

Molecular Characterization of Alkyd/Acrylic Latexes Prepared by Miniemulsion Polymerization

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Received 4 March 2009; accepted 1 June 2009

DOI 10.1002/app.30866

Published online 28 July 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The molecular characterization of alkyd/acrylic hybrid latexes produced by miniemulsion polymerization was characterized in terms of the resin degree of grafting, acrylic degree of grafting, reacted double bonds in the alkyd, gel content, and molecular weight distribution of the sol part. A simple method based on conventional size exclusion chromatography measurements was developed to estimate the fraction of alkyd resin grafted to the acrylic polymer. The method could be applied to completely soluble hybrids and to hybrids containing gel. Also, the limits of the extraction method used in the litera-

ture to estimate the fraction of acrylic polymer grafted to the alkyd was investigated; we found that this technique only provided accurate results at high values of the acrylic degree of grafting. The combination of this information with the reacted double bonds of the alkyd (determined by iodine titration) and the molecular weight distribution of the sol polymer provided a detailed characterization of the alkyd-acrylic hybrid polymer. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 3143–3151, 2009

Key words: coatings; composites; emulsion polymerization

INTRODUCTION

Waterborne alkyd/acrylic coatings have the potential to combine the positive properties of alkyd resins (e.g., autoxidative curing, high gloss, penetration in wood) with the fast drying and color retention of acrylic latexes. Nabuurs et al.¹ studied the emulsion polymerization of acrylate monomers in the presence of alkyds, finding that as the polymerization proceeded, polyacrylates and alkyd resin separated in different particles. A more promising route to the production of waterborne polymer-polymer composites is miniemulsion polymerization.^{2–7} In this process, the alkyd resin is dissolved in the monomer mixture containing a costabilizer (a highly water-insoluble compound of low molecular weight) and dispersed with the application of energy in an aqueous solution of surfactants to obtain a miniemulsion. Then, the submicrometer miniemulsion is polymerized with the addition of an initiator, with the aim of the nucleation of most of the droplets so that they are transformed into polymer-polymer composite particles and maintain the acrylic/alkyd ratio. Wang et al.⁸ described the development of alkyd/acrylic hybrid latexes via a miniemulsion polymerization

process, obtaining stable and small particle latexes that contained acrylic and alkyd components.

It is expected that the hybrid material will present a good balance between the application properties of the alkyd resins and those of the acrylic polymers when they are in intimate contact, namely, when they form a compatible mixture. Unfortunately, alkyd resins and acrylic polymer do not form a compatible blend. Therefore, to obtain a stable composite, the acrylic polymer should be chemically linked to the alkyd (i.e., grafting the alkyd resin with the acrylic polymer). Two possible grafting routes have been proposed:⁹ (1) radical addition to the alkyd carbon-carbon double bonds and (2) abstraction of alkyd allylic hydrogens. The acrylic monomers, initiators, and reaction conditions play an important role in determining the preferred grafting route.⁹ On the other hand, excessive grafting could negatively affect the end-use properties because it could considerably reduce the number of alkyd double bonds, which are needed for the ulterior autoxidation reaction. Therefore, the determination of the extent of grafting is critical to developing a successful polymerization strategy. So far, the characterization has been limited to the fraction of acrylic polymer that contained grafted alkyd [acrylic degree of grafting (ADG)]. The method for determining ADG is based on Soxhlet extraction with a selective solvent [e.g., diethyl ether (DEE)] that dissolves the free alkyd resin and the poly(acrylate-graft-alkyd) and the assumptions that the neat acrylic polymer is not

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Contract grant sponsor: European Union Project; contract grant number: Napoleon NMP3-CT-2005.

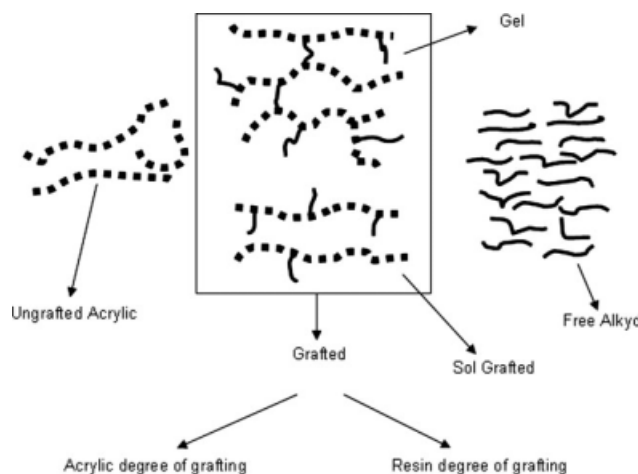


Figure 1 Scheme of the molecular heterogeneity of the acrylic-alkyd composite.

dissolved by DEE and that the undissolved part does not contain grafted polymer.⁸ This method was applied to estimate the ADG values of methyl methacrylate (MMA)/alkyd, butyl acrylate (BA)/alkyd, butyl methacrylate/alkyd; and MMA/BA/alkyd hybrid composites.^{9,10} However, assessment of the assumption that the neat acrylic polymer is not dissolved by the selective solvent has not been reported.

