

Effect of polymeric thickeners on pigment coatings: Adsorption, rheological behaviour and surface structures

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Polymeric thickeners play a vital role in controlling water retention in paper coating processes. In this work, the interactions between various polymer water retention agents (i.e., thickeners) and coating pigments were investigated, in an attempt to improve the understanding of the thickening mechanisms. Adsorption isotherms of the polymeric thickeners, up to four types of commercial thickeners based mainly on copolymers of acrylate and acrylic acid, onto mineral pigments (clay pigment and ground calcium carbonate, GCC) were determined. It was found that the adsorption behaviour was strongly affected by the surface structure of the pigment. All the selected thickeners showed greater affinity towards clay pigment than calcium carbonate. The influence of the selected thickeners on coating mixtures behaviour at low shear rate was also investigated. In coating mixture based on clay, it was found that HASE (hydrophobically modified alkali swellable emulsion) thickener that has the highest adsorption led to more effective thickening. All the selected thickeners showed moderate effect on the viscosity of the coating mixture based on GCC. The presence of thickeners also produced the coated paper with smooth and homogeneous surfaces, revealed by SEM observation.

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1. Introduction

Paper and paperboard are coated in order to improve their surface and subsequent printing performance. The coating mixtures are highly concentrated water based suspensions containing inorganic pigments such as clay and calcium carbonate, binder, soluble co-binders and thickeners, and other additives. When a coating mixture is applied to the paper, the wet coating will be subjected to dewatering and penetration into the base paper. Since paper is a porous substrate made of cellulose fibres, dewatering begins at the moment of coating application due to water absorption through the fibre walls and capillary penetration into the pores of the base paper [1]. The speed of penetration is dependent on several factors, such as the pore structure of the base paper, surface tension and viscosity of the water phase, and surface chemical properties of the base paper [2].

To prevent too rapid dewatering occurring, many different types of natural as well as synthetic water-soluble polymers have been used as thickeners. These thicken-

ers provide a viscofying effect on the coating mixture mainly by thickening the aqueous phase of the suspension. Polymers also interact with the other components in the mixture and improve the water retaining characteristics [3, 4]. Many researchers [5–7] proved that the interaction between pigments and water-soluble polymers (thickeners) has a significant effect on coating rheology, coating structure and consequently the final coated paper [6, 8]. The forces contributing to the colloidal interaction can be divided into the electrostatic repulsion forces between charged particles, steric repulsion forces resulting from the adsorbed polymer chains and depletion forces due to nonadsorbed polymers [2, 9].

The adsorption behaviour of various natural thickeners (including carboxymethyl cellulose and starch) onto clay coating pigment has been the subject of several studies [9–12]. The results indicated that these thickeners behave differently towards the pigment, affecting the viscosity of coating mixture in different manners. The viscosity the coating mixture does not only result

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TABLE I Thickener compositions

Name	Supplier	Compositions
T 1	BASF	25% aqueous dispersion of copolymer based on acrylate and carboxylic acid
T 2	BASF	Copolymer of acrylic and acrylamide water in oil emulsion
T 3	Ciba Chemicals	Aqueous solution of carboxylated polymer
T 4	Rohm and Hass	HASE (hydrophobically modified alkali swellable emulsion)

from the thickeners in the water phase, but also from their interaction with pigments.

The use of synthetic thickeners is steadily increasing in the paper coating industry. They have been designed to interact with the surface of the pigments in the coating mixture [13]. Little is known about their adsorption on pigments or their influence on particle-particle interactions. In this work, we have focused on the interaction between various synthetic water retention agents (i.e., thickeners) and coating pigments, in an attempt to improve the understanding of the thickening mechanisms.

2. Experimental

2.1. Materials

The coating mixture used in this study consisted of pigment, dispersant, binder and thickener only. The pigments were a standard grade of English China clay, SPS, obtained from Imerys UK, and Ground Calcium Carbonate, Hydrocarb 90-ME 78%, pre-dispersed slurry supplied by OMYA Croxton + Garry. The dispersant used was sodium polyacrylate (Polysalz S), supplied by BASF Germany. A copolymer based on n-butylacrylate, styrene and acrylonitrile, Acronal S 360 D, also supplied by BASF Germany, was used as a binder. Four various synthetic thickeners, were obtained from BASF, Ciba, and Rohm and Hass, respectively (see Table I). Polydiallyldimethyl ammonium chloride (PDADMAC) as a standard cationic polyelectrolyte was obtained from Aldrich.

