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COOL ROOFS AND HOLLOW MICROSPHERES

Spherical micron-sized fillers help improve the elastic properties of coatings. By Jan Nordin, Olof Sandin, Akzo Nobel Pulp and Performance Chemicals, Sweden, and Benjamin J Naden, PRA World, UK.

Low-density hollow microspheres as fillers in elastomeric waterproof/cool roof coatings can enhance a number of key properties. Compared with their mineral counterparts, low-density fillers help reduce the weight of the coating and provide a relatively strong boost to solar reflectance, reducing both the exterior surface temperature and the need for air-conditioning. Some coatings producers claim that hollow microspheres, and especially resilient hollow thermoplastic microspheres, also help maintain the elastomeric properties of the binder in filled coatings.

In this paper, we present data to support the idea that spherical micron-sized fillers enhance the elastic properties of a coating at a given pigment volume concentration relative to a standard inorganic filler. This is true for rigid glass microspheres and even more so for resilient thermoplastic microspheres.

Elastomeric waterproofing coatings are primarily applied to roofing materials to protect and seal them by providing a flexible, water-resistant seal that prevents leaks and mitigates the effects of weathering. In recent years, this class of coatings has also come to be known as elastomeric cool roof coatings [1]-[4], as they are often pigmented white for the purpose of strongly reflecting solar radiation. Pigments traditionally provide the bulk of a coating's reflective properties, whereas fillers are mainly added to reduce costs. However, adding fillers always modifies the properties of the material and they are now often selected carefully to enhance a particular aspect of performance.

UNEXPECTED COOLING

Hollow microspheres have increasingly served as fillers in elastomeric roof coatings over the last 15 years – mainly to reduce weight but also to provide insulation. A more unexpected characteristic of hollow microspheres is that they contribute to efficient cooling by reflecting solar energy. [5], [6]

Hollow microspheres are more efficient at reflecting near-infrared radiation than other additives. Reflection in this spectral region is important, because near-infrared radiation comprises just over 50% of solar energy. Using hollow microspheres as fillers, in combination with pigments, allows cost-effective cool roof coatings to be formulated that have excellent reflective properties across a broad region.

RESULTS AT A GLANCE

➞ Hollow microspheres can confer many advantages on elastomeric cool roof coatings when used as filler and as replacement for inorganic filler.

➞ They not only reduce the weight of the coating but will also improve its thermal insulation properties, help improve total solar reflectance and lower the need for air-conditioning, and extend the coating's service life.

➞ The results show that relatively coarse $CaCO_3$ filler exerts a greater adverse effect on coating elasticity than hollow microspheres.

➞ Resilient hollow thermoplastic microspheres help maintain coating elasticity to a greater extent than rigid glass microspheres.

➞ More research is needed.

EFFECT OF FILLERS ON MECHANICAL PROPERTIES

To accommodate the large temperature cycles experienced by roofs over the course of a day, cool roof coatings are often formulated with relatively soft binders that confer elastomeric properties. The coatings need to be able to accommodate thermal expansion of the roof during the day and contraction at night when it cools. Highly filled coatings normally lose a great deal of the elasticity contributed by the binder. In this paper, we compare three different types of filler and their effect on relevant mechanical properties, including elasticity, tear strength and adhesion. The three filler types are calcium carbonate, hollow glass microspheres and hollow thermoplastic microspheres.

EXPERIMENTAL

Elastomeric cool roof coatings of different filler compositions were formulated and evaluated. The reference coating was prepared with 37 vol.% $CaCO_3$ filler; coatings were also prepared with a filler combination of 17.5 vol.% $CaCO_3$ and 17.5 vol.% hollow microspheres, as well as with 37 vol.% hollow microspheres. Both hollow thermoplastic microspheres and hollow glass microspheres were evaluated (*Tables 1, 2* and *3*).