In most studies where the production of acrylic/alkyd composites has been investigated, almost all of the acrylic polymer had grafted some alkyd chain (i.e., ADG values closed to 100%), but a noticeable alkyd separated phase was observed in the particle morphology,^{8,10} which indicated that a large fraction of alkyd was without grafting. Figure 1 shows that ADG is an incomplete image of the acrylic-alkyd composites, which includes the neat acrylic polymer, grafted polymer, and free alkyd resin. The grafted polymer may contain both gel and soluble fractions. The resin degree of grafting (RDG) is the ratio between the amount of alkyd resin grafted to the acrylic polymer and the total amount of alkyd resin in the formulation. Because the molecular weight of the acrylic polymer is usually substantially higher than that of the alkyd resin, ADG is greater than RDG. To illustrate this point, let us consider that the average molecular weight of the acrylic chain is 200,000 g/mol and that of the alkyd resin is 10,000 g/mol; that is, there are 20 alkyd chains per acrylic chain. If 45% of the alkyd chains were grafted, as an average, each acrylic chain would have nine grafted alkyd chains, whereas 55% of the resin would remain free.

The fraction of the reacted double bonds (RDBs) in the alkyd resin is an important characteristic of the molecular characterization of the polymer because extensive crosslinking upon film formation is only possible if enough double bonds are available for auto-oxidation.

In this study, the molecular characterization of acrylic-alkyd hybrids produced by miniemulsion polymerization was studied. The gel fraction was determined by Soxhlet extraction. For the soluble part, two-dimensional chromatography is likely the technique that could give the more detailed information, provided that the solvent to separate the polymer according to their chemical composition is available.¹¹⁻¹³ However, this technique requires relatively sophisticated equipment (currently, there is only one two-dimensional chromatograph commercially available¹³). Therefore, taking advantage of the fact that the acrylic polymer did not produce any signal in the ultraviolet (UV) detector where the alkyd produced a strong UV signal, in this study, we developed a method based on conventional size exclusion chromatography (SEC) measurements using dual [UV and differential refractive index (DR)] detection. This approach could be of interest for the development of hybrid acrylic/alkyd composites in industry and for academic investigation of the basic kinetic mechanisms involved in the synthesis of hybrid polymers because valuable additional information can be obtained with commonly available equipment and a simple data treatment.

EXPERIMENTAL

Materials

Technical-grade monomers, MMA and BA, supplied by Quimidroga (Barcelona, Spain), and acrylic acid (AA), provided by Aldrich (Madrid, Spain) were used without purification. Two kinds of alkyd resin were used: a commercial Setal 293 and an experimental more reactive one, referred to as *Setal Reactive*; both were supplied by Nuplex Resins. Both alkyd resins had a similar number of double bonds per molecule (34-35 double bonds), but in the case of the Setal Reactive alkyd, a fraction of these double bonds were sterically more accessible. Stearyl acrylate (SA; Aldrich), Dowfax 2A1 (alkyldiphenyl oxide disulfonate, Dow Chemicals, Madrid, Spain), 2,2-azobis(2-methylbutyronitrile) (V59, Wako Chemicals, Zaragoza, Spain), *tert*-butyl hydroperoxide (TBHP; Panreac, Barcelona, Spain), ascorbic acid (AsAc; Panreac), and NaHCO₃ (Aldrich) were also used without purification. Gel-permeation-chromatography-grade tetrahydrofuran (THF; Scharlau, Barcelona, Spain), DEE (Sigma-Aldrich), Wijs reagent (Riedel-de Haën, Seelze, Germany), acetic acid (Aldrich), chloroform (Aldrich), sodium thiosulfate (Panreac), and starch soluble (Panreac) were used as received. Distilled water was used throughout the study.

Miniemulsion preparation and polymerization

The 50 wt % solid content miniemulsion was produced as follows. First, the organic phase was

prepared by dissolution of the alkyd resin (50 wt % on the basis of organic phase, wbop), SA (4% weight on the basis of the monomer, wbm), and V59 (1.6 wbm %) into the monomer mixture (BA/MMA/AA, 49.5/49.5/1 wt %). Then, the organic phase was poured into an aqueous solution of the surfactant (6 wbop % of Dowfax 2A1) and NaHCO_3 (0.039M) under intensive magnetic stirring (10 min at 1000 rpm) to create an emulsion. The resulting emulsion was sonicated for 15 min at power 9 and 80% duty cycle with a Branson 450 instrument (Danbury, CT). Finally, the miniemulsion was further treated (six cycles) with a two-valve high-pressure homogenizer (Niro Soavi, model NS1001L PANDA, Parma, Italy) with pressure of 410 and 41 bar in the first- and second-stage valves, respectively.

Polymerizations were carried out in batch in a 1-L glass reactor equipped with a reflux condenser, stirrer, sampling device, and nitrogen inlet. The miniemulsion was added to the reactor and kept under stirring and a nitrogen atmosphere (12–15 mL/min). We kept the reaction temperature constant at 70°C by controlling the temperature of the fluid in the jacket by means of a thermostatic bath and a heat exchanger. We carried out the postpolymerization processes at 70°C, feeding TBHP and AsAc independently over 90 min. Finally, the reaction was maintained for 30 min in batch.

Gel determination

The gel content was determined by Soxhlet extraction under THF reflux of vacuum-dried polymer samples over a period of 24 h.

