

Use of a polymer-treated mineral pigment in paper coatings*

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Mineral particles intended for the coating of paper and board were surface-treated with a copolymer based on styrene and acrylic acid. The mineral pigment used was ground CaCO_3 . The polymer was grafted to the mineral by first adsorbing the acrylic acid to the surface and then allowing this monomer to take part in the polymerization with the styrene. The grafting was performed in the aqueous phase, which was considered to be a prerequisite. The surface treatment of the mineral particles markedly improved the surface strength of papers coated with these pigments. This was interpreted as being a result of improved compatibility between the surface-treated pigment and the synthetic binder used in the coating layer. The surface treatment caused some decrease in the gloss of the coated papers but appeared otherwise not to impair important properties of the coated product. To some extent the surface treatment was also applied to kaolin particles. An improvement in the surface strength of papers coated with the modified particles was also observed with this pigment.

1. Introduction

The surface treatment of mineral fillers and reinforcing elements for use in polymer composites has during recent decades evolved into an area of great technical and scientific interest. Treatment of glass fibres with silane-based coupling agents is a familiar and important example of such a surface modification [1]. The purpose of the surface treatment is, in the majority of cases, to improve or control the adhesion between the filler and the polymeric matrix, which can in turn improve mechanical properties such as strength, creep resistance and dynamical-mechanical properties [2-6]. Often the compound used for the surface treatment promotes compatibility between the filler and the polymer or provides a coupling between the two phases. In the latter case, chemical bonding between the agent used and the two constituents is often assumed. The surface treatment of the filler particles or reinforcing elements may however also rest on physical adsorption and an improved compatibility.

An important class of composites are paper coatings which for simplicity may be regarded as consisting of mineral particles, e.g. kaolin, a polymeric binder and air. The porosity of these coatings is typically of the order of 30-35% and the mineral particles constitute the major part of the solid phase (80-90%), the remaining part being primarily the binder. The coatings are applied to the paper surface in the form of an aqueous suspension which, after drying, forms a thin layer (ca. 5-20 μm) on the surface.

The purpose of coating a paper is to improve its optical and printing properties (e.g. [7]).

In these types of composite the strength may also be a critical parameter. The coating must withstand the loadings and deformations imposed on it during the printing operation. This is the task of the polymeric binder which glues the mineral particles together and also anchors the coating to the paper substrate. In the printing operation, the strength of the coating in the thickness direction and its adhesion to the paper surface are important. These pigmented coatings are in general quite brittle with an elongation at rupture below 1% and they can also be anisotropic [8]. The ability of the coated paper to withstand loading without surface rupture in the coating, i.e. its surface strength, is evaluated by standard procedures [7]. It has been recognized that the surface failure mode of coated papers can be quite complicated, but it is generally believed that the properties of the pigment coating are of great significance. Several studies have consequently been undertaken to provide a better understanding of the relation between the structure of the coating and the mechanical properties of the coating and coated paper [7, 9-13]. These investigations have for instance pointed towards the importance for the mechanical performance of the coating of the choice of binder, the binder distribution in the porous structure etc.

It can be anticipated that the adhesion between the mineral pigment and the polymeric binder is also of

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considerable significance for this class of composites. The major difference between the pigmented coatings and polymeric composites is that the former are porous and the volume fraction of the polymer is substantially lower than that of the mineral component. It may thus be expected that a surface treatment of the mineral particles with the aim of promoting adhesion between the two phases can provide an interesting route to improve the surface strength of coated papers. This is the area of interest in this work. Within the paper coating field, surface treatment of the mineral particles to improve the adhesion between mineral and binder do not appear to have attracted much interest. It should however be mentioned that improvements in the rub resistance of coated paper were reported by Mlynar and McNamee [14] when kaolin pigments were reacted with an acrylic binder.

A more direct way to modify the surface characteristics of the mineral particles is to deposit or graft a polymer on to the mineral surface. The polymer should then be chosen to improve the compatibility of the particles with the polymeric binder. The mineral pigment used here was in most cases ground calcium carbonate, but some experiments were also performed with kaolin as the mineral. Both pigments are in common use for the coating of paper and board. In the paper coating field, latices based on carboxylated styrene-butadiene copolymers are commonly used as binders and a styrene-based polymer was therefore chosen for the surface treatment of the mineral particles. A method of grafting the polymer on to the mineral surface in the aqueous phase was developed, since this would certainly promote the technical use of the modification.