2.2. Characterization approaches

2.2.1. Determination of adsorption isotherms of polymer thickeners on clay and GCC

The clay was dispersed in 0.01 M NaCl solution with 0.25 pph (pph = part per 100 parts of dry pigment) sodium polyacrylate at a solids content of 65% and pH 8.5. The solids content was adjusted to 60% and pH 8 (typical of paper coating suspension). The dispersed clay slurry was equilibrated for 24 h. The suspension was diluted with distilled water to a clay concentration of 30%. Then, various amounts of thickeners, ranging from 0.01 to 0.6 pph, were added into the suspension. The mixtures were stirred for a further 5 min and transferred to sealed polyethylene bottles in water bath maintained at 25°C for 18 h to ensure the equilibration be reached. Afterwards, the coating suspension was centrifuged at 4000 rpm for 90 min.

The supernatant of the suspension was sampled, and the concentration of the un-reacted (i.e., non-adsorbed) thickener was determined with a standard cationic polyelectrolyte PDADMAC using a Mutek colloidal Titrator (PCD 03).

Ground calcium carbonate was supplied as slurry of 78% solids content. The suspension was diluted to 30%, then examined following the same procedure as in clay.

2.2.2. Rheological experiments

The coating mixture used to study the rheological properties contained 100 pph clay, 10 pph acrylic copolymer latex binder (Acronal S801, BASF). The clay was dispersed in distilled water in the presence of 0.25 pph sodium polyacrylate at a solids content of 65% and a pH of 8.5. The suspension was diluted to 60% and pH was adjusted to 8. The amount of thickeners added was varied from 0.01 to 0.2 pph or 0.11 to 2.21 mg/g pigment. The suspensions were then stirred for another 5 min. The rheological properties, at low shear, were measured using a rotary viscometer (Rheometer model ERV-8) at 25°C. The viscometer measured the torque necessary to overcome the viscous resistance to the rotation. A direct read-out of viscosity in centipoises was given.

2.2.3. Surface structure characterization using scanning electron microscope

Coated paper samples were prepared by coating 66 g/m² base paper using a laboratory blade coater. The coating mixture used consisted of 100 pph clay or GCC and 10 pph Acronal S801 binder. The solids content was adjusted to 50% and pH 8. The paper Samples were supercalendered at 50°C with a pressure of 87.5 kN/m in two nips using a pilot supercalender available in the Department of Paper Science at UMIST. A TOPCON SM300 Scanning Electron Microscope (SEM) was used to reveal the surface morphology of the coated samples.

2.2.4. Characterization of surface roughness

A Parker Print-Surf roughness tester (model ME 90) was used to obtain the S-10 values. Measurements were carried out by clamping the paper sample against a standard soft black rubber backing under a pressure of 980 kPa. The mean gaps between the sheet of paper and the flat rubber were measured, and the results of the test were expressed in micrometres.

3. Results and discussion

3.1. Adsorption isotherms of various polymer thickeners on pigments

Figs 1–4 show the adsorption isotherms of thickeners 1 to 4 onto clay (SPS) and GCC at pH 8. As can be seen, the amount of thickeners adsorbed onto clay and GCC was increased as the concentrations of thickeners increased. There is a significant difference in adsorption capacity among those thickeners at the similar addition dosage. All the selected thickeners show greater affinity towards clay pigment than calcium carbonate.

