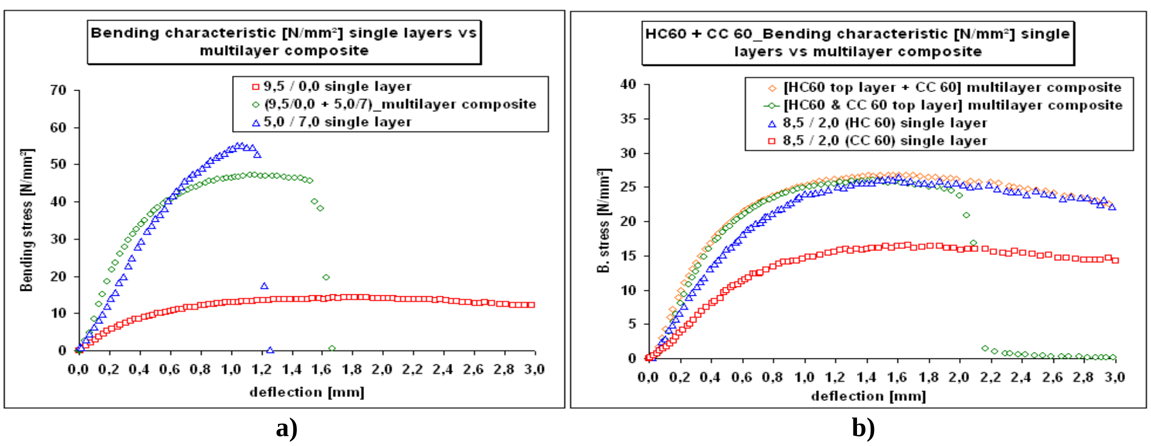
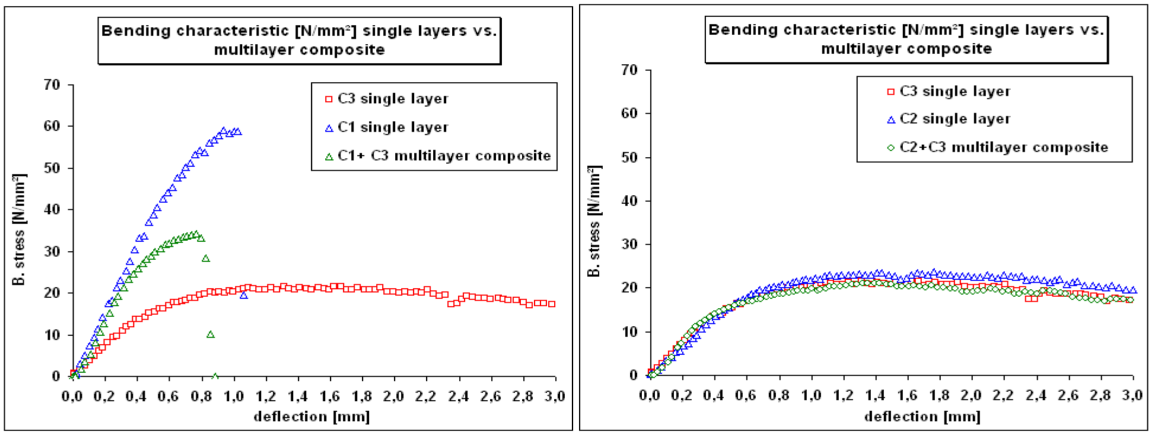


Figure 13. Bending characteristic of single coating layers and their multilayer composites depending on a) very rigid versus very soft behavior and b) pigment types

The commercial coating results showed similar bending material behavior of the coating composite layers. While the composite of C1 (rigid; no yielding behavior) and C3 (soft; strongly deformable) caused a very brittle bending characteristic (*Figure 14 a*) the composite of C2 (soft, medium deformable) and C3 caused additionally to high in-plane strength (*Figure 11 b*) soft (ductile) bending characteristic (*Figure 14 b*).



a) b)

Figure 14. Bending characteristic of commercial single coating layers and their multilayer composites depending on a) rigid/soft and b) soft/soft

CONCLUSION

Our work showed that synthetic binder (latex) replacement by starch has a substantial influence on the stress-strain characteristic and maximum stress-strain potential of unsupported single coating layers. Starch application causes "hardening" of the coating material properties and gives more stiff/rigid coating layers. Already low amounts of starch application caused substantial loss in yielding behaviour and decrease in elasticity. It was observed that a dramatical loss in strength and elongation potential took place with the used pigment system. Below a critical binder level which was 8.5% latex and 2% starch amount, no more latex can be replaced by starch without loss of strength and yielding behaviour.

Influence of pigment size and particle size distribution on unsupported single coating layers was less pronounced than that of starch application. Finer pigment with steep particle size distribution caused a softer material behaviour but less stress maximum potential. The E-modulus correlates well with the elongation at maximum stress.

The investigations of stress-strain characteristics showed that single coating layers are insufficient to describe the material behaviour of multilayer composites. Especially with large material behaviour differences between the composite layers the stress-strain characteristic determination has to be performed on multilayer composites. Whereas the E-modulus and stress-strain characteristic lay between those of the single coating layers parts, the stress and elongation maxima depend mainly on the properties of the weaker and rigid, more brittle composite part.
The yielding characteristic and elasticity (E-modulus) determine the bending behaviour of the coating layers. The bending characteristic and therefore the bending stress before cracking are strongly affected by the stress-strain characteristics differences within the multilayer composite. Soft single layer and soft modified multilayer coating composites with distinct yielding behaviour and accurate strength caused less bending stress development and reduced cracking of the coating layer.

This multilayer methodology enables investigations and modifications on double or triple coating layer composites concerning their in-plane stress-strain characteristics, bending behaviour and the resulting fold cracking propensity (CaF) which is affected by the single composite layers.

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