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Phase behavior and rheology in water and in model paint formulations thickened with HM-EHEC: influence of the chemical structure and the distribution of hydrophobic tails

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Abstract

The phase behavior and rheology of aqueous solutions of hydrophobically modified ethyl(hydroxyethyl) cellulose have been investigated. Effects of variations in the chemical structure of the hydrophobic tails grafted to the polymer backbone were followed. When the length of the polymer hydrophobic tails was increased the effects caused by association between different polymer chains became more pronounced. This was manifested by an increased tendency of the solution to phase separate, a higher viscosity, and a more elastic rheological response. The higher elasticity and viscosity was ascribed to slower polymer dynamics following from stronger hydrophobic associations. A separation of chemically different polymer chains into two coexisting phases was strongly promoted by modification with long hydrophobic tails. It was found that one of the coexisting phases contained highly substituted polymer chains, while in the other phase, less substituted polymer chains were found. It is proposed that this type of phase separation occurs because the highly substituted polymer chains have a pronounced tendency to form a network.

Model paint formulations prepared with the different polymers showed that an increasing length of the polymer hydrophobic tails slowed down the dynamics of the formulation. This was manifested as a higher thickening efficiency (a smaller amount of polymer material was needed to obtain the desired viscosity), and a more pronounced shear-thinning behavior of formulations comprising polymers with long hydrophobic tails. Compared to the simpler systems, which only contained polymer and water, the model paint formulations were less prone to phase separation. It is suggested that, in the paint formulation, surfactants, latex particles, pigment, and fillers increase the number of possible association sites for the polymer hydrophobic tails. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Hydrophobically modified polymer; Associative thickener; Ethyl(hydroxyethyl) cellulose; EHEC; Phase behavior; Viscosity; Rheology; Paint formulation

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1. Introduction

Associative polymers are a class of polymers that have found a widespread use in technical formulations. Their main function is as thickening compounds, and thus, they are added in order to obtain a desired consistency. Polymers belonging to this group are amphiphilic, containing lyophilic as well as lyophobic segments (Glass, 1989; Landoll, 1982). In an aqueous solution hydrophilic segments are responsible for the hydration and swelling, while the hydrophobic parts of the polymer chain minimize the contact with water by assembling in aggregates (cf. the micellization process of surfactants) (Cabane, Lindell, Engstrom & Lindman, 1996). As a result, hydrophobic modification of the polymer chains may decrease the viscosity of its aqueous solution. This is commonly seen at low concentrations where different polymer chains have a low probability to interact. This observation has been attributed to *intra*-aggregation of individual polymer chains, and the accompanying reduced size of the polymer coils (Bock, Siano, Valint & Pace, 1989; Gelman, 1987; Strauss, 1989; Tanaka, Meadows, Philips & Williams, 1990). However, at higher concentrations *inter*-aggregation becomes increasingly more important, and already at a concentration in the vicinity of the overlap concentration, c^*, of the unmodified parent polymer the viscosity is increased substantially by hydrophobic modification (Schaller, 1985; Semenov, Joanny & Khokhlov, 1995; Shaw & Leipold, 1985).

The polymer used in the present investigation, hydrophobically modified ethyl(hydroxyethyl) cellulose

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(HM-EHEC), is a technically important associative thickener that can be obtained in different grades. A common feature of different HM-EHEC fractions is that they all are cellulose ethers to which a low amount of hydrophobic side chains have been attached by a chemical reaction (Boström, Invarsson & Sundberg 1992). A typical grafting density of hydrophobic moieties is less than 5 per 100 repeating glucose units of the polymer chain. A growing commercial interest, but also more basic scientific interests regarding associative polymers, has recently prompted investigations regarding HM-EHEC. These studies dealt with the rheology and phase behavior of HM-EHEC in an aqueous solution. Focus was on the influence by a third additive (such as salt, alcohol (Thuresson, Nilsson & Lindman, 1996), or surfactant (Joabsson, Rosén, Thuresson, Piculell & Lindman, 1998; Thuresson & Lindman, 1997; Thuresson, Lindman & Nyström, 1997). Comparisons were always done with corresponding solutions based on the unmodified analogue in order to trace the effects of the modification step. Less work has been devoted to effects of a *variation* in the hydrophobic modification (density or type). Therefore, we have in the present investigation varied the length of the hydrophobic moiety in a controlled way, and followed changes in phase behavior and rheology of the quasi-binary solution (polymer + water). From a technical point of view it is important to know how an associative thickener influences more complex solutions. For this reason, some simple experiments (stability and rheology) in model paint formulations were also performed. Here interactions of the polymer chains with surfactants, latex particles, pigments, fillers, etc. can be anticipated.

2. Experimental

2.1. Materials

The cellulose used for the synthesis of the (HM-)EHEC polymers was supplied by Borregaard (Borregaard SVS 19T). Chloroethane was supplied by Hydro Polymers AB (Stenungsund, Sweden). Epichlorohydrin of Puriss grade was obtained from Fluka. Tintetrachloride ($SnCl_4$) of Puriss grade was purchased from Merck. Epoxyethane (EO) and nonylphenol (NP) were supplied by Akzo Nobel Surface Chemistry AB (Stenungsund, Sweden). Dodecanol (C_{12}), tetradecanol (C_{14}), hexadecanol (C_{16}), and a mixture of hexadecanol and octadecanol (C_{16-18}) were all obtained from Condea. Their trade names are Nacol 1296, Nacol 1495, Nacol 1695 and Nafol 1618, respectively. All have a purity which is better than 95% (w/w), except Nafol 1618 which is sold with the specification that beside 63 ± 4% (w/w) hexadecanol and 33 ± 4% (w/w) octadecanol, the mixture may also contain $< 0.2\%$ (w/w) C_{12}, $< 2\%$ (w/w) C_{14}, $< 3\%$ (w/w) C_{20}, and $< 0.2\%$ (w/w) C_{22}. Diethyleneglycol monobutyl ether (BDG) was of 97%-purity and purchased from BDH. Acetone of pro analysis grade was obtained from Merck.