RDG determination

A method to measure the mass fraction of the alkyd resin grafted to the acrylic polymer (RDG) was developed with SEC and a combination of two detectors: DR and UV absorption at 263 nm. The SEC measurements were carried out with an LC-20AD Shimadzu pump (Madrid, Spain) fitted with a set of three fractionation columns (Waters Styragel HQ2, HQ4, and HQ6, Madrid, Spain) and online DR and UV detectors (both Waters). Figure 2 shows the baseline-corrected detector signals (DR and UV at 263 nm) obtained when 1 mg/mL THF solutions of the neat acrylic polymer MMA/BA/AA [49.5/49.5/1 wt %; Fig. 2(a)] and the alkyd resin Setal 293 [Fig. 2(b)] were injected separately. Figure 2(a) shows that the UV signal of the neat acrylic polymer was almost zero, whereas Figure 2(b) shows that the alkyd resin presented a strong UV signal. The UV absorbance of the alkyd resin was mainly due to the presence of conjugated double bonds.

The determination of RDG values is based on the fact that the acrylic polymer is not detected by the

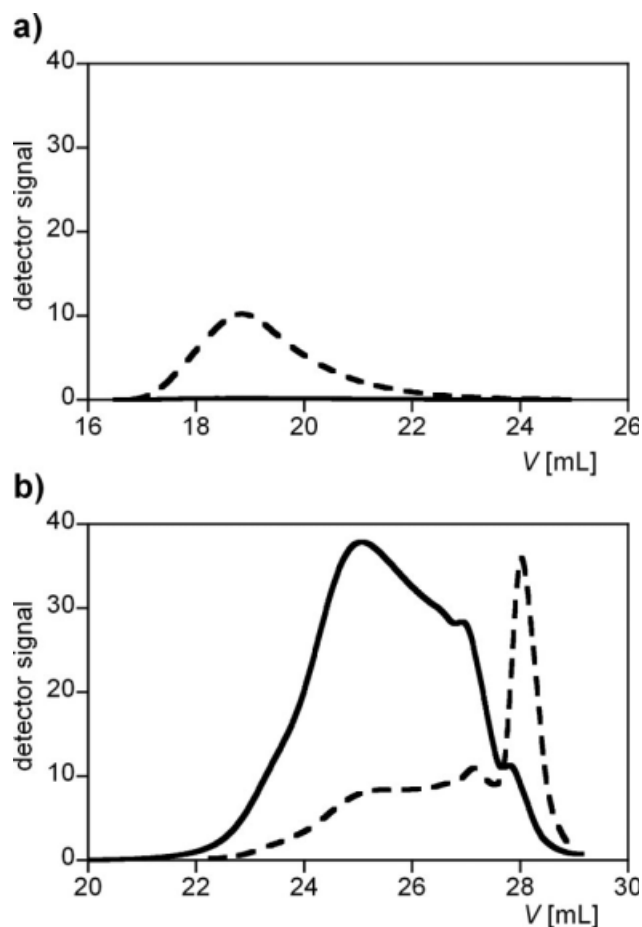


Figure 2 (—) UV at 263 nm and (- - -) DR signal for 1 mg/mL solutions of (a) the neat acrylic polymer and (b) the alkyd resin Setal 293 (V = volume).

UV sensor at a wavelength of 263 nm, and therefore, the area of the baseline-corrected UV chromatogram of an acrylic/alkyd hybrid material is proportional to the resin concentration in the sol fraction of the sample. In this study, both completely soluble hybrid polymers and hybrid polymers containing gel were considered.

In the case of hybrid samples without gel, namely, when the entire sample was soluble in THF, the RDG could be determined by direct comparison of the baseline-corrected UV chromatogram of the hybrid sample with the UV chromatogram of the original alkyd resin. Both UV chromatograms were normalized so that they had the same total area (i.e., they represented the equivalent resin concentration). Figure 3 shows the UV signal of an acrylic/alkyd hybrid obtained by miniemulsion polymerization (continuous line) and that of the original alkyd resin (dash line). The difference between both chromatograms was mainly due to the fact that the resin bound to acrylic chains increased its molecular weight, and hence, its signal was shifted toward lower retention volumes. Therefore, the surface area

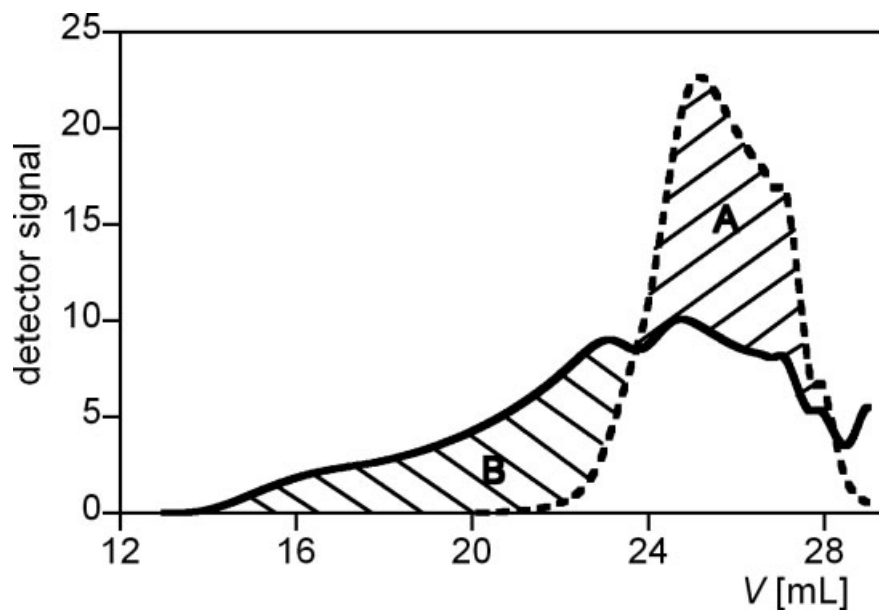


Figure 3 UV chromatograms (at 263 nm) of (—) a hybrid sample and (- - -) the alkyd resin Setal 293 (V = volume).