2. Experimental procedure

2.1. Materials

In most of the experiments, a commercial grade of ground calcium carbonate intended for the coating of paper or board was used. The average particle size according to a light diffraction technique (see also below) was ca. 1 μm . The particle size distribution is however quite broad, since this is an advantage for the rheology of the suspension. The average specific area of the pigment particles was $10\text{ m}^2\text{ g}^{-1}$ and the zeta-potential of the particles in water at pH 8 was -27 mV . A few experiments were also carried out using a commercial kaolin coating pigment. The average particle size of these particles was 2.4 μm according to the light diffraction method mentioned above.

A conventional carboxylated latex, based on a copolymer of styrene and butadiene (SB), was used as binder for the coating layers. The average size of the latex particles was ca. 150 nm. The glass transition temperature of the polymer was 20 °C as evaluated by differential scanning calorimetry. In this study, the amount of SB binder was constant at 10 parts by weight per 100 parts of pigment. The sodium salt of polyacrylic acid (0.35%) was used as dispersant for the mineral particles. The sodium salt of carboxymethyl cellulose (NaCMC) was used as cobinder, 1 part by weight of NaCMC per 100 parts of the pigment being

added to the suspension. The viscosity average molecular mass of the NaCMC was 30000.

The aqueous coating colours were prepared in a conventional manner.

2.2. Surface treatment of mineral particles

Grafting of a polymer to a mineral surface or encapsulating a particle has been described in several works and a good review of the field has been provided by Solomon and Howthorne [1]. In the present work, acrylic acid was adsorbed on to the basic surface, i.e. CaCO_3 , and the acid was then copolymerized with styrene. Several examples of this technique of surface modification using grafting via adsorbed monomers have been reported, e.g. the coating of calcite or titania with an acrylic acid-methyl methacrylate copolymer [1, 15]. The grafting of polystyrene on to sorbate-modified titanium oxide is another example [16]. In the present case, a previously developed method [17] of grafting a styrene-acrylic-acid-based polymer to CaCO_3 in an organic solvent (hexane or octane) was the starting point. However, when the organic solvent was evaporated, the modified particles could only with great difficulty be dispersed in water and it was decided that the surface treatment had to be performed *in situ* in the aqueous phase. The pigment slurry could then, after the appropriate concentration had been achieved, be used directly for preparation of the coating colour.

The grafting of inorganic particles in an aqueous slurry has not been reported to any great extent in the literature. Grafting on to leather [18], silk [19], asbestos and talc [20] and bentonite and kaolin [21] has been described. Using this information, a method of grafting polystyrene via the adsorbed acrylic acid on to the CaCO_3 particles was developed, the polymeric layer being in some cases crosslinked during the polymerization using divinyl benzene. An example of a typical grafting procedure is described in detail elsewhere [22].

The polymer, referred to hereafter as polystyrene-based (PS), appeared to adhere strongly to the CaCO_3 surface. Only a minor amount could be removed by Soxhlet extraction in acetone for 24 h, indicating that grafting via the adsorbed acrylic acid had taken place. The amount of PS grafted on to the mineral surfaces, determined by thermogravimetric analysis (TGA), was varied between 0.6 and 6.3% (relative to the weight of the mineral particles). The same surface treatment was to a limited extent also applied to kaolin particles. When using this pigment the grafted copolymer was cross linked.

2.3. Other methods

The size of the surface-treated particles was evaluated using a MasterSizer (Malvern Inc., UK). The amount of polymer grafted on to the mineral particles was determined thermogravimetrically with a Perkin-Elmer DSC 7.

The coating colours were drawn down using a small laboratory coater (K-Coater, R.K. Print-Coat

Instruments Ltd., Royston, UK) on a sized wood-free paper with a grammage of 77 g m^{-2} . The solids content of the colours was 45–50% (by weight) and the final coat weight was $10\text{--}13 \text{ g m}^{-2}$. In most cases, the coated papers were dried at room temperature, but some of them were dried at 80 and 130°C for 15 min. After conditioning at 23°C and 50% RH, the papers were calendered in a steel–steel nip (two passages) at a low line load. The rolls of the calender were not heated.

