

# Properties of keratin particles as a functional filler

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## Introduction

Fillers are present in high proportions in many coating systems. Above all, they contribute to mechanical stability and – because of their low price compared to binders – to cost savings. Therefore, mineral particles (e.g. CaCO<sub>3</sub>, BaSO<sub>4</sub>) are used as fillers. However, bio-based particles would also be conceivable as an alternative if they have sufficient stability and a low price. For example, keratin particles could be used. These can be produced cost-effectively from chicken feathers that are discarded in large quantities in slaughterhouses – 20,000 t annually in Germany alone. In contrast to mineral particles, keratin particles exhibit a rather low density. Another advantage is that their peptide surface functionalities – primarily as nucleophiles – can interact with the binder/hardener combination or other functional components such as corrosion inhibitors or UV absorbers, which could contribute to an improved coating performance.

## Preparation of keratin particles

The starting point was chicken feathers that have been obtained directly from the slaughterhouse. After pre-cleaning, this rough material was deep-frozen for transport and carefully separated from animal residues before washing in a household washing machine (60 °C, 129 min, addition of 15 g of non-ionic surfactant Triton X-100). After rinsing and drying (75 °C, 12 h), noticeably lightened feathers with the purity acceptable for the further processing were obtained.

Subsequently, various attempts were made to convert these cleaned feathers mechanically, mechano-chemically or chemo-mechanically into largely spherical keratin particles with sizes enabling their usage as filler particles in coatings.

As an example, the mechanical keratin particle preparation using a “PULVERISETTE 6 classic line” grinding system (Fritsch GmbH) is described below. This planetary ball mill was used with a 250 ml grinding bowl made of zirconium dioxide (ZrO<sub>2</sub>) and grinding balls of the same material (Fig. 1, left). Two sizes of grinding balls were used: 15 mm diameter for initial dry grinding and 5 mm diameter for thorough fine grinding. A high energy input at a rotation speed of up to 650 rpm enables rapid and uniform comminution of feather keratin particles both through collisions of balls with one another and of balls with the grinding bowl wall as well as through attrition as a result of high shear in the grinding bowl zones near the wall. In the first stage of the grinding process with the “PULVERISETTE 6 classic line” device, 45 ZrO<sub>2</sub> balls with a diameter of 15 mm were placed in the 250 ml grinding jar. The subsequent addition of approx. 10 g of feather keratin particles after pretreatment with a centrifugal mill (Retsch ZM-200 with ring sieve 0.08 mm) resulted in an almost completely filled grinding bowl. Dry grinding was started under the following conditions: One cycle consisted of: (i) 59 sec grinding phase (500 rpm) with inversion of the rotation direction; (ii) break of 3 min. After about 20 of these cycles, the grinding bowl was additionally filled with the further amount of particles performed in the centrifugal mill, so that finally a total amount of 33.1 g particles was obtained.

For fine grinding, these particles were then subjected to wet grinding (Fig. 2, left). For this purpose, the 15 mm grinding balls were replaced by 1200 5 mm grinding balls and 88.5 ml isopropanol were added to the mixture in the grinding bowl after the drying process. The resulting mixture was ground under the same milling conditions as above.



Figure 1. Planetary ball mill „PULVERISETTE 6 classic line“ (left); loading of its grinding bowl with feather particles after centrifugal mill treatment and dry milling using 15 mm grinding balls (right)

The total active grinding time for wet grinding was 159 minutes 20 seconds, with a three-minute break between grinding cycles. The results of the fine grinding of feathers with the “PULVERISETTE 6 classic line” planetary monomill are shown on the particle size distribution diagram in Fig. 2.