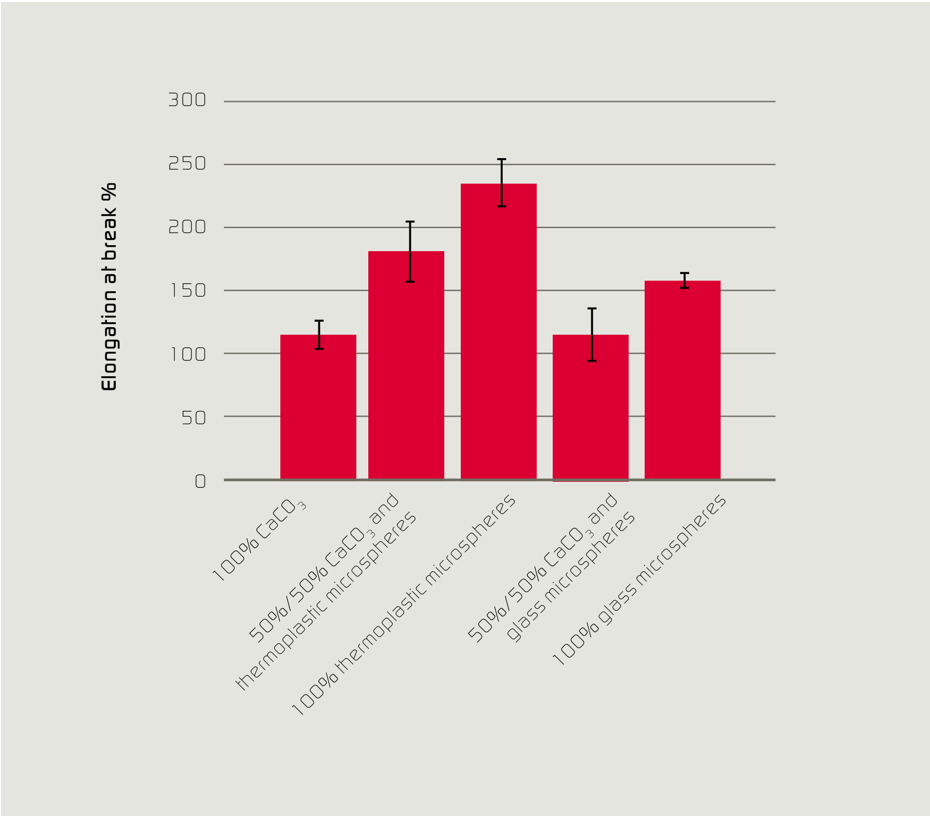
The calcium carbonate filler was "Snowhite 12", a ground $CaCO_3$ from Omya, with a reported median size of 13 µm. Hollow glass microspheres from 3M are rigid and have a low density and the product evaluated in this study ("3M S38HS") had an average size of 44 µm and a density of ~380 g/l. This grade was chosen to provide an optimum balance of thermal properties and high crush strength. "Expancel Microspheres" are thermally expandable core/shell particles containing a blowing agent, typically a low-boiling hydrocarbon, such as isobutane, encapsulated in a thermoplastic polymer shell. [7]-[9] Pre-expanded microspheres are common in many coating applications. Unlike glass microspheres, thermoplastic microspheres exhibit resilience, even at temperatures well below 0 °C. The product evaluated here, "Expancel 461WEA20d30" (from AkzoNobel Pulp and Performance Chemicals, now trading under the name Nouryon), has an average size of 20 µm and a density of ~30 g/l.

Oil absorption by $CaCO_3$ and the microspheres was measured as per the ASTM D281 standard test method for oil absorption of pigments by spatula rub-out. The elasticity of the dry coatings was evaluated as per ASTM D2370, which covers the determination of elongation at break, tensile strength and Young's modulus. Ten specimens measuring 20 mm x 150 mm x 250 µm were prepared from each material. The initial gauge length was 75 mm and the specimen strain rate was 67 %/min until break. Tear strength was measured as per ASTM D624. Five specimens measuring 15 mm x 150 mm x 250 µm were prepared from each material. Type T (or trouser tear strength) measurement was conducted from an initial cut of 40 mm, under a jaw-separation rate of 50 mm/min. Adhesion of the coatings to a cement board was evaluated as per ASTM D903, which permits extensible materials to be backed with a suitable non-extensible material – self-adhesive polypropylene tape was used in this case.

GREATER ELONGATION AT BREAK

There was an apparent increase in elongation at break of films cast from formulations in which $CaCO_3$ was replaced by hollow thermoplastic microspheres, with 100% replacement causing the greatest elongation (*Figure 1, Table 4*). Elongation at break more than doubles from 114 % for the reference containing $CaCO_3$ to 235 % for the coating con-

Figure 1: Elongation at break of the 5 coatings with various fillers; (1) 100 % $CaCO_3$;(2) 50 %/50 % $CaCO_3$ and thermoplastic microspheres; (3) 100 % thermoplastic microspheres; (4) 50%/50% $CaCO_3$ and glass microspheres; (5) 100 % glass microspheres.



taining hollow thermoplastic microspheres. There seems to be a weak correlation with material tensile strength; the more elastic material is often weaker and breaks at higher deformation (*Table 4*). However, the distribution of the results for tensile strength, as represented by the calculated standard deviation, suggests the need for caution in drawing firm conclusions about any relationship observed here. There does, however, seem to be a clear relationship between elongation and Young's modulus of the coatings, with increasingly stiffer films exhibiting less elongation (*Table 4*). Replacing 50% $CaCO_3$ with an equal volume of glass microspheres seems to have little effect upon elongation at break, although the standard deviation of the result is highly distributed (*Table 4*). The results for 100% replacement indicate a substantial increase in elongation at break. Again, the tensile strength results do not evidence a distinct relationship with elongation performance, and Young's modulus is inversely proportional to elongation.