The surface strength of the coated papers was evaluated as the IGT pick strength [7]. This technique provides a measure of the out-of-plane strength of the coating. The IGT surface strength denotes the limiting speed at which a standard oil with a prescribed viscosity applied with a special disc can simulate printing of the paper without rupturing the coated surface.

The main interest is here focused on the strength characteristics of the paper, but some other paper properties are also briefly reported. The effect of the treatment on properties other than the surface strength has been described in more detail elsewhere [22]. The paper properties were evaluated using conventional techniques. To measure the ink absorbency of the coated sheet, an excess of Croda red draw-down ink was applied to the coated surface and after a contact time of 30 s the excess was wiped off. The optical intensity of the remaining stain (the Croda value) was then assessed and taken as a measure of the ink absorptivity of the paper.

3. Results

3.1. Size of surface-treated particles

Fig. 1 shows how the PS modification affects the average size (equivalent spherical diameter) of the CaCO_3 particles. Both crosslinked and uncrosslinked PS were used. The size of the particles increased as the amount of grafted PS increased. It is not obvious how the polymer is localized on the mineral surface. It may form a film on the surface or be deposited as patches. The latter is not unlikely, and this may be of consequence for the size measurements performed here, since it is known that the light diffraction technique used is sensitive to deviations in particle shape. Agglomeration can also increase the apparent size of the

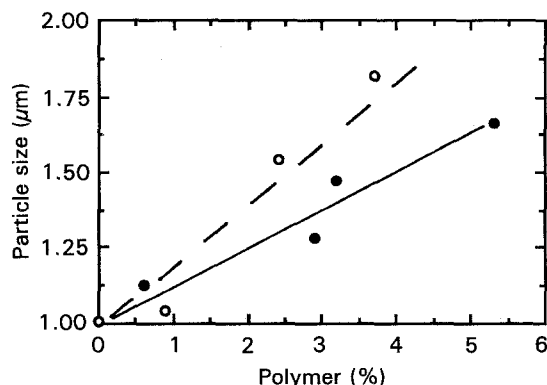


Figure 1 Average size of surface-treated CaCO_3 particles as a function of the amount of grafted polymer: (●) crosslinked, (○) not crosslinked.

treated particles, although care was taken to minimize this tendency. It seemed that the particle size increased more with increasing amount of PS if the polymer was not crosslinked. This may be the result of a more pronounced aggregation of the treated mineral particles when the uncrosslinked polymer is used, especially at higher levels of grafting.

The surface treatment also yielded a broadening of the particle size distribution, as is evident in Fig. 2. Here the particle size distribution is shown for CaCO_3 particles grafted with 0.6 and 5.3% crosslinked PS. That the broadening of the size distribution increased with increasing amount of PS on the particles is also evident in Fig. 3. The width of the size distribution (W) is defined as

$$W = \frac{D_{90} - D_{10}}{D_{50}} \quad (1)$$

where D_A denotes the value of the equivalent spherical diameter of the treated CaCO_3 particles than which $A\%$ of the particles are smaller. Obviously particles grafted with uncrosslinked PS have a broader particle size distribution than the other type of treated particles. This may be a consequence of the more pronounced tendency of the former to aggregate; the broadening of the size distribution may in itself be indicative of particle flocculation.

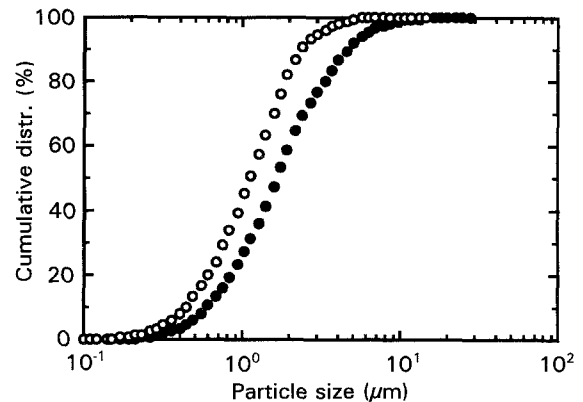


Figure 2 Cumulative particle size distribution for CaCO_3 -particles grafted with (○) 0.6 and (●) 5.3% polymer.