The following components were used to formulate the model paints; a defoamer from BYK Chemie (trade name Byk 022), a dispersing agent from Rohm & Haas (trade name Tamol 731), a preservative from Angus Chemie GmbH (trade name Canguard), a filler from Omya (trade name Hydrocarb), a pigment from Kronos AS (trade name Kronos 2190), and a binder from Vinamul (trade name Vinamul 3650).

2.2. Synthesis

The hydrophobically modified EHECs were synthesized according to a standard procedure (Boström et al., 1992).

2.3. Purification

The purification of the synthesized polymers from by-products originating from the reaction process was made in several steps. First the polymer products were washed with hot water containing 10% (w/w) Na_2SO_4. The temperature (95°C) of the water was far above the cloud point of the polymer. At these conditions only a small fraction of the polymer material is soluble in water. In a recent investigation it was found that at equilibrium (at such high temperatures) the polymer-rich phase, which has a concentration of 20–30% (w/w), is in equilibrium with a phase of a much lower polymer concentration containing only about 20% dry weight of the total polymer material (Joabsson et al., 1998). Salt, and in particular salt with highly charged ions, like SO_4^{2-}, is expected to reduce the solubility of EHEC significantly. By taking into account that the equilibrium situation is far from reached we expect to lose insignificant quantities of the polymer via the rinsing water, while reducing the content of NaCl and low molecular weight poly(ethyleneglycol) (PEG). After washing with hot water each polymer sample was dried and ground into granules with a size of ca. 0.3 mm. To get rid of remaining PEG and hydrophobic material which not has been successfully attached to the polymer chains, the dry granules were washed with acetone under vigorous stirring for 30 min. After washing, the product was collected by vacuum filtration with a Büchner funnel. This procedure was repeated two or three times. After the final acetone aliquot had been removed by filtration the polymer powder was dried, and later dissolved in water to a concentration of ca. 1% (w/w). This solution was centrifuged during 1 h at ca. 10 000*g* to eliminate water insoluble impurities, such as non-modified cellulose. In the final step of the purification procedure, the supernatant was dialyzed against an excess of Millipore water for several days with a repeated exchange of the dialysis water, to get rid of small water soluble impurities (remaining salt, traces of PEG etc.). The dialysis was performed by using a Spectra/Por® membrane tubing with a molecular

Table 1
The substitution degrees of ethyleneoxide (MS_{EO}), ethyl (DS_{ethyl}), and hydrophobic tails ($MS_{hydrophobe}$) of each of the polymer samples given as average numbers of substituents per repeating glucose unit. Independent repeated determinations render an uncertainty in the numerical values of about 5%. The abbreviations given in the 'Hydrophobe' column refers to the unmodified parent EHEC (0), HM-EHEC modified with, nonylphenol groups (NP), C_{12} groups (C_{12}), C_{14} groups (C_{14}), C_{16} groups (C_{16}), and with C_{16}–C_{18} groups (C_{16-18}). Values within brackets are determined for polymer samples after the dialysis, while the other numbers refer to the polymer samples before the dialysis step

Hydrophobe	MS_{EO}	DS_{ethyl}	$MS_{hydrophobe}$
0	2.1	0.8	0
NP	2.1	0.8	(0.0079)
C_{12}	2.1	0.8	0.0086 (0.0090)
C_{14}	2.1	0.8	0.0082 (0.0074)
C_{16}	2.1	0.8	0.0081 (0.0068)
C_{16-18}	2.1	0.8	0.0091

weight cut off of 6–8000. After the dialysis the polymer material was recovered by freeze-drying.

2.4. Characterization

The degrees of substitution of hydroxyethyl and ethyl groups, $MS_{EO} = 2.1$ and $DS_{ethyl} = 0.8$, were determined by gas chromatography following degradation of the products with HBr in glacial acetic acid (Stead & Hindley, 1969. The given values (MS_{EO} and DS_{ethyl}) correspond to the average numbers of EO and ethyl groups per sugar unit, respectively. The substitution degrees of hydrophobic tails (C_{12}, C_{14}, C_{16}, $C_{16}{-}{18}$), $MS_{hydrophobe}$, were determined by a procedure given by Landoll (1982). In one HM-EHEC sample (hydrophobically modified with NP), $MS_{hydrophobe}$ was determined by measuring the absorption of light at 275 nm with a UV-vis spectrophotometer using phenol in aqueous solution as a reference. All numbers (MS_{EO}, DS_{ethyl}, $MS_{hydrophobe}$) for the six different polymers are summarized in Table 1. Below the different polymers will be referred to as EHEC, HM(NP)-EHEC, HM(C_{12})-EHEC, HM(C_{14})-EHEC, HM(C_{16})-EHEC, and HM(C_{16-18})-EHEC, respectively.

2.5. Methods

All samples (except the model paint formulations) were prepared by weighing the different components into test tubes which were sealed with Teflon tightened screw caps. If possible, the samples were carefully mixed for an extended time (several days) at a temperature where they did not phase separate. After complete mixing each sample was equilibrated at the temperature of interest.

The model paint formulations were prepared by slowly adding the thickener (the (HM-)EHEC polymer) to the water under vigorous stirring with a magnetic bar. After about 3 h the thickener was completely dissolved. A 'pigment paste' was prepared by adding part of the defoamer, the dispersing agent, the preservative, the filler, and the pigment to the thickener solution. The mixture was dispersed with a mixer from Diat. The rotating part of the mixer had a diameter of 4 cm and the mixing was performed at 3000 rpm for 20 min. The binder and the remaining part of the defoamer were then added to the pigment paste under vigorous stirring. Finally, the paint was stirred for another 20 min (see also Table 3).

(HM-)EHEC polymers in aqueous solution have a reversed temperature dependency and a lower critical consolute temperature. The behavior is unexpected from simple thermodynamic considerations, and in passing we note that different theoretical models have dealt with this subject (Goldstein, 1984; Karlström, 1985; Karlström, Carlsson & Lindman, 1990; Kjellander & Florin, 1981). Because of the concomitant scattering of light when the solution phase separates this temperature is often referred to as the cloud point, T_{cp}. In the present investigation the T_{cp} was taken as the temperature where the solution first became hazy as determined by visual inspection. The determinations were conducted on 1% (w/w) solutions in spectrophotometer cuvettes immersed in a temperature controlled water bath. The T_{cp} was approached by increasing the temperature in steps of 2°C with a waiting time of 20 min after each temperature step to allow for thermal equilibrium before observation of the samples.