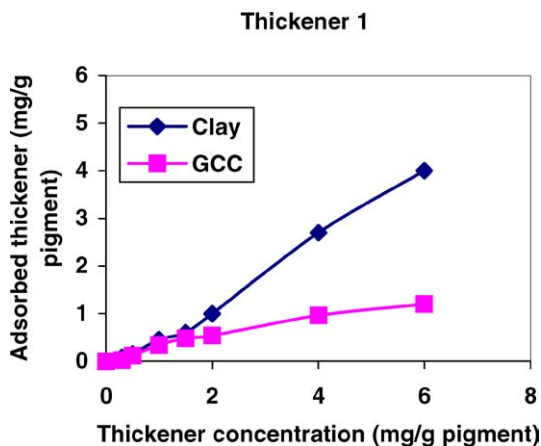


Figure 1 Adsorbed amount of thickener 1 onto clay (SPS) and GCC at pH 8 and 30% solids content.

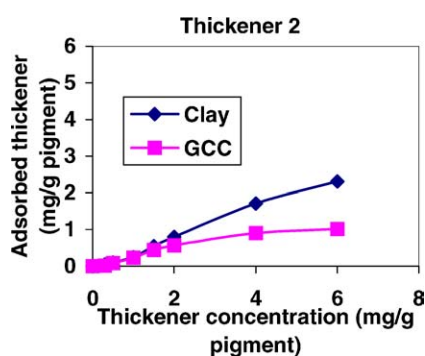


Figure 2 Adsorbed amount of thickener 2 onto clay (SPS) and GCC at pH 8 and 30% solids content.

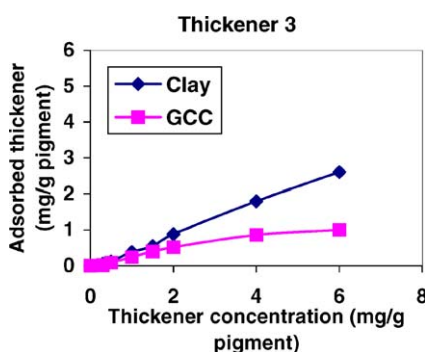


Figure 3 Adsorbed amount of thickener 3 onto clay (SPS) and GCC at pH 8 and 30% solids content.

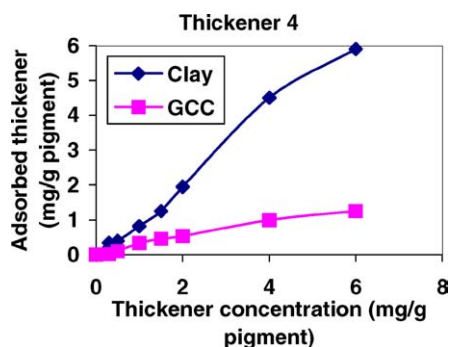


Figure 4 Adsorbed amount of thickener 4 onto clay (SPS) and GCC at pH 8 and 30% solids content.

Clay pigments have proven to be more structure creating than calcium carbonate, due to their shape, higher aspect ratio and layered characteristics [14]. It is likely that the polymeric thickener chains preferably adsorb on the cationic edge of clay platelets. A coating mixture based on ground calcium carbonate, however, did not create such a structure, due to its limited interaction with the thickener chains. This is consistent with previous studies based on natural polymeric thickener [5, 6].

Apparently, the selected thickeners belong to two groups. One group (thickeners 1 to 3) is conventional acrylate thickeners and another (thickener 4) is hydrophobically modified alkali swellable emulsion (HASE). HASE thickener has higher adsorption than the other types of thickeners. Thickeners 2 and 3 (based on acrylamide and carboxylated polymers) have relatively low adsorption on clay pigment and behaved similarly; whereas Thickener 1 has an intermediate effect. There are no appreciable differences between the adsorption isotherms of the selected thickeners onto GCC pigment. Thickener 2 shows slightly higher adsorption than the other thickeners.

It should be pointed out the determination of adsorption of polymer thickeners was indeed performed in the presence of free dispersant in the system. Since the adsorption of dispersant is an equilibrium process, implying the existence of some free dispersants in the aqueous phase. However, the effect of the free dispersant on colloidal titration is trivial. The principle of the titration relies on the complex formation between standard polyelectrolyte (i.e., PDADMAC) and free polymer thickeners. Such complex association becomes more significant for the polymer with relatively long chains or colloidal particles. In other words, the titration is sensitive to polymers with high molecular weights. Apparently, the molecular weight of polymeric thickeners tends to be higher than that of dispersant. Consequently, the polyelectrolytes were mainly associated with polymeric thickeners instead of the free dispersants in the system. From the results of adsorption, no any dispersant was detected by colloidal titration in the absence of thickeners (i.e., the control samples). This further indicates little association between standard polyelectrolyte and dispersant.