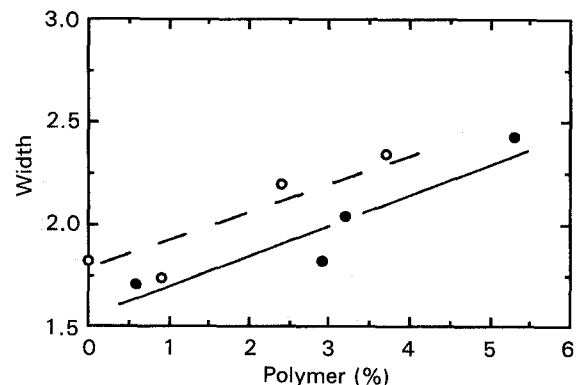


Figure 3 Width of the particle size distribution, according to Equation 1, for surface-treated mineral particles as a function of the amount of grafted polymer: (●) crosslinked, (○) not crosslinked.

3.2. Influence of surface treatment on surface strength

Papers coated with ground CaCO_3 are in general considered to have a good surface strength [12, 23, 24]. The primary aim of this work was to investigate whether an improvement in this property could be achieved with the polymer modification used here. Fig. 4 shows the effect of crosslinked PS on the surface strength of coated papers dried at room temperature. The grafting of PS significantly improved the surface strength, the effect being more pronounced at lower grafting degrees. The increased strength is here attributed to an improved adhesion between the PS-treated mineral particles and the styrene-butadiene binder, although the conditions under which the polymerization and the grafting were performed could also influence the surface strength [22].

If the grafted styrene-acrylic acid copolymer is not crosslinked, there is a further increase in the IGT surface strength, as shown in Fig. 5. In this case the amount of grafted polymer was 1% and the coated sheets had been dried at room temperature. The improvement over the crosslinked system can be due to an enhanced diffusion of polymer molecules over the interface between the grafted polymer and the SB binder [25], due to the greater mobility of the PS molecules. When the amount of uncrosslinked PS on the mineral surface was raised to ca. 4% no further

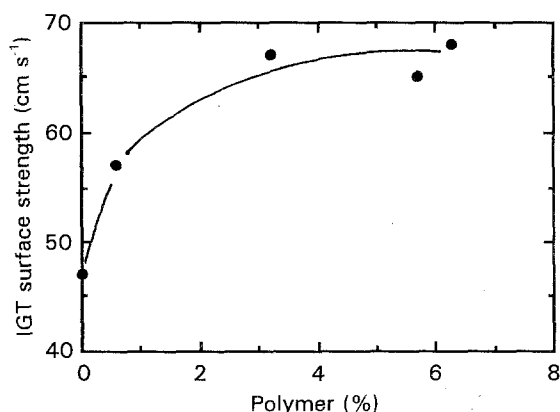


Figure 4 The surface strength of the coated papers increased as the amount of grafted polymer increased. The grafted polymer was crosslinked and the papers were dried at room temperature.

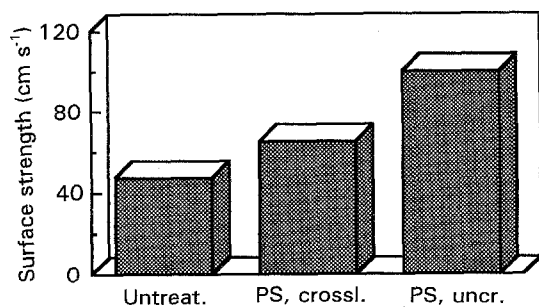


Figure 5 Surface strength of sheets coated with untreated CaCO_3 and with the same pigment treated with 1% crosslinked or uncrosslinked polymer. The sheets were dried at room temperature.

improvement in surface strength was noticed. Actually a decrease was noted at the highest degrees of grafting, probably because of an aggregation of the pigment particles at higher amounts of grafted polymer.