OIL ABSORPTION

The results for oil absorption confirm a small difference in the surface area of $CaCO_3$ compared with that of glass and thermoplastic microspheres (*Table 5*). The two types of hollow microspheres are very similar in this respect. Oil absorption values for fillers and pigments can be used to roughly calculate the critical pigment volume concentration (CPVC) of a formulation, provided that all fillers and pigments in the formulation are accounted for. Lower oil absorption equates to a higher CPVC for the formulation. In this study, the formulations differ only in their fillers; all other components remain constant. Consequently, the CPVC is somewhat higher for the formulations containing hollow microspheres. As the PVC is the same for all formulations, it follows that the PVC/CPVC ratio is slightly lower for the formulations filled with hollow microspheres (*Tables 1* and *2*). A lower PVC/CPVC ratio has a documented positive effect on coating quality and may partly explain the lower elasticity observed for the $CaCO_3$-filled coatings. [10]-[11]

FILLER-BINDER CONSIDERATIONS

With small filler particles, the breaking strain is low and rupture itself is sudden. Large filler particles yield a lower tensile strength, but rupture is preceded by large strain deformation and necking. [12] If the filler-binder adhesion at the interface is poor, the composite might be seriously weakened, and the filler might behave not as reinforcement but rather as a defect in the matrix. In such a scenario, the strength would be reduced and elongation at break would increase. The aspect ratios of the three different fillers studied here are quite low and the possible reinforcement effects at the same volume fraction should be low and quite similar. The three fillers have somewhat different surface chemistries and so the interfaces are of different strength. Were any of the fillers evaluated in this paper to have a deviating surface chemistry, it would most likely be the thermoplastic microspheres. However, there is also the possibility of quite good compatibility between the acrylic binder and the acrylic polymer surface of the thermoplastic microspheres. Also, the smooth surface of hollow fillers, their spherical morphology and relatively large particle size may affect the filler-binder interaction and partly explain why coatings containing them are more elastic. Kohls and Beaucage [13] noted that fillers can affect tensile modulus, flexural strength and impact strength of polymeric systems, so that these properties are enhanced with increase in filler content and decrease in filler size.

RESILIENCE MAKES THE DIFFERENCE

The effect on elongation at break is less pronounced for the films filled with glass microspheres than those filled with thermoplastic microspheres. This difference cannot be ex-

Table 1: Formulations

		37vol% $CaCO_3$	18.5vol% $CaCO_3$, 18.5 vol% 461WEA20d30	37 vol% 461WEA20d30
Formulation		1	2	3
Mill Base	**Commercial name**		wt%	
Solvent	Water	12.31	13.91	16.33
Dispersant	"Orotan 850"	0.13	0.16	0.19
Dispersant	"KTPP Calgon TK"	0.11	0.14	0.17
Defoamer	"DAPRO DF 7580"	0.15	0.18	0.23
$CaCO_3$	"Snowhite 12-PT"	34.08	20.48	0.00
TiO_2	"Kronos 2160"	7.26	8.73	10.95
ZnO	"Zachem 800H"	1.61	1.94	2.43
Let-Down				
Binder	"Primal EC-1791E"	37.98	45.66	57.23
Defoamer	"DAPRO DF 7005"	0.15	0.18	0.23
Solvent	"DAPRO FX 511"	0.56	0.68	0.85
Mildewcide	"Acticide MBS"	0.17	0.20	0.26
	"Acticide MKW2"	0.10	0.12	0.15
Solvent	Propylene glycol	1.97	2.37	2.97
DINP	DINP	0.24	0.29	0.36
	"Hexamoll DINCH"	2.82	3.40	4.26
Rheological modifier	"Bermocoll EBM 8000"	0.34	1.15	0.51
Microspheres	"Expancel 461WEA20d30"	0.00	1.15	2.88
Microspheres	"3M S38 HS"	0.00	0.00	0.00
Total		100.00	100.00	100.00
PVC %		43.00	42.99	42.97
CPVC* %		59.31	63.95	69.80
Volume solids %		49.44	48.99	49.42
Solids content %		63.85	56.11	45.52