In the phase studies the samples were carefully equilibrated and macroscopically separated at the temperature

Table 2
The relative weight of the two coexisting phases (including water) and the concentration of HM-EHEC, c_p, in the top and the bottom phases in samples that phase separated macroscopically at 30°C. The values of the average hydrophobic modification degree, $MS_{hydrophobe}$, of the HM-EHEC chains in each phase is also given. 'TP' refers to top phase, 'BP' to bottom phase and 'mean' refers to the average value of both phases. Two numbers given in the same box corresponds to independent phase separations and composition analyses. Upper and lower halves is for HM-EHEC substituted with C_{14} and C_{16} hydrophobic moieties, respectively

Weight fraction, BP	c_p, TP	c_p, BP	c_p, mean	MS_{hyd}, TP	MS_{hyd}, BP	MS_{hyd}, mean
C_{14}						
42% (w/w)	0.83% (w/w)	1.37% (w/w)	1.05% (w/w)	0.006	0.010	0.009
30% (w/w)	0.83% (w/w)	1.33% (w/w)	0.99% (w/w)	0.010	0.013	0.011
C_{16}						
47% (w/w)	0.62% (w/w)	1.48% (w/w)	1.03% (w/w)	0.004	0.011	0.009
52% (w/w)	0.59% (w/w)	1.35% (w/w)	0.99% (w/w)	0.004	0.010	0.009

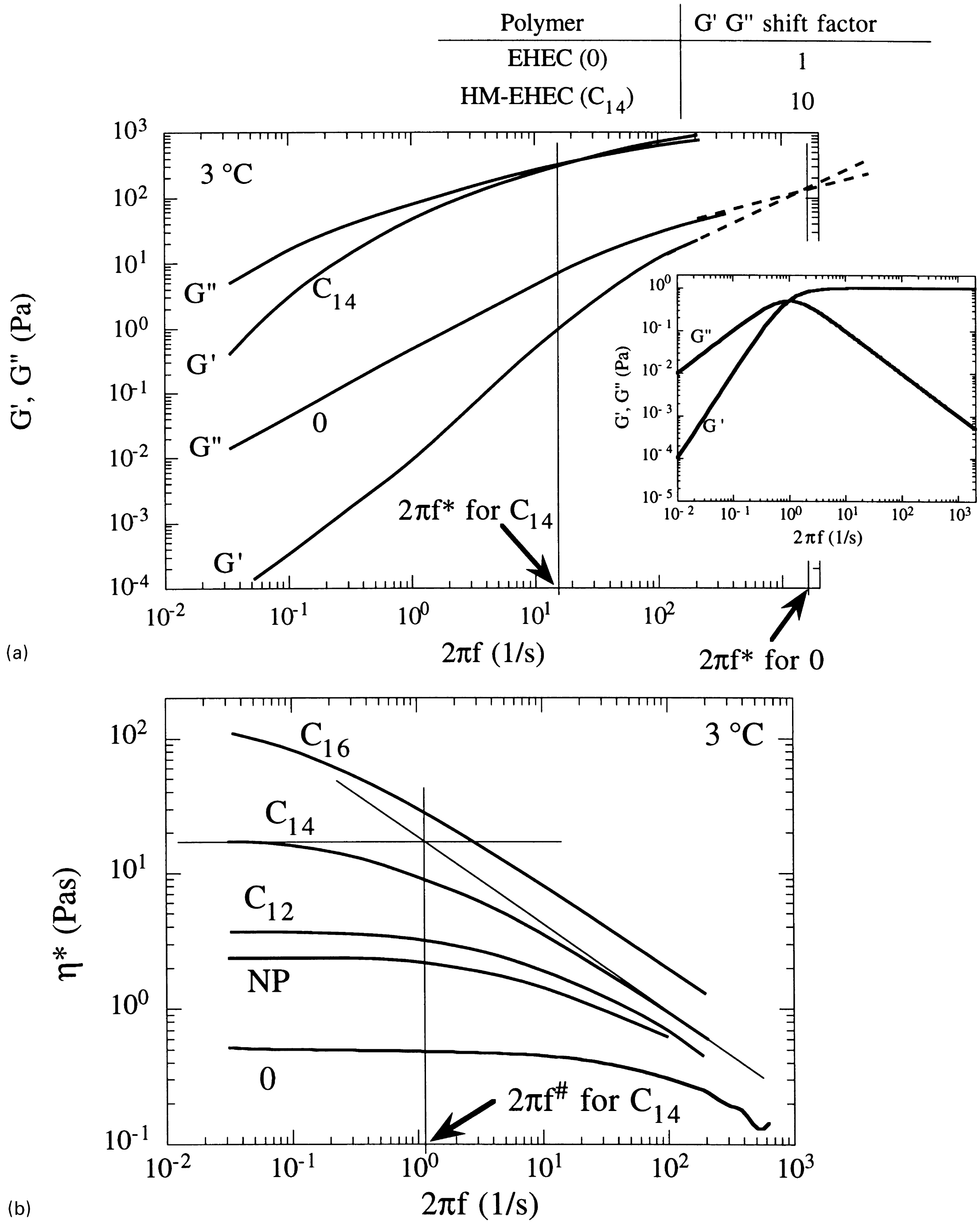

Fig. 1. (a) The viscoelastic response (G' and G'' vs. angular frequency) of a 2% (w/w) EHEC solution (0) and a 2% (w/w) HM-EHEC solution modified with C_{14} chains (C_{14}). The cross over angular frequencies used to calculate the characteristic times τ^* are indicated. For the EHEC solution the cross over was estimated by a linear extrapolation of G' and G''. Note that G' and G'' for HM(C_{14})-EHEC (upper set of curves) have been shifted upwards. The insert shows the suggested evolution of G' and G'' by the Maxwell model (see text). $G_\infty = 1$ Pa and $\tau^* = 1$ s were used in the calculation. The measurements were performed at 3°C. (b). The complex viscosity, η^*, from oscillatory shear experiments vs. angular frequency for 2% (w/w) aqueous solutions of the different (HM-)EHECs. The angular frequency, $2\pi f^{\#}$, used to calculate the characteristic time $\tau^{\#}$ is indicated for the solution prepared with HM(C_{14})-EHEC. The full lines represents, from bottom to top, unmodified EHEC (0), HM-EHEC modified with nonylphenol groups (NP), with C_{12}, C_{14} and C_{16} groups. The measurements were performed at 3°C.

of interest (30°C). If needed, the separation process was speeded up with a centrifuge. During centrifugation the temperature was kept at 30 ± 0.5°C. The polymer concentration in each phase was determined by freeze-drying and weighing. The average hydrophobic modification degree of the polymer material in each phase was determined by either of the two procedures described above.