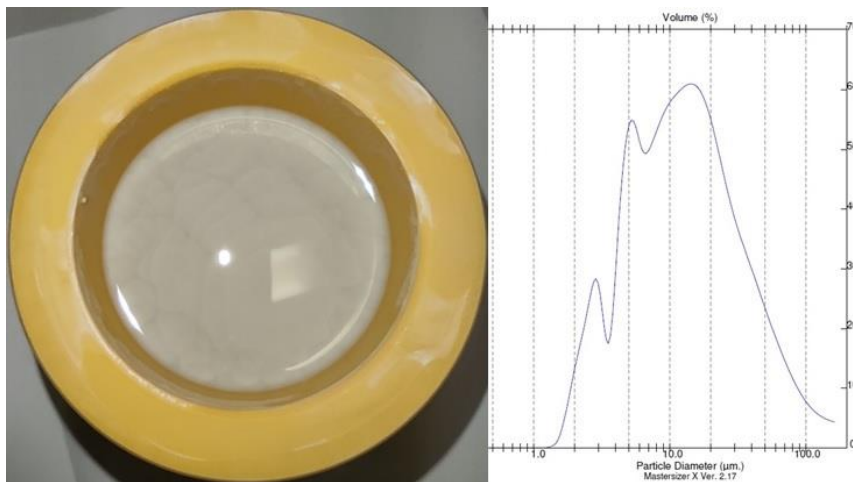


Figure 2. Mixture of dry-milled feather particles and iso-propanol before starting the wet grinding using the “PULVERISETTE 6 classic line” device (left) and the particle size distribution of the resulting dispersion (right)

BET isotherm characteristics indicated a significantly increased specific particle surface area compared to light diffraction experiments. This supports the assumption that the particle size distribution obtained (Fig. 2, right) is largely determined by agglomerates. The agglomeration can be explained by the increased influence of the electrostatic charge, because the surface plays an increasingly larger role in the particles’ interaction as they become smaller and smaller. As a result, the keratin particles attract each other electrostatically. From this and from microscopic images, primary particle sizes in the small single-digit micrometer range and below can be derived.

This process enabled a significantly higher throughput (> 30 g of product per process) and was advantageous over alternatively tested processes in that only a load of maximum 1.5 g in a single cycle was possible and a continuous cooling with the liquid nitrogen was necessary.

### Interaction of keratin particles with the coating matrix

In principle, the peptide nucleophilic S/N moieties of keratin – similar to the hardener – can interact directly with epoxy binders. Therefore, there are at least two preparative ways of replacing the filler by keratin particles (K) in a 2-Pack (epoxy/amine) formulation (2PF, cf. Table 1), which could cause different crosslinking (EP: “epoxy” part of the formulation, AM: “amine” part of the formulation):

1. Disperse K into EP, then add AM (usual for filler component)
2. Disperse K into AM, then add EP

For eggshell powder - which like K has nucleophilic groups on the surface - additions of 0.1-0.3 wt% based on the epoxy component are sufficient to achieve a significant increase of hardness and barrier effect in the resulting matrix [1]. Based on this, water was proportionally replaced in 2PF by a 3.33 wt% dispersion until the keratin particles had reached concentrations between 0.15 wt% and 0.60 wt%. In this way, a value was obtained once within and once above the concentration range mentioned above. In total, five 2PF formulation variants were created to determine the effects, with the sample named K401 being identical to 2PF and used as a reference:

- K401a: 0.15 wt% K in epoxy, then in amine
- K401b: 0.60 wt% K in epoxy, then in amine
- K401: Part I, then Part II (standard 2PF)
- K401c: 0.15 wt% K in amine, then in epoxy
- K401d: 0.60 wt% K in amine, then in epoxy

The two cases that can be distinguished in terms of reaction mechanisms are sketched in Fig. 3.

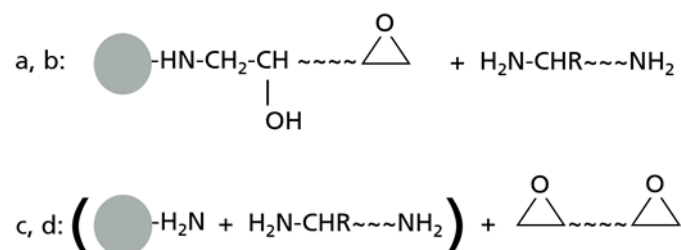


Figure 3. Reaction mechanistically distinguishable cases after substitution of the filler by keratin particles (gray circles) in 2PF

After 300 μm squeegee application on Al substrate and conditioning for 7 days, the resulting coatings were overlaid with a 5 wt% NaCl solution and detected using EIS after 5 min und 3.5 h. The Nyquist plots of the EIS data obtained are shown in Figure 4.

After five minutes of electrolyte exposure, the “reference” K401 has the highest barrier; Apparently, the system with the most homogeneous matrix dominates in this phase, i.e. the one that offers the electrolyte the fewest diffusion paths along the particles. However, the sequence of the remaining four samples cannot be interpreted well in the initial phase.

After 3.5 hours of exposure, the types with the initially strongest barrier (K401, K401b) show the lowest barrier stability. Conversely, the two “K in amine” systems K401d (weakest after 5 min) and K401c now have the largest barrier.