It has been reported that other techniques such as colorimetric method has also been used to determine the adsorption of thickeners on clay in the presence of dispersant, and positive results were obtained [9–12]. Therefore, the influence of dispersant on adsorption behaviour of thickeners appears to be limited.

3.2. Effect of thickeners on rheological behaviour of clay-based coating mixtures

Figs 5–8 show the viscosity of the clay-based coating mixtures as a function of shear rate in the presence of various amounts of Thickeners 1 to 4. Clearly, the coating mixtures behave as shear thinning in the range of shear rate studied. As the amount of the polymer added increases, the viscosity increases. The higher the

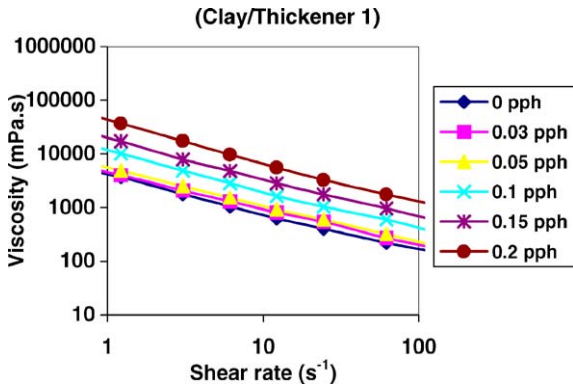


Figure 5 Effect of thickener level on low shear viscosity of coating mixture based on clay/Thickener 1 at pH 8 and 60% solids content.

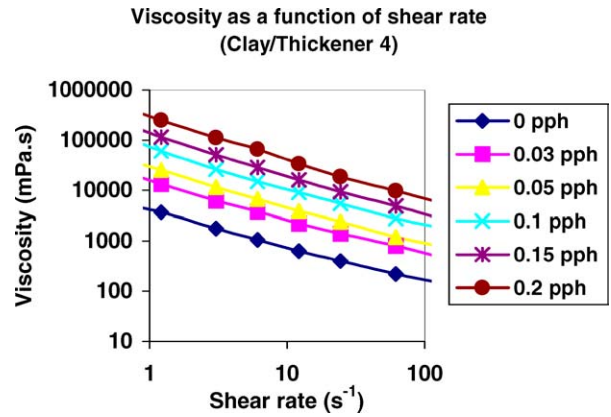


Figure 8 Effect of thickener level on low shear viscosity of coating mixture based on clay/Thickener 4 at pH 8 and 60% solids content.

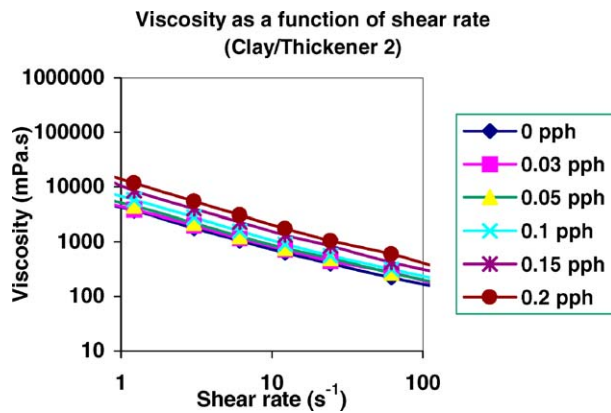


Figure 6 Effect of thickener level on low shear viscosity of coating mixture based on clay/Thickener 2 at pH 8 and 60% solids content.