A was proportional to the amount of alkyd grafted to the acrylic polymer. Similarly, the amount of alkyd grafted to the acrylic polymer was linked to surface area B . The values of areas A and B may have been different because the double bonds of the alkyd resin could disappear during the grafting reactions. Consequently, for a given amount of alkyd resin, the UV signal of the hybrid polymer was lower than that of the unreacted original alkyd resin. This means that area A may have been overestimated and area B underestimated. We obtained an average of their values by making equal the area of the UV chromatogram of the hybrid sample to that of the original alkyd resin. In this way, the same values for areas A and B were obtained, which were an estimation of the actual value. Then, the RDG was estimated as follows: A/A_{resin} or B/A_{resin} , where A_{resin} is the total area of the UV trace of the original resin.

The analysis of hybrid samples containing gel was more complex because the gel was not soluble in THF, and hence, it could not be measured by SEC. Consequently, the alkyd resin grafted to the acrylic in the gel did not appear in the SEC of the sol part. This means that the UV trace of the soluble part of the hybrid resin could not be compared with that of the original alkyd resin to calculate the fraction of the grafted alkyd resin.

The characteristics of the DR and UV signal of the alkyd resin opened the possibility of overcoming this limitation. Figure 2(b) shows that the peak at a volume around 28 mL had a DR/UV signal ratio higher than 1, whereas for the rest of the chromatogram, this ratio was lower than 1. This indicated that the resin was not a pure component and that the relative content of UV-sensitive groups (i.e., the

conjugated double bonds) in this peak of the sample was much lower than in the other fractions of the alkyd resin. After analyzing the polymerized hybrid samples, we noted that the substance associated with this peak remained unaffected. For this reason, this peak was used as an internal standard for estimating the resin incorporation in the sample with a significant amount of gel.

Figure 4 illustrates the procedure. In this figure, the UV chromatograms of a hybrid sample acrylic/alkyd resin with 45% of gel and that of the original alkyd resin are plotted. The height of the chromatograms was varied to match the height of the 28-mL peak of the hybrid sample to that of the original alkyd resin. In this figure, the A/A_{resin} ratio is the fraction of alkyd resin that was grafted to the acrylic polymer (either to the gel or to the soluble part). The

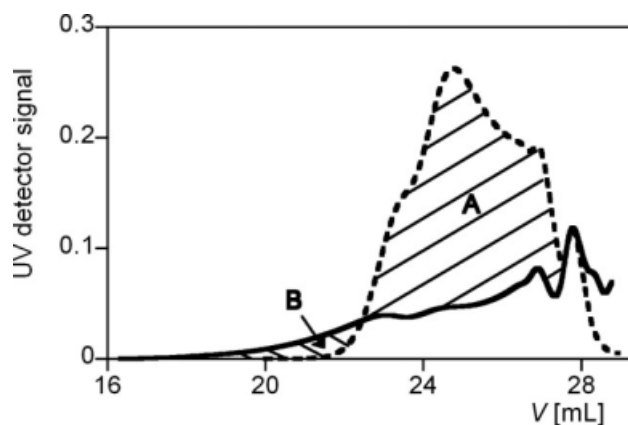


Figure 4 UV chromatograms (at 263 nm) of (—) a hybrid sample with 45% gel and (- - -) the alkyd resin (V = volume).

B/A_{resin} ratio is an estimation of the fraction of the alkyd resin incorporated to the acrylic polymer that was soluble (RDC_{sol}). Because of the reaction of the double bonds of the alkyd resin during polymerization, the B/A_{resin} ratio could be underestimated.

Molecular weight determination

The molecular weight distribution (MWD) and the corresponding average values [number-average molecular weight (M_n) and weight-average molecular weight (M_w)] of the sol part were determined with the baseline-corrected DR chromatogram and a third-order direct calibration obtained with 20 narrow polystyrene standards in the range 10^3 – 10^6 .

The MWD of the hybrids were very broad [Fig. 5(a)] because they included the relatively high-molecular-weight acrylic polymer (both neat acrylic and alkyd grafted to acrylic) and the low-molecular-weight ungrafted alkyd resin. The molecular weight of the ungrafted alkyd resin was obtained by comparison of the UV baseline-corrected chromatograms of the total hybrid sample and that of the original alkyd resin. Area C in Figure 5(b) corresponds to the UV chromatogram of the ungrafted alkyd resin ($S_{\text{UV,uA}}$). The DR baseline-corrected chromatogram for the ungrafted alkyd ($S_{\text{DR,uA}}$) was calculated as follows:

$$S_{\text{DR,uA}} = S_{\text{UV,uA}} \frac{S_{\text{DR,A}}}{S_{\text{UV,A}}} \quad (1)$$

where $S_{\text{DR,A}}$ and $S_{\text{UV,A}}$ are the DR and UV baseline-corrected chromatograms of the original alkyd, respectively. Figure 5(c) presents the DR baseline-corrected chromatogram for the ungrafted alkyd resin calculated with eq. (1) and that of the acrylic (grafted and neat) polymer calculated as the difference between the chromatogram of the total sample and that of the ungrafted resin. The corresponding MWDs are presented in Figure 5(a).