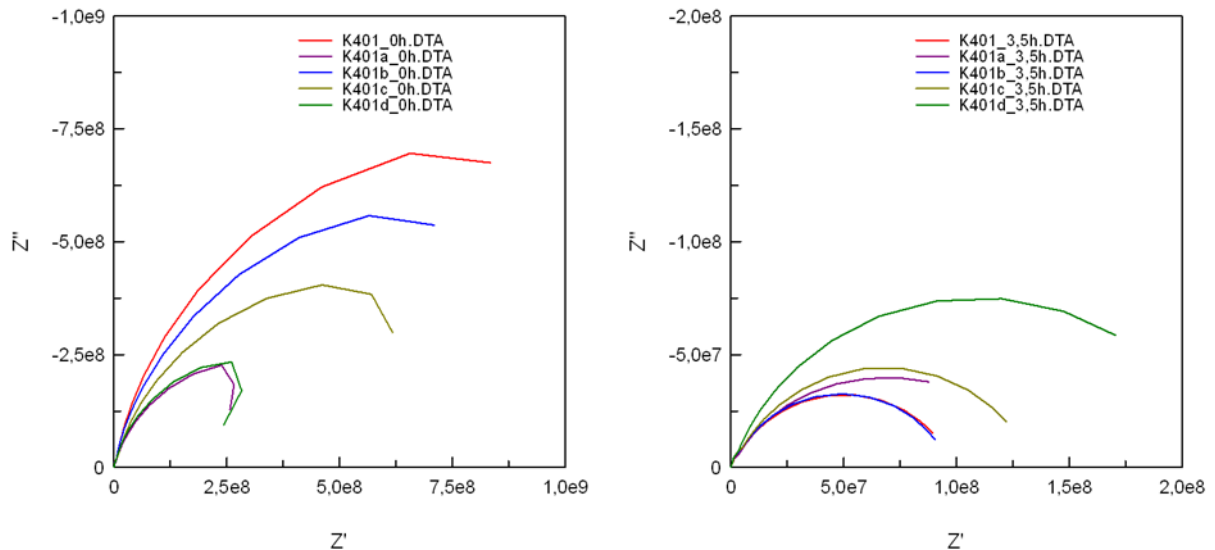


Figure 4. EIS data of the K401 coatings immediately after the start of electrolyte coating (left) and 3.5 h later (right).

These findings could be explained as follows: The high K content in K401d leads to more diffusion paths. However, the structure created in this way could have caused the matrix to swell more than in the other systems. The curing behavior of the samples may provide further information about the specific structure formation:

1. *Curing rate immediately after application (visually and haptically, i.e. determined qualitatively):*

- $c \approx d > \text{standard} > b > a$
- Lower hardening rate of a, b: Epoxy is “immobilized”, no longer migrating freely through amine in the volume
- c, d (initially) tend to remain somewhat softer than K401 despite the presence of polycrosslinking points, because part of the epoxy is more likely to multiply crosslink with K.

2. *(Martens) hardness determination during the hardening or post-hardening phase:*

Fig. 5 shows the results of (Martens) hardness determinations ten and 30 days after application of the films.

This results in the following findings (cf. Fig. 3):

- While a, b had the lowest curing speed immediately after application, the greatest hardness is finally achieved for these, perhaps because K acts particularly prominently as a “polycrosslinking point” due to the kinetics.
- However, it is possible that “too much” K was added in b compared to a, so that the “side reaction” of a double or multiple reaction of the epoxy components with the same K compromises the curing somewhat.
- c, d tend to remain somewhat softer than K401 despite the presence of polycrosslinking points, perhaps because some of the epoxy components are more likely to be multicrosslinked with K.

- Regarding d: Since the epoxy component is “immobilized” at K and d contains more K than c, d could initially remain softer than c. In the second curing phase, however, the formation of more polycrosslinking points could have a positive effect on the hardness, so that d shows the greatest increase in hardness in this phase.
- a and d are opposite in the following respect:
  - d shows the lowest hardness after 10 days, a the largest; however, the post-curing of d is very high up to 30 days, that of the standard is the lowest → without K the curing occurs earlier in the final state.
  - Curing rate immediately after application:  $c \approx d > \text{Standard} > b > a$  → highest initial dynamics when the epoxy component meets the combination of amine component and high K concentration.
  - Both initially have an almost identical, significantly worse barrier than the standard; however, after 3.5 h only d can form a clearly better barrier than the standard → possibly this creates a highly swellable system with a balanced ratio of K network points and epoxy/amine matrix; an optimization option could therefore lie in increasing the proportion of epoxy components (compensation for “epoxy loss” through K surface consumption)