The surface strength of the coated papers is also influenced by the drying of the sheets. Here the coated papers were, after application and metering of the coating colour, dried at room temperature, at 80 or at 130 °C for 15 min. Fig. 6 illustrates the influence of the drying temperature when 0.9% uncrosslinked polymer had been grafted to the CaCO_3 particles. The increase in drying temperature evidently raised the surface strength of the sheets. The same behaviour was observed at the other degrees of grafting and with the crosslinked polymer. This improvement may be a result of an increased mobility of the grafted polymer and of the SB binder leading to an increased adhesion and a more favourable polymer distribution in the coating structure. The flow of the binder is certainly not unimportant, since an improvement in surface strength with increasing drying temperature also occurred when untreated CaCO_3 particles were used as coating pigments.

When the kaolin pigment was treated with the PS-based polymer a positive influence on the surface strength was also noted. The amount of grafted polymer was ca. 4% in this case. Fig. 7 shows that the surface strength was improved by the grafting and that the strength was further increased by an increase in the drying temperature. The improvement in surface strength at higher drying temperatures was also observed when untreated kaolin particles were used.

A straightforward way to improve the surface strength of a coated paper is simply to raise the binder content [7]. The grafting procedure used here was, however, at a given total amount of polymer (grafted polymer + binder), more effective in improving the IGT strength, at least at low levels of grafting. This is shown in Fig. 8, which compares the surface strength of papers coated with surface-treated (crosslinked PS) CaCO_3 and 10 parts of the SB latex with that of paper coated with untreated CaCO_3 and 10, 12 or 14 parts of the SB binder.

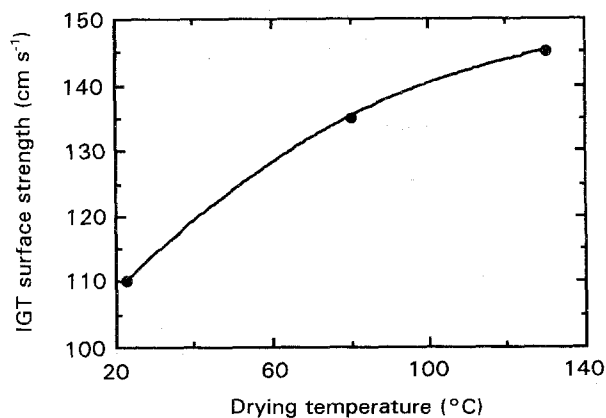


Figure 6 Surface strength of the coated papers as a function of the drying temperature. In this case the 0.9% uncrosslinked copolymer had been grafted on to the CaCO_3 particles.

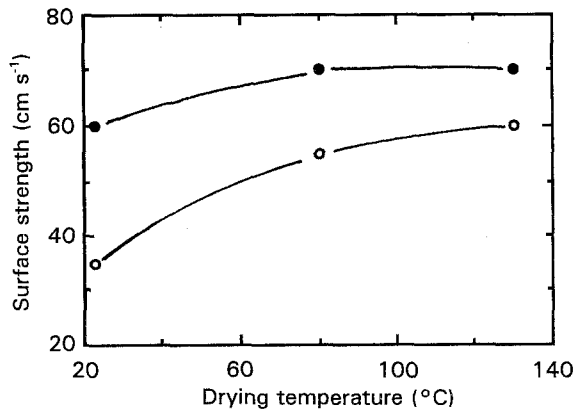


Figure 7 Effect of drying temperature on the surface strength of paper coated with (○) unmodified kaolin and (●) kaolin grafted with ca.4% polymer.