The rheological measurements were performed with a

StressTech rheometer from Rheologica equipped with a 4 cm, 1° cone and plate system. The temperature of the sample during a rheological measurement was controlled to within ± 0.1°C by an external water bath connected to the measuring geometry. Measurements were performed at (HM-)EHEC concentrations of 1% (w/w) or 2% (w/w). For samples with a polymer concentration of 1% (w/w), and for measurements on the solvent mixtures containing BDG and water at different mixing ratios, the rheometer was put in the constant shear mode. For these solutions the Newtonian plateau, characterized by a shear rate independent viscosity, was always reached.

In order to slow down polymer dynamics and to facilitate the determination of the cross-over times, τ^* and $\tau^\#$, (defined below) a (HM-)EHEC concentration of 2% (w/w) was employed. The rheometer was put in the oscillatory shear mode, and all measurements were performed in the 'linear' regime, where the response was independent of the applied stress. An oscillatory shear measurement reports the storage, G', and loss, G'', moduli as a function of the frequency, f, of the oscillation. The complex viscosity, η^*, was calculated as $\eta^* = \sqrt{G^2 + G''^2}/2\pi f$. The low frequency limit characterized by a Newtonian behavior (viscosity independent of f) was reached for all samples except for the aqueous solution containing 2% (w/w) HM(C_{16})-EHEC (see Fig. 1(b)).

In this investigation two methods, which both use a cross-over from a viscous to an elastic behavior of the solution, have been used to indirectly probe polymer dynamics. τ^* is the characteristic time corresponding to the inverse angular frequency, $1/2\pi f^*$, where $G' = G''$. At frequencies higher than f^* the response is mainly elastic. An elastic response indicates that on the experimental time scale, the polymer chains do not have the time to relax to the new equilibrium position due to the applied deformation. In the low-viscous samples (i.e. the samples prepared with EHEC, HM(NP)-EHEC, and HM(C_{12})-EHEC) this frequency is not directly accessible with the present rheometer. Here, the presented τ^* values have been estimated by linearly extrapolating the evolution of G' and G'' vs. frequency in a log–log representation, Fig. 1(a). An alternative way to probe the crossover from a viscous to an elastic behavior of the solution is to determine the angular frequency at which the viscosity profile (η^* vs. $2\pi f$) changes from being Newtonian to shear thinning, Fig. 1(b). The characteristic time, $\tau^\# = 1/2\pi f^\#$, corresponding to the inverse of this angular frequency, is for the present samples longer than τ^*, and the two methods become complementary. Indeed τ^* and $\tau^\#$ follow the same trend (cf. Fig. 6).

If the rheological data from a polymer system are determined by only one relaxation time, the simplest model of a viscoelastic fluid, namely the Maxwell model, can be used to describe the frequency dependencies of the dynamic moduli. Then the evolutions of G' and G'' with f are given by:

$$G' = G_\infty \frac{(2\pi f)^2}{1 + (2\pi f)^2} \qquad \textit{and} \qquad G'' = G_\infty \frac{2\pi f}{1 + (2\pi f)^2}.$$

Here G_∞ is the plateau value of G' at high frequencies. In this model τ^* equals $\tau^\#$ In particular it follows from the Maxwell model that $\log(G')$ has the slope $+2$ as a function of $\log(f)$ and $\log(G'')$ has the slope $+1$ in the terminal zone (low frequencies), while at frequencies above τ^*, $\log(G'')$ has the slope -1 while G' approaches G_∞. However, this model cannot satisfactorily describe our data as is evident from the different shapes of the curves (compare data in Fig. 1(a) with insert). Rather the frequency dependencies of the dynamic moduli indicate that a range of relaxation times has to be used to give a proper representation. In light of the expected polydispersity regarding the molecular weight as well as the chemical structure of the (HM-)EHEC polymers this is not surprising. Thus, the reason for the differences in τ^* and $\tau^\#$ can probably be traced to the fact that the relaxation in solutions of (HM-)EHEC is due to a range of different processes with different characteristic times.

In the industry one method to characterize paints is to measure the viscosity at one low and one high shear rate. The two values are referred to as the 'Stormer' and 'ICI' viscosities, respectively. Here the Stormer viscosity was measured with a Stormer viscometer at a shear rate in the range 10–100 s^{-1}. The values are given in Krebs units (KU). The conversion of the numerical values from KU to the SI-quantity Pa s can to our knowledge only be made with an approximate formula (Reisser, M. & Oleinitec, A.B., private communication).[1] These measurements were made in accordance with the ASTM D 562-81 standard. The ICI viscosity was obtained at a shear rate corresponding to approximately 12 000 s^{-1} and is usually given in Poise. However, here we have chosen to present these data in Pa s to facilitate comparison with other measurements (10 P = 1 Pa s). The measurements were made in accordance with the ASTM D 4287-94 standard.

The model paints were characterized according to color acceptance (ASTM D 5326), leveling (ASTM D 4062-81), spatter resistance, gloss (ASTM D 523-89), and storage stability. For the color acceptance test a universal colorant was added to the paint formulation. After shaking the paint for 5 min it was applied to a white chart. A 'rub-out test' in which one part of the surface of the painted chart was rubbed while another part was untouched was performed. The paint was judged by means of color differences between the two different parts, and by a comparison with standard charts the paint formulation was given a rating of 1–10; 1 corresponds to a poor resistance, while 10 to an excellent resistance to mechanical rubbing.