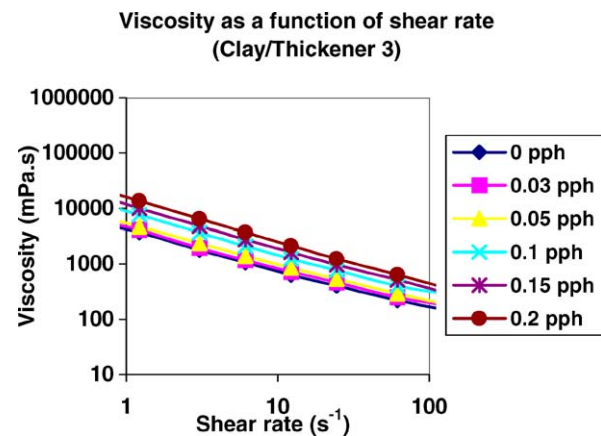


Figure 7 Effect of thickener level on low shear viscosity of coating mixture based on clay/Thickener 3 at pH 8 and 60% solids content.

viscosity, the more significant the network formation between the clay and the thickener might occur [6, 7]. HASE thickener (i.e., Thickener 4) generated the highest viscosity values.

A network structure is created within the coating mixture when it is not subjected to any deformation forces. As a deformation force is applied to the coating mixture, the network will start to break into aggregates. The strength of this network structure depends on the different interactions among coating mixture components. In the current situation, the interaction is mainly attributed to the bridging of clay pigments with the adsorbed polymeric thickeners.

Acrylic thickeners are often supplied in the form of very mobile dispersions with a low pH. In the acid pH range, the acid groups contained in the polymer chain remain un-dissociated, and is present in the form of dispersed spherical coils. With an increase in pH the carboxyl groups dissociate and donate protons, which cause them to become anionic. The formation of anionic charges along the polymer chain causes it to stretch out owing to mutual repulsion, and water molecules are attracted to the polymer chain and become attached to it. The dispersed thickener particles then dissolve, which allows them to unfold their effects. It only takes a few minutes to dissolve them completely. Maximum viscosity is achieved when all acid groups are completely neutralised [2]. The high number of acid groups presents in the acrylic emulsion polymer probably accounts for the improved viscosity at low shear over the natural thickeners.

The pronounced high viscosity caused by the selected thickeners is related to their strong adsorption onto pigment particles, as shown in adsorption results (Figs 1–4). As the polymer chains adsorb on the surface of the pigment particles, the particles are bounded together via a bridging mechanism, leading to a higher degree of cross-linking within the entire system [2].

It is interesting that the addition of thickener 4 (HASE), which has the highest adsorption amount on clay, substantially increases the viscosity of the clay coating mixture (see Fig. 8), implying there is a correlation between adsorption capacity and rheological behaviour for the coating mixture containing polymer thickeners. HASE (known also as associative thickener) is a water-soluble polymer containing some hydrophobic pendent chains. In addition to the strong affinity towards clay pigment, the hydrophobic groups in the thickener tend to associate each other in water to form a structure similar to micelle [15, 16]. The associative interaction between the hydrophobic side chains increases the degree of internal coordination of the entire system. The mobility of the aqueous phase is reduced due to intramolecular and intermolecular cross-linking. As a result, the coating mixture has an extremely high viscosity at low shear. This means that even a small amount of the addition of this thickener will produce coating mixtures with the desired viscosity and runnability.

3.3. Effect of thickeners on rheological behaviour of GCC-based coating mixtures

Figs 9–12 show the viscosity of the coating mixtures, based on GCC, containing various amounts of Thickeners 1 to 4 as a function of shear rate. There is only a slight increase in viscosity as the addition of polymer increases. The low adsorption amount of the thickeners onto GCC pigment seems to have not created such network structure as done in clay-based coating mixture. Consequently, when the coating mixture