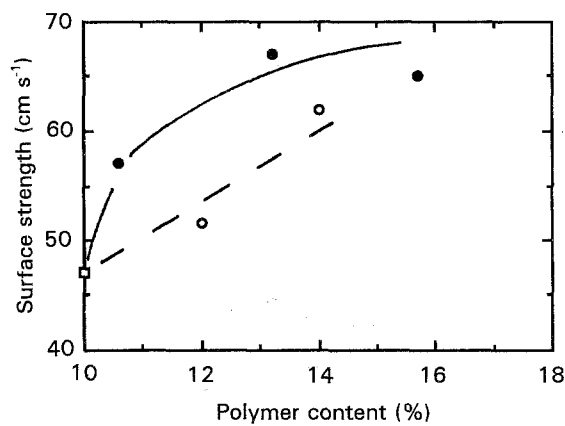


Figure 8 Surface strength of paper coated with grafted (crosslinked) CaCO_3 pigment and with the same unmodified pigment versus the total amount of synthetic polymer in the coating layer. With untreated pigment, the amount of SB binder was 10, 12 or 14% relative to the weight of the mineral pigment. (□) Untreated, (●) PS-treated, (○) with SB latex.

3.3. Effect of surface treatment on other properties of the coated sheets

The effect of surface treatment of the CaCO_3 on paper properties other than the surface strength has been described in some detail elsewhere when using the crosslinked system [22]. Surface treatment of the particles led to a reduction in gloss and in general the gloss decreased with increasing levels of grafting. The amount of grafted polymer should therefore be kept low, since high gloss is an important quality requirement. Higher gloss levels were however obtained when the crosslinking of the grafted polymer was omitted (Fig. 9). In this case the amount of PS polymer was 4%. Fig. 10 shows that another pattern emerges when kaolin is used as the coating pigment. In this case the surface-treated particles imparted a higher gloss to the coated papers than the untreated kaolin. As expected, the gloss levels were significantly higher than with the ground CaCO_3 pigment. The graph also indicates that the gloss of the coated papers decreased as the drying temperature was raised. The effect of the drying temperature is thus the same as that noted with the CaCO_3 pigment [22].

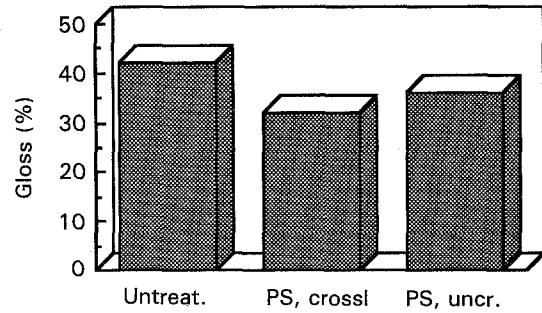


Figure 9 Gloss of papers coated with unmodified CaCO_3 pigment and with the same pigment with 4% crosslinked and uncrosslinked polymer grafted to the mineral surface. The sheets were dried at room temperature.

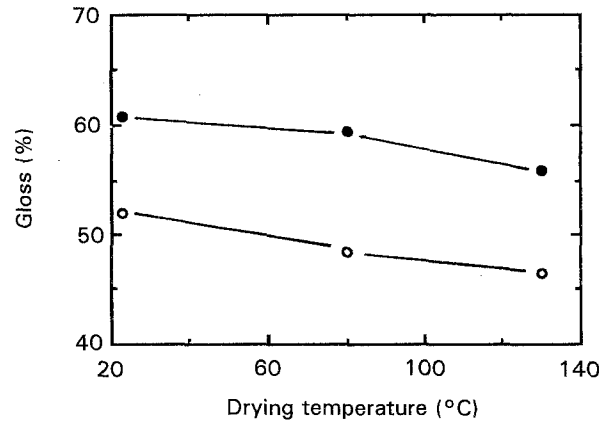


Figure 10 Paper gloss for sheets coated with (○) unmodified and (●) surface-treated (ca.4%) kaolin as a function of the drying temperature.

It is desirable that the finished surface should be as smooth as possible. The surface roughness is often given as the PPS-10 value for the coated surface [7]. When untreated CaCO_3 was used as pigment, the PPS value was ca.1.4 μm . The surface treatment did not significantly influence the surface roughness. If the amount of grafted polymer was kept lower than 5% and the coating was dried at room temperature, the PPS value was generally of the order of or lower than 1.6 μm . Increasing the drying temperature resulted in a slight increase in the surface roughness. The surface treatment of the kaolin pigment led to a somewhat smoother coated surface, which parallels the improvement in gloss (e.g. [26]).