Table 2: Formulations continued

		18.5 vol% $CaCO_3$, 18.5 vol% S38	37 vol% S38
Formulation		4	5
Mill Base	**Commercial name**		wt%
Solvent	Water	14.42	17.41
Dispersant	Orotan 850	0.15	0.18
Dispersant	KTPP Calgon TK	0.13	0.16
Defoamer	DAPRO DF 7580	0.18	0.22
$CaCO_3$	Snowhite 12-PT	19.96	0.00
TiO_2	Kronos 2160	8.51	10.27
ZnO	Zachem 800H	1.89	2.28
Let-Down			
Binder	"Primal EC-1791E"	44.50	53.72
Defoamer	"DAPRO DF 7005"	0.18	0.22
Solvent	"DAPRO FX 511"	0.66	0.80
Mildewcide	"Acticide MBS"	0.20	0.24
	"Acticide MKW2"	0.11	0.14
Solvent	Propylene glycol	2.31	2.79
DINP	DINP	0.28	0.34
	Hexamoll DINCH	3.31	4.00
Rheological modifier	"Bermocoll EBM 8000"	1.20	0.48
Microspheres	"Expancel 461WEA20d30"	0.00	0.00
Microspheres	"3M S38 HS"	2.80	6.76
Total		100.00	100.00
PVC %		43.00	43.00
CPVC* %		63.24	67.73
Volume solids %		48.95	49.42
Solids content %		57.18	48.85

Table 3: Filler volumes in the various formulations.

Formulation	1	2	3	4	5
	Vol% dry filler				
"Snowhite 12-PT"	37	18.5	0	18.5	0
"Expancel 461WEA20 d30"	0	18.5	37	0	0
"3M S38 HS"	0	0	0	18.5	37

plained in terms of size, surface area, oil absorption (CPVC) or shape of the filler. Instead, we propose that a possible explanation is that hollow glass microspheres are rigid and hollow thermoplastic microspheres are resilient and capable of deforming with the binder upon application of strain. If the filler has a higher modulus than the polymer, stiffness will be enhanced. [12] Our proposal is in agreement with the experimental results.

ENHANCED TEAR STRENGTH

Tear strength seems to be enhanced by replacing $CaCO_3$ with hollow thermoplastic microspheres, although the standard deviations of the tear strength results make it difficult to draw any firm conclusions from these tests.

ADHESION RESULTS INCONCLUSIVE

Adhesion of the coatings to a cement board was evaluated as per ASTM D903 but the results unfortunately provide no insights. Despite the use of self-adhesive polypropylene tape to reinforce the coating film, cohesive failure of the film was observed in all samples tested. This indicates that the films adhered more strongly to the cement-board substrate than the strength of the coating film and the tape together. Nordin et al. [6] reported that adhesion and wet adhesion to galvanised steel seem to be improved by replacing $CaCO_3$ filler with hollow thermoplastic microspheres. The waterproofing properties of elastomeric roof coatings are contingent on excellent adhesion of the coating to the substrate. It is likely that polymeric fillers with a relatively low T_g contribute more to coating adhesion than inorganic fillers. This is a corollary of the tackier nature of the system and is true for the hollow thermoplastic microspheres evaluated here.
Hollow microspheres can confer many advantages on elastomeric cool roof coatings when used as filler and as replacement for inorganic filler. They not only reduce the weight of the coating but will also improve its thermal insulation properties, help improve total solar reflectance and lower the need for air-conditioning,

Table 4: Elasticity (ASTM D2370) (standard deviation in brackets)

	1	2	3	4	5
Elongation at break (%)	114.78 (12.14)	180.16 (25.17)	235.37 (19.72)	114.01 (22.83)	152.06 (12.48)
Tensile strength (MPa)	1.36 (0.56)	1.15 (0.10)	1.14 (0.03)	1.29 (0.12)	1.13 (0.07)
Young's Modulus (MPa)	11.14 (0.40)	5.60 (0.43)	3.59 (0.36)	7.03 (0.21)	5.55 (0.35)

Table 5: Oil absorption by the fillers

Filler	g oil / cm^3 pigment
Snowhite 12-PT	0.62
3M S38 HS	0.38
Expancel 461WEA20d30	0.35

"Cost-optimise coatings formulations."

Jan Nordin

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2 questions to Jan Nordin

In addition to roof coatings, where do you see other fields of application for hollow microspheres? *Microspheres are sold to hundreds of different applications. Everything between wine stoppers to shoe soles. Within coatings applications I can mention elastomeric roof and wall coatings, anti-condensation coatings, insulation coatings (pipe coatings) and indoor ceiling paints.*

What further research is planned? *We currently look more closely at optical properties of different combinations of pigments and hollow microspheres in coatings. The objectives are to cost-optimise coatings formulations and to try maximise solar reflection for colored coatings.*

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and extend the coating's service life. The results presented here indicate that relatively coarse $CaCO_3$ filler exerts a greater adverse effect on coating elasticity than the hollow microspheres studied here. It is also apparent from the results that resilient hollow thermoplastic microspheres help maintain coating elasticity to a greater extent than rigid glass microspheres. More research is needed in order to fully understand the nature of the different systems studied here.

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