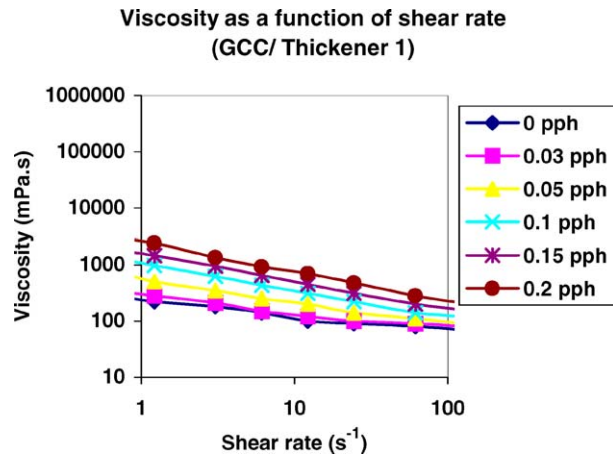


Figure 9 Effect of thickener level on low shear viscosity of coating mixture based on GCC/Thickener 1 at pH 8 and 60% solids content.

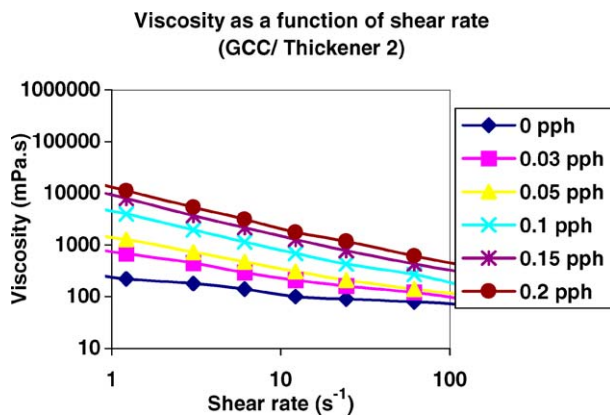


Figure 10 Effect of thickener level on low shear viscosity of coating mixture based on GCC/Thickener 2 at pH 8 and 60% solids content.

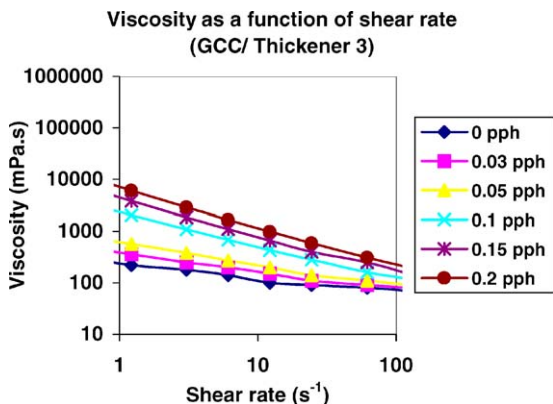


Figure 11 Effect of thickener level on low shear viscosity of coating mixture based on GCC/Thickener 3 at pH 8 and 60% solids content.

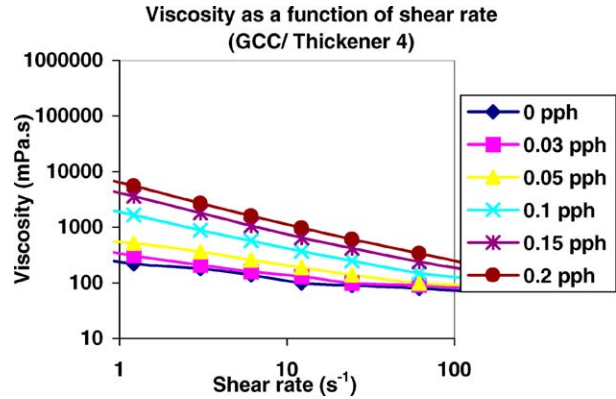


Figure 12 Effect of thickener level on low shear viscosity of coating mixture based on GCC/Thickener 4 at pH 8 and 60% solids content.

was subjected to shear forces, there is no detectable resistance to the applied force, which was reflected by low viscosity readings. Among four thickeners, Thickener 2 shows a slightly better increase in the viscosity of the coating mixtures, compared with other types.