ADG determination

For samples that did not contain gel, the mass fraction of acrylic polymer containing grafted alkyd resin, defined as ADG, was determined by Soxhlet extraction with DEE, mainly because it has been reported that DEE dissolves the free alkyd resin and the hybrid alkyd–acrylic components but not the neat acrylic polymer.⁸ Filters containing the latex sample were dried in a vacuum oven at room temperature and weighed before and after the extraction. Assuming that the neat acrylic polymer was not dissolved, we calculated ADG as follows:

$$\text{ADG} = \frac{\text{Acrylic grafted to resin}}{\text{Total acrylic}} \quad (2)$$

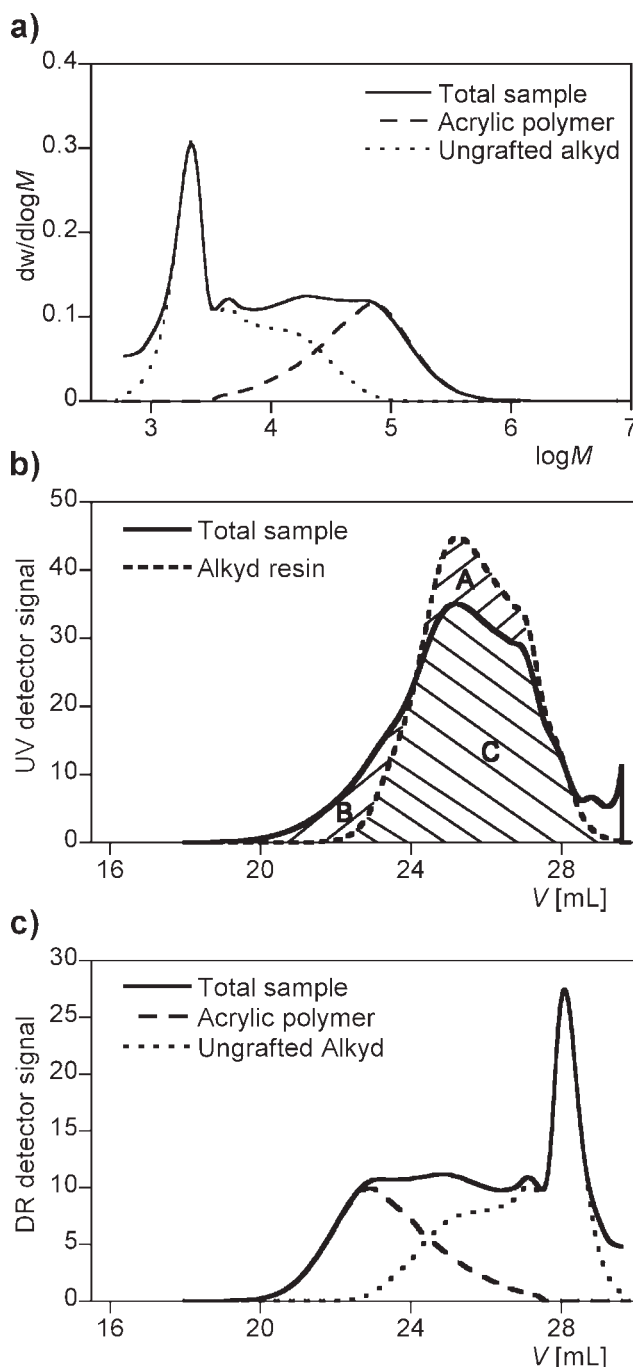


Figure 5 Calculation of MWDs: (a) MWDs of a total hybrid sample, the ungrafted alkyd resin, and the acrylic polymer; (b) UV (at 263 nm) chromatograms of the hybrid sample and the alkyd resin; and (c) DR chromatograms of the hybrid sample, the ungrafted alkyd, and the acrylic polymer (V = volume).

that is

$$\text{ADG} = \frac{(\text{Total polymer weight}) \times p_A - \text{Neat acrylic}}{(\text{Total polymer weight}) \times p_A} \quad (3)$$

with

$$p_A = \frac{(\text{monomer}_{\text{formulation}}) \cdot x}{(\text{monomer}_{\text{formulation}}) \cdot x + \text{Alkyd}_{\text{formulation}} + \text{initiator}_{\text{formulation}} + \text{emulsifier}_{\text{formulation}}} \quad (4)$$

where p_A is the mass fraction of acrylic in the dried sample, neat acrylic is the weight of the insoluble polymer after the extraction in samples without gel, and x is the acrylic conversion.

When the gel was present, ADG could not be estimated by eq. (3) because the insoluble gel may have also contained some grafted alkyd, that is

$$\text{Insoluble weight} = \text{Neat acrylic} + (\text{Total polymer weight}) \times \text{Gel} \quad (5)$$

where gel is the mass fraction of the gel in the sample. Therefore, in samples containing gel, ADG was estimated as follows:

$$\text{ADG} = \frac{(\text{Total polymer weight}) \times (p_A + \text{Gel}) - \text{Insoluble weight}}{(\text{Total polymer weight}) \times p_A} \quad (6)$$

The use of eqs. (3) and (6) to estimate ADG involved the assumption that the neat acrylic polymer was not dissolved by DEE. This point is discussed later in this article.