Leveling of the model paint formulations was measured by the 'Lenata draw-down method'. The results were

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[1] Over the viscosity range of 0.2–2.1 Pa s the following equation may be used to convert Stormer viscosity values from Krebs units to Pa s: $\ln(\mathrm{KU}) = 1.1187 + 0.8542 \ln(193.8\ \mathrm{Pa\,s} + 36) - 0.0443[\ln(193.8\ \mathrm{Pa\,s} + 36)]^2$. Over the viscosity range of 2.1–5.0 Pa s it is more appropriate to use: $\ln(\mathrm{KU}) = 1.8118 + 0.596 \ln(193.8\ \mathrm{Pa\,s} + 36) - 0.0206[\ln(193.8\ \mathrm{Pa\,s} + 36)]^2$. Here KU corresponds to the viscosity at 25°C in Krebs units, while Pa s is the viscosity at 25°C in Pa s.

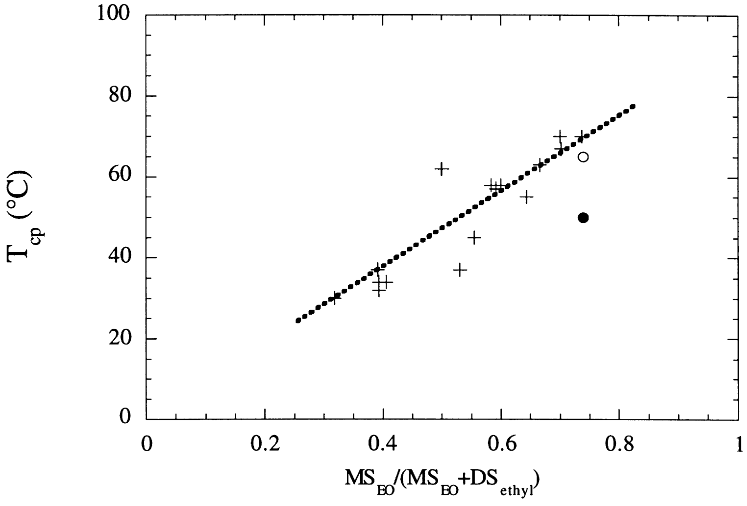

Fig. 2. The cloud point of a collection of different EHEC samples (1% (w/w)) plotted against the fraction of hydroxyethyl groups, $MS_{EO}/(MS_{EO} + DS_{ethyl})$. The data is reproduced from Thuresson et al. (1995). An open circle and a filled circle represent the unmodified EHEC and the HM(NP)-EHEC corresponding to the samples in the present investigation, respectively. The dashed line is only drawn as a guide to the eye.

compared with standards and given ratings from 1 to 10 where 1 is a low degree of leveling and 10 is an excellent degree of leveling.

The spatter resistance was measured by applying the paint formulation with a roller onto a 'wall' with an area of 0.25 m^2 at a frequency of 60 strokes/min. The spatter was collected on a test chart located below the rolled surface, and the result was compared with a standard. Again the paint formulation was given a rating from 1 to 10 where 1 is a poor performance and 10 corresponds to a low spatter and excellent spatter resistance.

To evaluate the gloss properties of the paint formulation it was applied to a glass panel. The reflectance was measured after 10 days at an angle of 60° and is reported in percentage of the reflectance of a standard surface of polished glass.

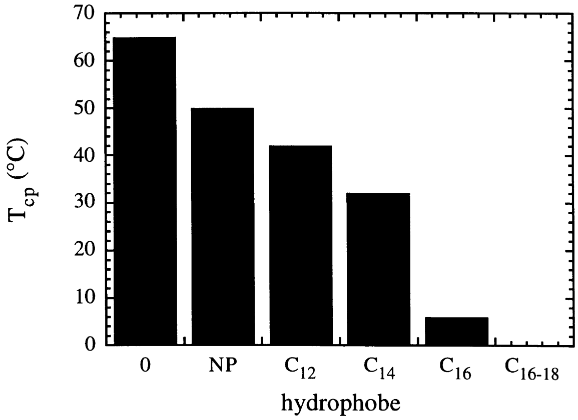

Fig. 3. The cloud point, T_{cp}, for the different (HM-)EHEC samples in 1% (w/w) aqueous solutions. From left to right; unmodified EHEC (0), HM-EHEC modified with nonylphenol groups (NP), with C_{12}, C_{14} and C_{16} groups, and with C_{16}–C_{18} groups(C_{16-18}). The one phase region of the last sample, HM(C_{16-18})-EHEC, is not experimentally accessible ($T_{cp} < 0$°C).

The storage stability of the paint was estimated by a repeated measurement of the Stormer viscosity after 28 days of storage at 50°C.

3. Results and discussion

This section is divided into three parts, each of which contains a discussion of the effect of hydrophobic modification of the polymer chains.

3.1. Phase behavior

It has been found that for EHEC (without hydrophobic modification) the T_{cp} can be correlated to MS_{EO} and DS_{ethyl} in a way such that T_{cp} increases with increasing MS_{EO}, while it decreases with increasing DS_{ethyl}, Fig. 2 (Thuresson, Karlström & Lindman, 1995). It was also found that the conversion of EHEC to HM(NP)-EHEC had a drastic influence on T_{cp}. This is also found in the present investigation, Fig. 3. The longer the aliphatic chain, the more pronounced is the shift in T_{cp} (relative to that of the unmodified EHEC). It is important to note that the overall hydrophilic/hydrophobic balance is only slightly changed by a variation in hydrophobic tail length, and consequently this cannot be the explanation to the pronounced shifts in T_{cp}. It is therefore reasonable to invoke a mechanism in which the phase separation is influenced by the association of polymer hydrophobic tails into micellar aggregates (Thuresson & Joabsson, 1999). These connect different polymer chains into a network. The swelling of the polymer matrix is then restricted by finite extension of the part of the cellulose chains connecting different micellar aggregates. This favors the formation of one phase that is concentrated in polymer. This phase is in equilibrium with a phase depleted in polymer (cf. a bridging flocculation in a polymer/particle system or the restricted