3.4. Surface structures characterized using SEM

Fig. 13 is the SEM image of the surface morphology of the paper coated with clay-based pigment without thickener. It shows that the clay platelets are oriented randomly and the coating layer follows the tangent of the underlying fibres giving an open and rough surface. Figs 14 and 15 are the electron micrographs of paper coated with coating mixtures containing 0.2 pph of thickeners 2 and 4, respectively. It is shown that smooth and homogeneous coated paper surfaces have been obtained. The greatest smoothing effect has been generated with the use of Thickener 4. The adsorption isotherm of Thickener 4 on clay has already showed a great affinity of the thickener towards clay pigment, which has also increased the viscosity of the coating mixture. Consequently, a more bulky coating and a higher coating hold have been achieved.

The SEM image (Fig. 16) of the paper coated with GCC-based pigment without thickener revealed the unidentified particle shape of Hydrocarb pigment, some cracks and rough and open surface. The addition of thickener has been found to generate a more uniform and smooth surface—similar to those obtained in clay systems. Fig. 17 presents one of the SEM images of GCC systems as an example, which contained 0.2 pph of Thickener 4. In contrary to the clay system, Thickener 2 seems to generate a more uniform and smooth surface (Fig. 17), compared with Thicker 4 (Fig. 18). It should be addressed that the coating weight in all SEM micrographs were attempted to maintain at the same levels; and there is no significant changes in coating weights for the samples observed under SEM.

The results of Parker Print-Surf roughness have been included in the captions of Figs 13 to 18. Obviously, the surface roughness has been improved for

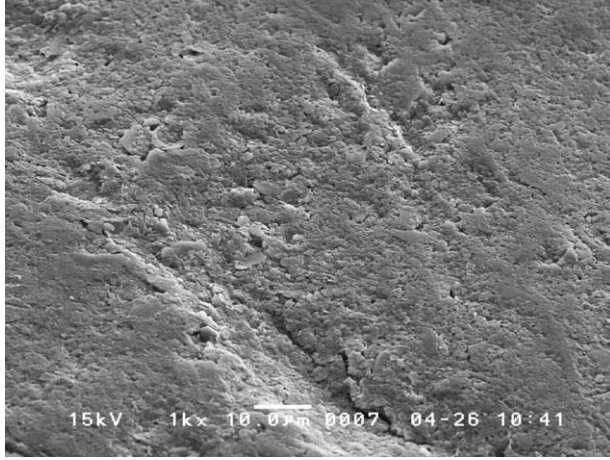


Figure 13 Scanning electron micrograph of paper coated with clay based pigment (Without thickener) and supercalendered at 87.5 kN/m and 50°C (Parker Print Surf. Roughness is 1.69 micron). Magnification = 1000×.



Figure 16 Scanning electron micrograph of paper coated with GCC based pigment (without thickener) and supercalendered at 87.5 kN/m and 50°C (Parker Print Surf. Roughness is 1.75 micron). Magnification = 1000×.

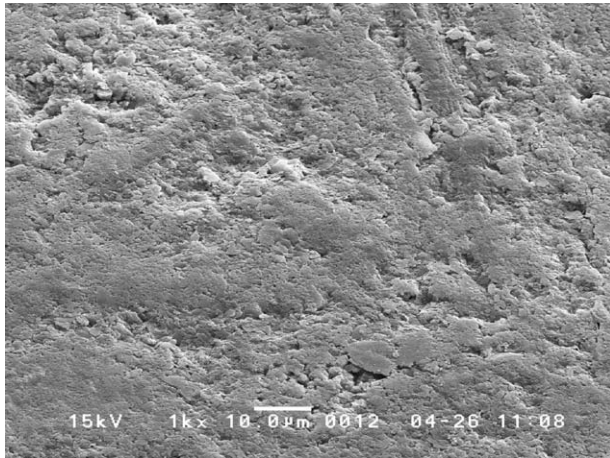


Figure 14 Scanning electron micrograph of paper coated with sample clay based pigment having 0.2 pph of thickener 2 and supercalendered at 87.5 kN/m and 50°C (Parker Print Surf. Roughness is 1.4 micron). Magnification = 1000×.