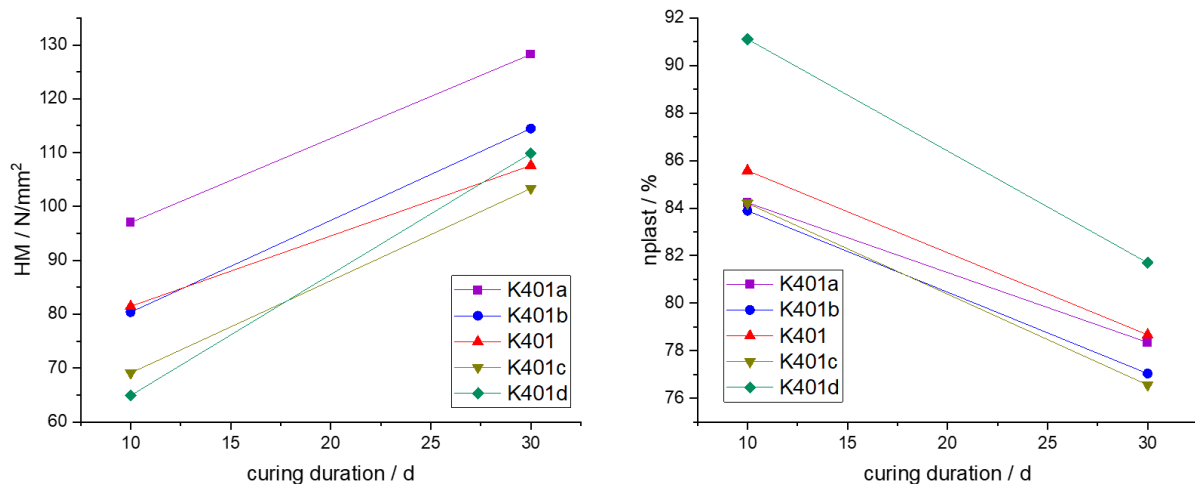


Figure 5. Martens hardness determination on the K401 coatings after ten and 30 days of curing

In (epoxy/amine) 2-Pack systems, with the primary addition of keratin particles to the binder, a high hardness but a low barrier effect is achieved. When the hardener is added initially, the situation is reversed. Since in the latter case the barrier of the standard formulation (with conventional fillers) is clearly exceeded, keratin particle fillers should tend to be dispersed into the hardener component during formulation process.

### Interaction of keratin particles with $\text{Cu}^{0/2+}$ and hBN

The nucleophilic surface moieties of keratin particles could not only interact with the electrophilic epoxy function of the binder, but also with electrophilic moieties of particles or cations. Literature gives some reasons, why such interactions could result in properties, which could contribute to improved performance of coatings:

*Keratin/ $\text{Cu}^{0/2+}$  interaction:* According to literature, keratin/ $\text{Cu}^{0/2+}$  complexes can act as good radical scavengers - and thus potentially as UV protection additives in binders. This is based on the structural similarity of the expected complexes to Cu,Zn-superoxide dismutase (SOD) [2].

*Keratin/hBN interaction:* The literature describes intensive interactions between peptide chains and the surface of hexagonal boron nitride (hBN) [3]. Such interactions (see Fig. 6) could possibly be exploited to improve the barrier and mechanical properties if they are formed in binder matrices [4].

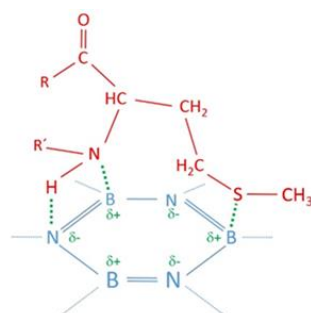


Figure 6. Illustration of possible interactions between a hBN surface and a peptide chain

However, a prerequisite for the efficient, structure-giving formation of such interactions is the activation of the B-N bonds - for example with DMSO [5]. As a result of some tests, we found that a combination of DMSO and acetone was suitable for activation in this case.