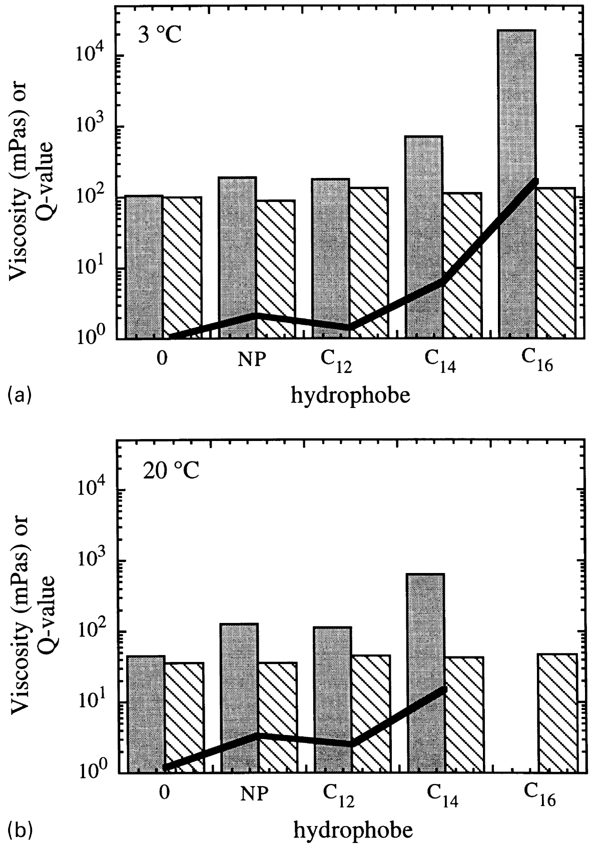

Fig. 4. (a) The bar to the left in each collection (gray) reports the viscosity of the polymer in water, and the bar to the right (striped) reports the viscosity in a 80:20 mixture of water and BDG (see text). To compensate for the higher viscosity of the solvent (water/BDG compared to water), the numerical values for the viscosity in water/BDG mixtures were divided with 2.7 before presentation (cf. insert Fig. 5). The line reports on the '*Q*-value', which is the ratio between the viscosity of the aqueous polymer solution and the viscosity of the polymer dissolved in the water/BDG mixture. The different groups of bars correspond from left to right to, unmodified EHEC (0); EHEC modified with nonylphenol groups (NP), with C_{12}, C_{14}, and C_{16} groups. All solutions contain 1% (w/w) polymer and the measurements were performed at 3°C. The reported values correspond to the viscosity at the Newtonian plateau and they were obtained with the rheometer put in the constant shear mode. (b) Same as Fig. 4(a), but at 20°C. At this temperature it was impossible to measure the viscosity of the aqueous solution of HM(C_{16})-EHEC due to a phase separation. Note that the solution of this polymer in the water/BDG mixture has a one phase behavior.

swelling of a covalently crosslinked gel). The outlined scenario requires the hydrophobic associations to be strong enough to overcome the decrease in entropy that accompanies the formation of the phase concentrated in polymer. However, the unfavorable reduction of the entropy is significantly reduced if both phases contain approximately the same polymer concentration. This has recently been discussed by Annable and Ettelaie (1994) in an experimental and theoretical study, based on a simple Flory–Huggins approach. They discovered that a mixture of a hydrophobically modified polymer with its unmodified analogue might phase separate. After the phase separation the two different polymers are enriched in separate phases. Below we will refer to this behavior as a segregative phase separation, or alternatively that the polymers phase separate segregatively (Piculell & Lindman, 1992).

Table 3
Recipe for the preparation of the model paints formulation. *x* is the weight per mille (‰w/w) of thickener in the model formulation. The different components are added to the mixture in the same order as listed in the table (top to bottom). Note that the defoamer is added in two portions. For details, see Section 2.5

Water (‰ w/w)	$243.2 - x$
Thickener, HM-EHEC (‰ w/w)	x
Defoamer, Byk 022 (‰ w/w)	2
Dispersing agent, Tamol 731 (‰ w/w)	6.5
Preservative, Canguard (‰ w/w)	1
Filler, Hydrocarb (‰ w/w)	110
Pigment, Kronos 2190 (‰ w/w)	180
Binder, Vinamul 3650 (‰ w/w)	454.3
Defoamer, Byk 022 (‰ w/w)	3
$\sum$ (‰ w/w)	1000

Based on this knowledge, mixtures prepared with the HM(C_{16})-EHEC and the HM(C_{14})-EHEC polymers, respectively, were macroscopically phase separated at 30°C into two liquid phases in equilibrium. In each sample, the two phases had similar volumes (Table 2). Each phase was analyzed with respect to polymer concentration and the average hydrophobic modification degree. Despite the uncertainty in the data, the trend is clear and it was found that the samples separated segregatively with one phase containing HM-EHEC chains with a higher substitution degree than the chains residing in the other phase. Thus, the HM-EHEC sample contains a range of polymer molecules differing in molecular weight, a normal situation for all polymer samples, and also in chemical composition, and the 'binary' aqueous solution has a behavior reminiscent of a multi-component system. This conclusion was also drawn in a previous publication in which the phase behavior of EHEC and HM(NP)-EHEC at high temperatures was investigated (Joabsson et al., 1998). In connection with this discussion it is valuable to comment on the fact that although T_{cp} for a 1% (w/w) HM(C_{14})-EHEC solution is reported to be ca. 32°C (Fig. 3), a macroscopic segregative phase separation is observed already at 30°C (Table 2). This reflects the difficulties in observing this type of phase separation by means of the clouding phenomenon. We think the disagreement is due to the fact that in the vicinity of the phase separation temperature the two phases have similar compositions (segregative phase separation with similar polymer concentrations), differing mainly in a small variation of hydrophobic modification as shown above. Thus, at such conditions the two phases can be expected to have a similar refractive index and light is not scattered (no clouding is observed). The conjecture is that there is a risk of overestimating the true phase separation temperature by visual detection of T_{cp}. In the present HM-EHEC systems we estimate the uncertainty in the phase