The brightness of a paper is strongly dependent on the light scattering coefficient of the porous structure, i.e. on the porosity and pore size distribution of the coating layer. If surface treatment has a profound influence on the pore structure, this should be clearly evident in the brightness of the coated paper. Brightness measurements were performed at an effective wavelength of 457 nm. Fig. 11 shows that there was a small increase in brightness of the coated papers when the amount of grafted polymer was increased. The uncrosslinked polymer appeared to be slightly more effective in this respect than the crosslinked type. The change in brightness may be due to a change either in

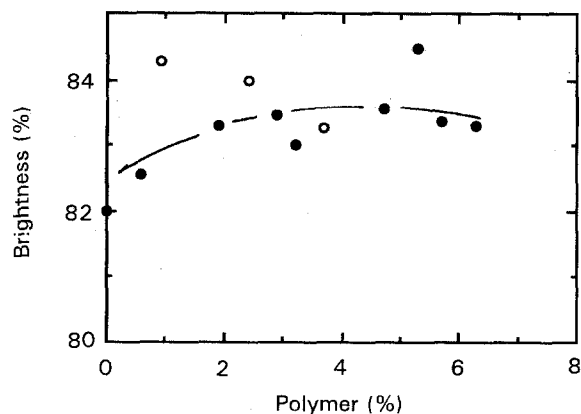


Figure 11 Brightness of coated papers as a function of the amount of polymer grafted to the CaCO_3 particles. The sheets were dried at room temperature. (●) Crosslinked, (○) not crosslinked.

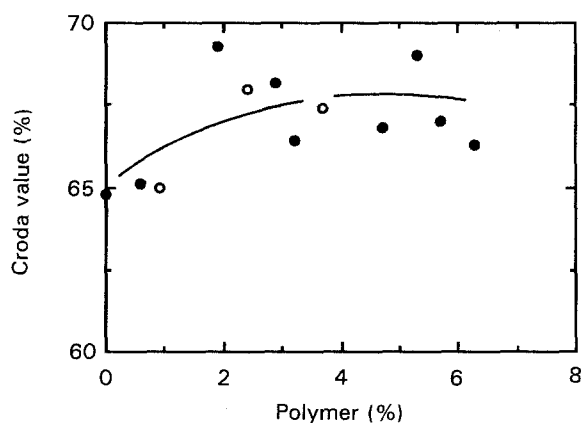


Figure 12 Croda ink-stain value of the coated sheets versus the amount of polymer grafted on to the CaCO_3 particles. The sheets were dried at room temperature. (●) Crosslinked, (○) not crosslinked.

pore structure of the coating or in its light absorption characteristics. An increase in the drying temperature can lead to a decrease in the brightness of the coated paper. This decrease is however not very pronounced, being less than 0.5% in most cases [22]. In the case of the kaolin pigment, the surface treatment had no significant influence on the optical properties of the coated sheets.

Ink absorptivity is another important property of coated products. Stain tests, like the Croda red draw-down ink test, are often used as simple methods to obtain an estimate of the ink absorbency of paper products [27]. Fig. 12 shows the effect of the grafting on the Croda value of the coated sheets. In general a small increase in the intensity of the stain was observed when the amount of polymer on the mineral particles was increased. The same behaviour was found for both the crosslinked and the uncrosslinked systems. The Croda value also increased slightly when the drying temperature was raised. These results indicate no deterioration in the ink absorbency of the coated papers as a result of the surface treatment of the CaCO_3 particles. The same behaviour was observed when kaolin was used as coating pigment

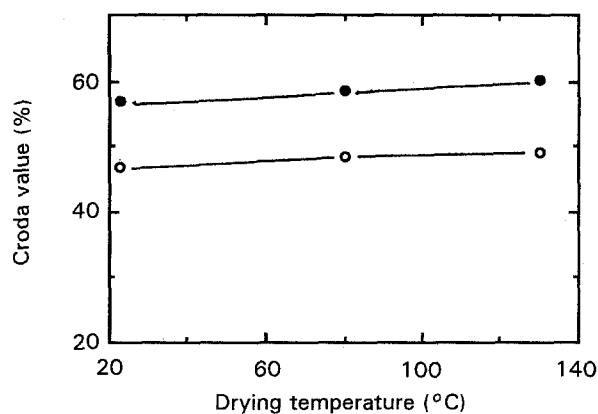


Figure 13 Croda ink-stain value of papers coated with (○) untreated kaolin and (●) kaolin grafted with ca.4% polymer versus the drying temperature.