Total hybrid polymer (THP) content

The mass fraction of THP was estimated as follows:

$$\text{THP} = \text{ADG} \times p_A + \text{RDG} \times p_R \quad (7)$$

where p_R is the mass fraction of the alkyd in the dried sample:

$$p_R = \frac{\text{Alkyd}_{\text{Formulation}}}{(\text{Monomer}_{\text{Formulation}}) \times x + \text{Alkyd}_{\text{Formulation}} + \text{Initiator}_{\text{Formulation}} + \text{Emulsifier}_{\text{Formulation}}} \quad (8)$$

Determination of the RDBs of the alkyd resin

The fraction of RDBs of the resin was determined by iodine titration with the standard Wijs method.¹⁴

RESULTS AND DISCUSSION

Assessment of the method for RDG determination

The method for determining RDG was first tested with blends of acrylic polymers and alkyd resins with different alkyd/acrylic ratios. The first two rows of Table I present the average molecular weights of both the polyacrylic (MMA/BA/AA, 49.5/49.5/1 wt %) and alkyd resins (Setal 293) used to prepare these blends. The DR and UV chromatograms of these blends and the corresponding UV chromatogram of the original resin are shown in Figure 6. Because the acrylic polymer was not detected by the UV sensor, almost no difference between the UV chromatograms of the resin and those of the

blends was observed (Fig. 6). The predicted RDG values calculated by comparison of the two areas were close to the real one for hybrid systems containing large amounts of resin. The errors were mainly due to the presence of small-molecular-weight components (probably emulsifier, which appeared around a 30-mL volume) contained in the acrylic latex.

TABLE I
Test of the RDG Estimation Technique with Physical Mixtures of the Acrylic Polymer and Alkyd Resin (Setal 293)

Sample	Alkyd content (%)	M_n (g/mol)	M_w (g/mol)	RDG (%)
Pure acrylic	0	553,000	1,437,000	0
Pure alkyd	100	2,600	7,800	0
Mixture 1	86	2,700	132,700	1.1
Mixture 2	50	3,300	315,000	1.9
Mixture 3	34	3,100	350,000	3.9
Mixture 4	23	4,100	630,000	5.2

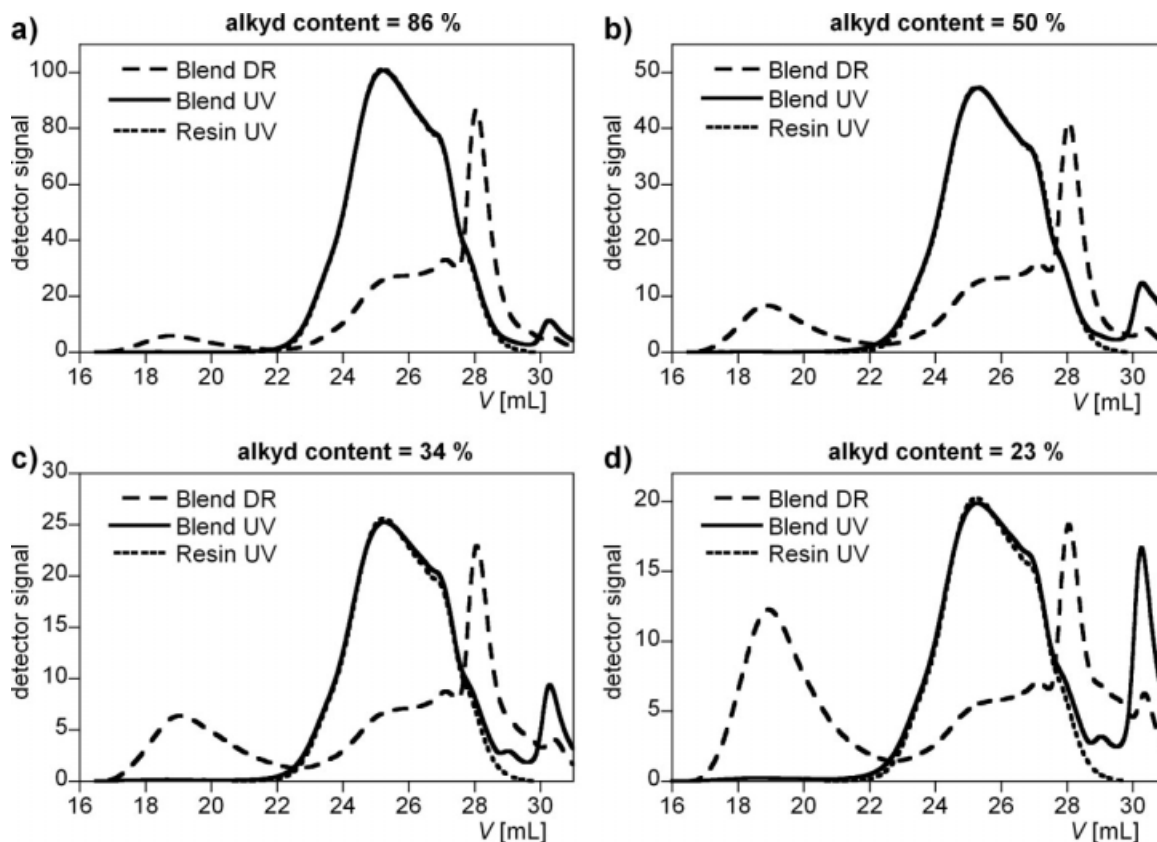


Figure 6 UV and DR chromatograms of physical mixtures of the acrylic polymer and alkyd resin and UV chromatogram of the original resin (V = volume).