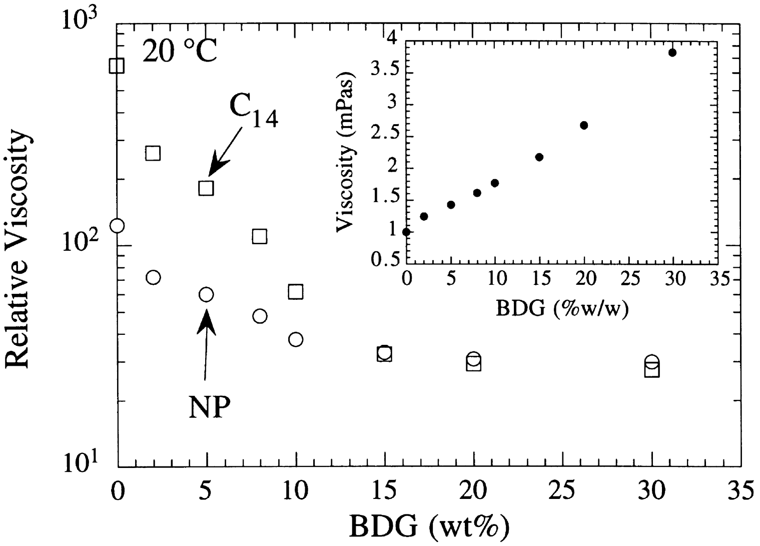

Fig. 5. The influence on viscosity of the composition of the solvent in solutions of associating HM-EHECs as exemplified with 1% (w/w) solutions of HM-EHEC modified with nonylphenol groups (NP) or with C_{14} groups (C_{14}). It can be seen that the viscosity levels off at an approximate weight mixing ratio of BDG:water corresponding to 15:85. The data are presented as a relative viscosity (the viscosity of the polymer solution divided with the viscosity of the solvent mixture). The insert reports the viscosity of the BDG:water mixture at different compositions. All measurements were performed at 20°C with the rheometer put in the constant shear mode.

separation temperature, by using the clouding phenomena, to ± 5°C.

3.2. Rheology in quasi-binary solutions

Usually the expectation is that the viscosity of an aqueous solution of a hydrophobically modified polymer increases with the length of the hydrophobic tails. The higher viscosity has been ascribed to slower motions of individual polymer chains as the residence time of the hydrophobic tails in ‘polymer micelles’ increases (Annable, Buscall, Ettelaie & Whittlestone, 1993; Leibler, Rubinstein & Colby, 1991). The present results follow that trend. Measurements performed on aqueous solutions at two different temperatures (3 and 20°C) are reported in Fig. 4. The viscosity for the HM(C_{16})-EHEC solution at 20°C could not be measured as a natural consequence of the phase separation which occurred already at a much lower temperature (cf. Fig. 3). Fig. 4 also gives the viscosity of the different polymers in a solvent mixture composed of 80% (w/w) water and 20% (w/w) BDG. The knowledge that a ‘saturation level’ of BDG usually is observed was decisive when the ratio between water and BDG was chosen. This is exemplified in Fig. 5, where data for 1% (w/w) HM(C_{14})-EHEC and 1% (w/w) HM(NP)-EHEC solutions are presented. Initially the viscosity decreases strongly, but at about 15% w/w BDG the decrease levels off and above that BDG concentration the relative viscosity of both the investigated polymer solutions is constant within the experimental uncertainty. The effect of BDG can be rationalized by comparison with the well-known influence of surfactants on aqueous solutions of hydrophobically modified polymers. These are regarded to break intermolecular hydrophobic associations by ‘individually dissolving’ hydrophobic patches (or hydrophobic tails) within micellar-like aggregates (Piculell, Thuresson & Ericsson, 1995). Indeed, BDG has an amphiphilic structure and is expected to adsorb at polar/non-polar interfaces. As a consequence of decreased hydrophobic associations, addition of BDG can also be anticipated to decrease the tendency to segregative phase separation. In particular the phase separation of an aqueous solution of HM(C_{16})-EHEC was inhibited in the water/BDG mixture and the viscosity of that solution could be determined (Fig. 4(b)). It is also interesting that all (HM-)EHEC polymers, independent of the nature of the polymer hydrophobic tail, give virtually the same viscosity when they are dissolved in the water/BDG mixture. This indicates that the different (HM-)EHEC polymers have similar molecular weights, and that the differences observed between the *aqueous* solutions can be referred to variations in the aggregation process of the polymer hydrophobic tails. Thus, the *Q*-value, which is the ratio between the value of the (Newtonian) viscosity in water to that observed in water/BDG, can be regarded as a phenomenological measurement of the influence of hydrophobic associations on the viscosity of the aqueous solution. In this way different polymer samples (variation in chemical structure of the hydrophobic tails, variation in modification degree, variation in modification pattern etc.) can be ranked. In line with this, we note that the unmodified EHEC has a *Q*-value close to 1. However, comparisons of *Q*-values should be done with care because the evolution of *Q* with polymer molecular weight has not been investigated.

Generally a shift towards longer relaxation times is expected when the polymer chains in a solution become more entangled (increased polymer concentration or higher polymer molecular weight) or when the life time of

Table 4
Summary of the observations in the model paint formulations. The different columns refer to unmodified EHEC (0), HM-EHEC modified with nonylphenol groups (NP), with C_{12}, C_{14}, and C_{16} groups, and with C_{16}–C_{18} groups ($C_{16–18}$). The numbers given for color acceptance, spatter resistance, and leveling are ratings obtained by visual comparisons to standards. 1 is poor and 10 is excellent. *x* is the ‰ (w/w) of the thickener that is needed to obtain the desired Stormer viscosity

	0	NP	C_{12}	C_{14}	C_{16}	$C_{16–18}$
x (‰ w/w)	7.5	4.5	5.75	4.5	4	3.9
Stormer viscosity (KU)	110	113	112	112	113	109
ICI viscosity (Pa s)	0.18	0.15	0.16	0.11	0.10	0.10
Colour acceptance	10	8	6	6	6	6
Spatter resistance	4	7	7	7	7	6
Levelling	1	1	1	1	1	1
Gloss (%)	24	27	26	24	26	24
Storage stability (KU)	123	120	119	120	121	119
Consistency	flowing	flowing	flowing	flowing	jelly	jelly

intermolecular hydrophobic associations becomes longer (in case of hydrophobically modified polymers). Extracted from an oscillatory shear experiment, which reports indirectly on polymer dynamics, the change in the characteristic times, τ^* and $\tau^\#$, may be taken to reflect such variations. At experimental times exceeding τ^* and $\tau^\#$ the viscous behavior of the solution dominates, while at shorter times the elastic behavior prevails. Indeed, τ^* and $\tau^\#$ increase with an increasing length of the hydrophobic tail (Fig. 6). We stress that τ^* and $\tau^\#$ not are expected to correspond to any characteristic time of any process on a molecular level, but we do believe that they capture trends correctly and therefore can be used to compare different HM-EHEC polymers. We note that a shift towards longer relaxation times, following an increased hydrophobicity of the hydrophobic tails, will on a fixed experimental time scale (as in applications) show up as a more elastic behavior of the solution.