(Fig. 13), although the Croda values were lower when this pigment was used. This difference is probably due to the greater tortuosity of the kaolin structure than that of the CaCO_3 coating.

4. Discussion

One of the most important results arrived at in this study is that it is possible to prepare coating colours based on polymer-treated CaCO_3 or kaolin. It is an advantage if the surface treatment can be carried out in the aqueous phase, since the pigment can then be dispersed without any greater difficulty. In principle the grafting of the polymer to the mineral surface is a rather straightforward procedure.

The grafting of the copolymer to the mineral surface can obviously improve the surface strength of the coated paper quite significantly. Low levels of grafting were here relatively more effective. This may not in general be the case since some aggregation of the pigment particles probably occurred at higher grafting levels, and this can yield a slight increase in the porosity of the coating layers and thus in turn a reduction of the surface strength [9]. If the aggregation could be prevented, coating layers which performed better at higher levels of grafting could probably also be produced. The mechanical performance of the coated papers was markedly influenced by the drying temperature. This applied to coatings based on both surface-treated and untreated pigments. Diffusion of polymer segments over the interface between the SB binder and the grafted polymer may be one controlling factor in this case, as well as an improved spreading of the binder on the available pigment surfaces. The improvement in surface strength when the crosslinking of the grafted polymer is omitted may be attributed to the former mechanism, i.e. an enhanced diffusion of polymer segments over the mutual polymeric interface.

The grafting of polymers was more effective in improving the surface strength than was merely raising the binder content of the coating colour. One reason for this may be that the grafting results in a more favourable polymer distribution on the pigment

surfaces. This may then to some extent explain why the difference in surface strength between the two systems is clearer at low levels of grafting. However, it should once again be pointed out that aggregation of the surface-treated pigment particles may hide the potential of the surface treatment at higher grafting levels.

For the papers coated with CaCO₃, the decrease in gloss is certainly not desirable and the level of grafting should be kept rather low, i.e. in the range where the positive effect on the surface strength was more marked and problems with pigment aggregation were not obvious. It is not surprising that the gloss decreases when the amount of synthetic polymer in the coating structure increases [7], but the gloss values were here lower than that attained with the untreated pigment and on increasing the amount of SB binder. The surface treatment did however bring about an increase in gloss when kaolin was used as the coating pigment. The reason for this is not clear, and more experimental work is undoubtedly required with the kaolin pigment.

In general the optical properties were not strongly affected by the surface treatment of the pigment particles. A slight increase in the brightness was in most cases observed. The surface treatment of the coating pigments can bring about a change in the pore structure, e.g. an increase in the porosity or a change in the effective pore dimension which is then observed as an increase in the light-scattering ability of the coating. This is also supported by the increase in the ink absorptivity as revealed by the slight increase in the Croda ink-stain values. Drying the coating at higher temperatures may give a redistribution of the binder and thus also a change in the pore structure, which lowers the brightness of the coating [28]. Another possibility or contributing factor is that the light absorption coefficient is increased by the heat treatment.

The aim of this work was merely to show whether it is possible to adopt the concepts and techniques used within the polymer composite field and use them to improve the mechanical performance of coated paper products by a suitable surface treatment of the coating pigments. It was however important that this surface treatment could be performed in the aqueous phase. Obviously there are several possibilities of improving the surface strength further by this type of surface modification. It is quite clear that the ratio of binder content to amount of grafted polymer can be optimized to obtain a higher surface strength. The role of the glass transition temperatures of the polymeric binder and the grafted polymer deserves further attention. Different binders may yield results that differ from those arrived at here and, of course, other types of polymer treatment of the pigment particles can be of great interest [1]. The results obtained here indicate that it is possible to improve the surface strength of coated paper products without significant negative effects on other important properties. More work is, however, definitely required in order to ascertain this.

This is especially true with respect to the printing properties of the paper, which require a separate study on papers produced on a larger scale.

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