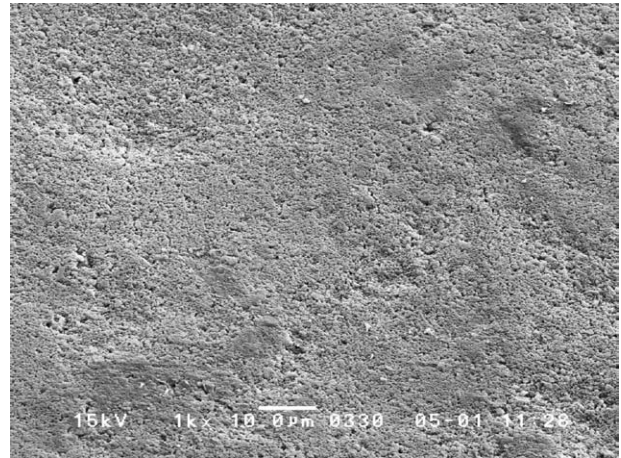


Figure 17 Scanning electron micrograph of paper coated with sample GCC based pigment having 0.2 pph of thickener 2 and supercalendered at 87.5 kN/m and 50°C (Parker Print Surf. Roughness is 1.44 micron). Magnification = 1000×.

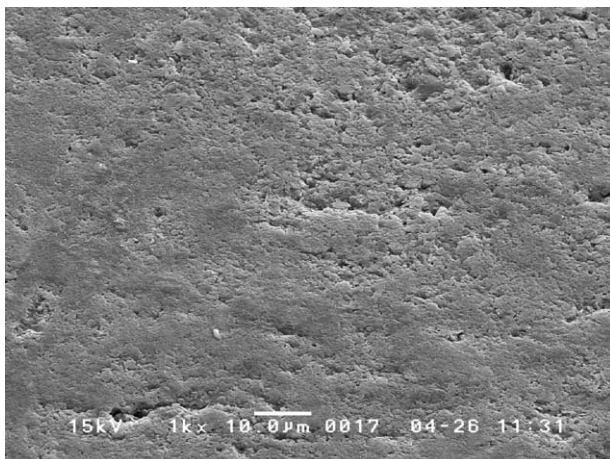


Figure 15 Scanning electron micrograph of paper coated with sample clay based pigment having 0.2 pph of thickener 4 and supercalendered at 87.5 kN/m and 50°C (Parker Print Surf. Roughness is 1.2 micron). Magnification = 1000×.

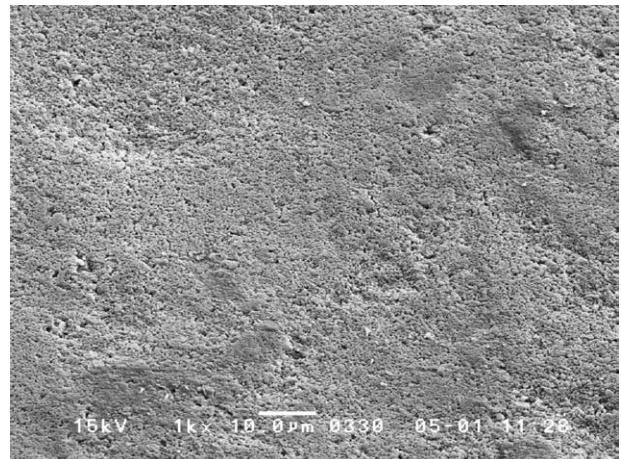


Figure 18 Scanning electron micrograph of paper coated with sample GCC based pigment having 0.2 pph of thickener 4 and supercalendered at 87.5 kN/m and 50°C (Parker Print Surf. Roughness is 1.69 micron). Magnification = 1000×.

the samples containing thickeners whereas clay samples appeared to be even smoother than those GCC samples.

4. Conclusions

The conclusions from this work are:

- Polymeric thickeners have different affinities towards mineral pigments, depending on polymer compositions and surface structure of the pigment.
- All the selected thickeners showed greater affinity towards clay pigment than calcium carbonate.
- Adsorption or interaction between thickeners and pigment plays a vital role in controlling rheological behaviour or water retention in paper coating processes.
- Higher adsorption (e.g., HASE as thickener) tends to produce more effective thickening (i.e., high viscosity of coating mixtures).
- Smooth and homogeneous coated paper surfaces have been achieved with the aid of polymeric thickeners.

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