Assessment of the method for ADG determination

A technique to determine the fraction of acrylic polymer that contained grafted alkyd (ADG) reported elsewhere⁸ was further investigated. In this study, the technique was tested with two physical mixtures containing alkyd resin (63 and 83 wt %) and acrylic polymer (49.5/49.5/1 wt % MMA/BA/AA). The Soxhlet extractions were carried out with DEE over 24 h. The filters were dried in a vacuum oven at room temperature and weighed before and after the extraction. Then, assuming that the alkyd resin was totally soluble in the solvent, we calculated the ADG using eq. (3). The values are presented in Table II. The method estimated that about 25% of the neat acrylic polymer contained grafted alkyd, although no graft copolymer existed in these

samples. This simply means that about 25% of the neat acrylic polymer was dissolved by DEE, and therefore, ADG was overestimated. Figure 7 shows the influence of the dissolution of 25% of the neat acrylic polymer on the estimation of ADG. At high ADG values, the error was small because the total amount of dissolved neat acrylic polymer was low, and hence, that of the dissolved neat acrylic was

TABLE II
ADG of Physical Mixtures of the Alkyd Resin (Setal 293) and Neat Acrylic Polymer Obtained by Soxhlet Extraction with DEE as the Solvent

Sample	Alkyd content (%)	ADG (%)
Mixture 5	63	26
Mixture 6	83	27

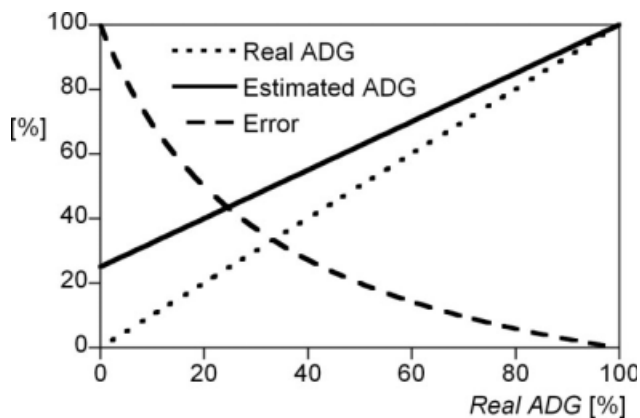


Figure 7 ADG estimation errors calculated under the assumption that 25% of the neat acrylic could be dissolved in DEE.

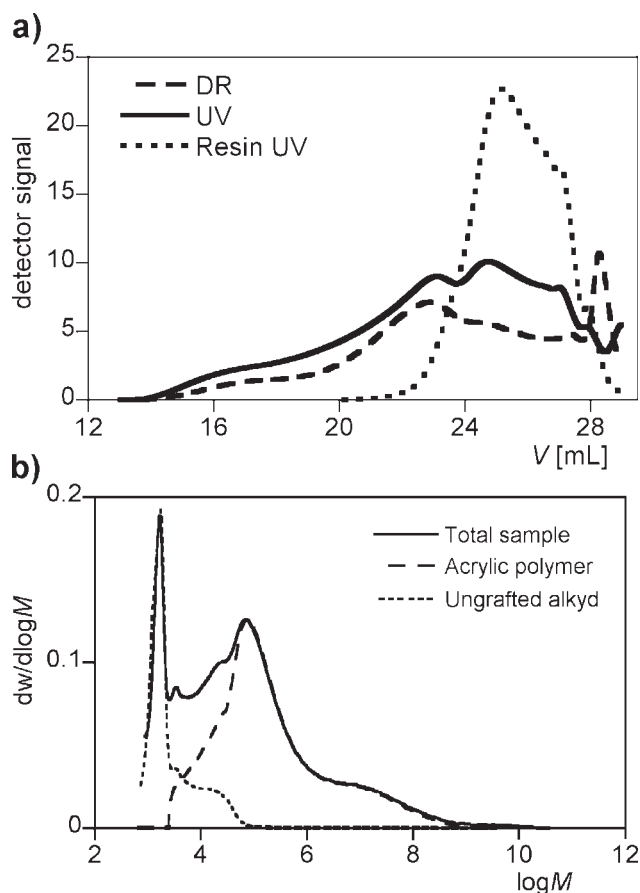


Figure 8 SEC analysis of hybrid sample A: (a) UV and DR chromatograms of the sample and UV chromatogram of the original resin and (b) MWDs (V = volume).

almost negligible. On the other hand, substantial errors could be incorporated in the ADG estimation in samples with low ADG values.

Gel-free alkyd–acrylic hybrids

Miniemulsion polymerization with the low reactive alkyd resin yielded gel-free hybrid latexes. Figure 8(a) presents the DR and UV signals of the SEC of the hybrid polymer and the UV signal of the original alkyd resin, and Table III presents the characterization results (sample A). The RDG calculated from

the SEC trace was 45%. The ADG estimated with eq. (3) was about 89%. However, as shown in the previous section, this value was overestimated. With the assumption that about 25% of the neat acrylic polymer was dissolved, the corrected ADG value was 85%; namely, a relatively small error was made with eq. (3). The value of ADG was substantially higher than the value of RDG. The reason was that the molecular weight of the acrylic chains was much higher than that of the alkyd resin; therefore, the likelihood of finding an acrylic chain containing an alkyd chain was higher than that of finding an alkyd chain grafted to an acrylic chain. The total fraction of grafted polymer was 65 wt %, and about 20% of the double bonds of the alkyd resin reacted during polymerization. MWD is presented in Figure 8(b), and the average molecular weights are given in Table III. A very broad MWD was obtained. For the total sample, the low value of M_n resulted from the relatively high amount of unreacted alkyd resin. A higher M_n value was obtained for the hybrid sample without the ungrafted resin. A very high molecular weight tail is shown in Figure 8(b), which likely resulted from intermolecular chain transfer to the polymer. Because this high-molecular-weight tail was out of the columns fractionation range (100 to 1×10^7 g/mol), the M_w value in Table III is expressed as higher than the higher standard used (3×10^6 g/mol)