3.3. Model paint formulations

A recipe of the formulations is given in Table 3. The concentration of (HM-)EHEC in the final mixtures varies because a paint is formulated aiming at a certain (Stormer) viscosity, rather than a certain polymer concentration (Table 4). The amount of polymer that is needed decreases when the polymer hydrophobic tails becomes longer. In other words; HM-EHECs with strongly associating hydrophobic tails have a high thickening efficiency. It is interesting to note that despite the rather extreme conditions which the model paint formulations were exposed to (50°C for 28 days was used in the storage stability test) no phase separation was observed. Rather the model paint formulations had a good stability and only minor changes in the viscosity with time could be detected (compare the storage stability column with the Stormer viscosity column in Table 4). This is in direct contrast to the results obtained in the simpler ‘binary’ solutions. We recall that certain HM-EHEC solutions phase separated already at room temperature (see Fig. 3). This can be taken as an indication of the fact that surfactants, pigments, latex particles, fillers etc. influence the aggregation process. The phase separation may be inhibited by an increased number of sites where the polymer hydrophobic tails can adsorb. However, at this stage it is too early to draw any further conclusions.

Another interesting result, which follows from Table 4, is that HM-EHEC with long hydrophobic tails give paints with a more elastic consistency as compared with paints prepared with thickeners with shorter hydrophobic tails. This correlates to the slower relaxation process with increasing strength of the inter-molecular associations which was observed as a higher elasticity by oscillatory shear measurements already in the ‘binary’ solutions. The slower relaxation process of solutions prepared with HM-EHEC modified with long aliphatic chains is also reflected in the viscosity values reported in Table 4. The more pronounced shear-thinning behavior of solutions of HM-EHEC comprising long hydrophobic tails follows from lower ICI viscosity values.

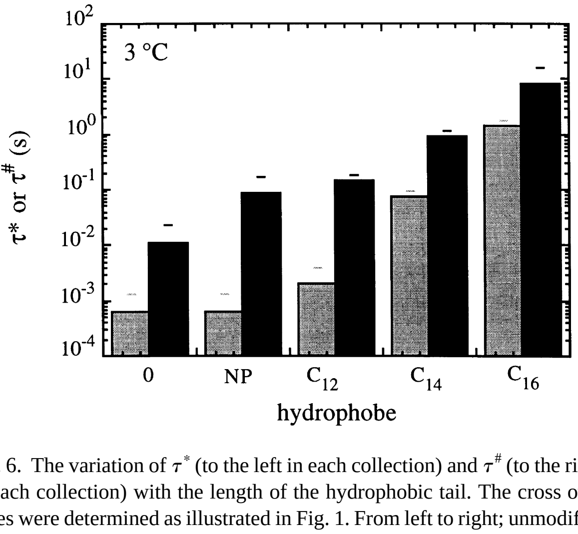

Fig. 6. The variation of τ^* (to the left in each collection) and $\tau^\#$ (to the right in each collection) with the length of the hydrophobic tail. The cross over times were determined as illustrated in Fig. 1. From left to right; unmodified EHEC (0), HM-EHEC modified with nonylphenol groups (NP), with C_{12}, C_{14}, and C_{16} groups. The line over each bar represents an estimated error. The polymer concentration was kept constant at 2% (w/w) and the temperature was 3°C.

4. Conclusions

One of the reasons why hydrophobically modified polymers have appeared on the market, and sold as thickeners, is that they often have been found to provide a better thickening efficiency in aqueous solutions than their unmodified analogues. In this paper we have in a systematic way varied the chemical structure of the hydrophobic moieties that were grafted to the polymer backbone when ethyl(hydroxyethyl) cellulose, EHEC, was converted to obtain the hydrophobically modified HM-EHEC. By changing the length of hydrophobic tails the strength of the associations between different polymer molecules was modulated. At the conditions in the present investigation—HM-EHEC with a substitution degree of $MS_{\text{hydrophobe}} = 0.008$ dissolved in an aqueous solution to a concentration of 1% (w/w)—we observed that the hydrophobic tails should contain more than 12 carbon atoms to give a thickening efficiency significantly better than that of the unmodified analogue (see Fig. 4(a)). It was also found that the strong hydrophobic associations that accompanied the modification with long hydrophobic tails resulted in solutions that were more elastic on a given time scale. This may be a problem in applications (such as water borne paints). Thus, in the design of an effective associative thickener, other aspects apart from high viscosity following strong hydrophobic associations have to be taken into account, and it is not sufficient to rank different HM-polymers only by thickening efficiency.

The literature reports that, provided inter molecular associations are strong enough; increasing water content of an aqueous solution of HM-EHEC induces a phase separation. Under such circumstances one of the phases contains virtually pure water, while most of the polymer material can be found in the other phase. The observation was rationalized in terms of a behavior reminiscent of restricted swelling of a covalently bonded gel (Thuresson & Joabsson, 1998). In the present investigation we found that also a modification of the polymer chains with tails of a quite modest hydrophobicity can induce a phase separation. The reason is an inhomogeneous distribution of hydrophobic tails among the polymer chains. At such conditions, the solution has a tendency to phase separate segregatively into one phase containing polymer chains with a high substitution degree, and the other phase containing polymer chains with a lower substitution degree. The mechanism is related to that of the ‘restricted swelling’, but in addition the tendency towards phase separation is increased because both phases have similar polymer concentration.

Finally, it is interesting to note that when the HM-EHEC polymers were in model paint formulations the tendency to segregative phase separation was decreased. One explanation to this observation can be that surfactants, latex particles, pigment, and fillers supply association sites for the polymer hydrophobic tails. This is expected to promote a single-phase behavior if the reason for a phase separation can be traced to a restricted swelling of the HM-EHEC matrix.

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