Component	2PF	P1	P2	T1	T2
Araldite PZ 3961-1	11.748	12.923	12.923	12.923	12.932
Additol VWX 6208	0.042	0.042	0.042	0.042	0.042
Kronos 2310	3.5	3.5	3.5	3.5	3.5
<b>hBN-K</b>		<b>1.75</b>		<b>1.75</b>	
<b>Cu/K</b>				<b>1.75</b>	<b>0.83</b>
<b>ZnO/K</b>			<b>0.5</b>		<b>0.5</b>
<b>Ca-K</b>		<b>1.75</b>	<b>3</b>		
<b>K</b>					<b>2.17</b>
Talkum EL 10	3.5				
H <sub>2</sub> O demin.	1.855	0.455	0.855	0.587	1.855
Aradur 3986	3.897	3.897	3.897	3.897	3.897
H <sub>2</sub> O demin.	0.695	0.695	0.695	0.695	0.695

Table 1. Standard (“reference”) 2-Pack formulation (2PF) and variants (P1, P2, T1, T2), in which the Talkum filler is replaced by keratin-based filler systems; their given numbers represent the overall solid mass of the respective filler alternative

The keratin filler systems hBN-K and Ca-K were generated by addition/mixing of K with Ca-salt and hBN, respectively, whereas the keratin filler systems Cu/K and ZnO/K were prepared as composite fillers. Details about their preparation are given elsewhere [6].

In all five formulations the total filler mass part adds to 3.5. H<sub>2</sub>O demin. was added in the amount necessary for a sufficient dispersion of the filler-containing part. After homogenization of the epoxy/amine parts the formulation was applied on Al substrates via 300 μm doctor blade and conditioned for 14 days under standard climate conditions.

Unfortunately, it was not possible to suppress the formation of matrix defects (pores, pinholes) during curing process in case of the P and T formulations. Apparently, the K-containing filler particles adsorbed air during dispersion, which was released slowly. Attempts to solve this problem by addition of potentially suitable additives were not fully successful yet. However, we think the results of the following characterizations allow certain conclusions about the potential of the K-based filler:

1. 500 h fluorescence UV irradiation test according to DIN EN ISO 16474-3: 2014-03; detection of L\* before and after irradiation.  $\Delta L^*$  (double determination)
2. Pull-off test according to DIN EN ISO 4624)
3. Cross cut test before and after 500 h of neutral salt spray test (NSS according to DIN EN ISO 2409)

The averaged results of these tests are given in Table 2.

Sample	$\Delta L^*$	Pull-off / MPa	Cross cut before / after irradiation test
P1 (hBN-K Ca-K)	-1.93	5.36	1 / 3.5
P2 (ZnO/K Ca-K)	-1.78	4.12	3.5 / 5
T1 (hBN-K Cu/K)	4.23	4.35	2 / 3
T2 (ZnO/K Cu/K)	0.60	3.79	2.5 / 5
2PF	-6.47	5.75	0.5 / 3

Table 2. Averaged test results obtained from the five samples described in Table 1.

Regarding  $\Delta L^*$  one obtains:

- The strongest darkening is obtained for the keratin particle-free reference system.
- In contrast, T1 (with a high Cu content) shows the strongest lightening; the smallest deviation from the initial state is obtained for the coating in which a keratin with a moderate Cu content was used as a filler.
- Keratin/ZnO systems also appear to contribute (albeit to a lesser extent) to colour stabilisation.

Considering that only 2PF was able to cure completely without air accumulated during the dispersion phase, the following findings indicate barrier- and network-enhancing effects of (2:1)K/hBN combinations:

- P1, T1 outperform the analogue P2, T2 in pull-off test.
- Despite significant air inclusions, P1 is only slightly weaker in pull-off test than 2PF.

Cross-section results before and after NSS show:

- Formulations with hBN (P1, T1) are better than without hBN (P2, T2).
- After NSS 2PF is only slightly better than P1 and the same as T1, although the latter are provided with air entrapment handicap (i.e. matrix defects).

## Summary

- Methods were identified with which chemically or mechan(ochem)ically prepared keratin particles ( $< 10 \mu\text{m}$  or  $< 20 \mu\text{m}$ ) can be produced from chicken feathers in a reproducible and scalable manner.
- Coordinative or composite fillers with other functional particles or ions can be produced from these keratin particles - primarily via their nucleophilic peptide functionalities. The effects of such binary fillers were determined by combining keratin particles with the following components, among others:
  - Cu/Cu<sup>2+</sup>: according to the literature, noticeable radical scavenging properties should be detectable - analogue to Cu,Zn-SOD. In fact, a reduced UV-induced binder degradation could be detected with "Cu/K" filler.
  - hBN: Barrier and adhesion/cohesion tests on different "hBN-K" formulations suggest that the addition of such composite particles can strengthen the network and the barrier.

- In 2-Pack systems, the initial addition of keratin particles to the binder part results in high hardness but a low barrier effect; the reverse is true for initial dispersion in the hardener part. Since in the latter case the barrier of the standard formulation (with conventional fillers) is clearly exceeded, keratin particle fillers should tend to be dispersed in the hardener part in such formulations.

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