Gel-containing alkyd–acrylic hybrid polymer

The miniemulsion polymerization carried out with the highly reactive alkyd resin yielded a polymer containing 45% gel. Figure 9(a) presents the DR and UV signals of the SEC of the soluble part of this hybrid polymers and the UV signal of the original alkyd resin, and Table III presents the characterization results (sample B). The RDG calculated from the SEC trace was 65%, whereas the corrected value of the ADG was 89%, which was also substantially higher than the value of RDG. The total fraction of grafted polymer was 78%, and about 15% of the double bonds of the alkyd resin reacted during

TABLE III
Summary of the Degree of Grafting Results

Sample	Resin reactivity	Gel (%)	THP (%)	ADG (%)	ADG (%) ^a	RDG (%)	RDB (%)	RDG _{sol} (%)	M_n (g/mol)	M_w (g/mol)
A	Low	0	65	89	85	45	20	45	7,000 ^b 31,000 ^c	$>3 \times 10^6$
B	High	45	78	92	89	65	15	5	3,400 ^b 15,200 ^c	36,200 ^b 81,700 ^c

^a The value was corrected under the assumption that 25% of the neat acrylic polymer was dissolved by DEE.

^b Average molecular weight of the total sample.

^c Average molecular weight of the acrylic polymer.

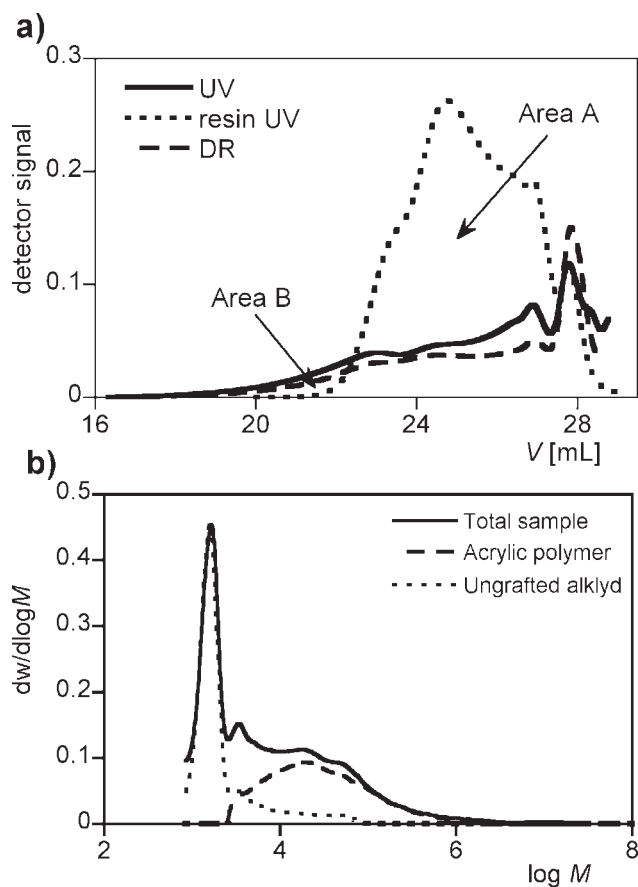


Figure 9 SEC analysis of hybrid sample B: (a) UV and DR chromatograms of the sample and UV chromatogram of the original resin and (b) MWDs (V = volume).

polymerization. Figure 9(a) shows that area B was significantly smaller than area A, which indicated that only 5% of the grafted resin was in the sol part; namely, almost all of the grafted resin was in the gel. The sol MWD corresponding to the total hybrid sample is presented in Figure 9(b), and the average molecular weights are given in Table III. Again, a very broad MWD was obtained with a low value of M_n of the total sample, which was the result of the relatively high amount of unreacted alkyd resin. The M_w was smaller than that of the completely soluble hybrid polymer [Fig. 9(b)] because the higher molecular weight species were forming the gel.

CONCLUSIONS

In this study, the molecular characterization of alkyd/acrylic hybrid latexes produced by miniemulsion polymerization was studied. This involved the determination of RDG, ADG, THP, gel content, sol

MWD, and fraction of unreacted double bonds in the alkyd. The polymer hybrid was analyzed by a new method based on SEC and dual (UV and DR) detection. This method was based on the fact that the acrylic polymer did not practically absorb the UV signal at a wavelength of 263 nm. Therefore, the area of the baseline-corrected UV chromatogram of the hybrid material was proportional to the alkyd resin content of the hybrid. We showed that the method can be applied to completely soluble hybrids and to gel-containing hybrids. Although this technique is not as rigorous as two-dimensional chromatography, it allows one to obtain very useful information for either industry or academia in the development of hybrid acrylic/alkyd composites with just a routine measurement carried out in a conventional SEC. The limits of the extraction method used in literature to measure the fraction of acrylic polymer that contain grafted alkyd (ADG) were investigated. This technique did not provide accurate results at low values of ADG because a considerable fraction of the neat acrylic polymer ($\sim 25\%$) was dissolved by the solvent (DEE). The errors were relatively low at high ADG values. The combination of this information (resin and ADG) with the MWD of the sol polymer and with the RDBs of the alkyd determined by iodine titration provided a detailed characterization of the alkyd-acrylic hybrid polymer.

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