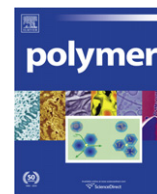


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A new strategy to improve alkyd/acrylic compatibilization in waterborne hybrid dispersions

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ABSTRACT

Grafting of alkyd resin to the acrylic polymer is needed to fully exploit the possibilities of these hybrids; but in the current technology, grafting is accompanied by an important reduction of the unsaturated groups of the alkyds, which adversely affects the curing of the film and its properties. A novel strategy that overcomes these limitations is presented. The strategy is based on the use of alkyd resin functionalized with methacrylic groups, that substantially improved the incorporation of the resin to the growing acrylic polymer chain, and the polymer particle homogeneity, without decreasing the degree of unsaturation in the alkyd resin.

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1. Introduction

Alkyd/acrylic waterborne hybrid coatings are attractive materials as they have the potential of combining the advantageous properties of the alkyd resins (e.g. auto-oxidative curing, high gloss and penetration in wood) with the quick curing and color retention of acrylic latexes. Furthermore, the coatings based on alkyd-modified hybrid dispersions can improve film formation properties, due to the presence of alkyd moieties, which typically have low glass transition temperatures. However, alkyd resins and acrylic dispersions are incompatible, and therefore, prone to suffer phase separation, that results in haziness and lower gloss. The great challenge in this kind of materials is to compatibilize both phases [1]. Compatibilization requires both, intimate contact between the materials and grafting of the acrylic and the alkyd resin, yielding a graft copolymer able to act as compatibilizer between the pure acrylic and the free alkyd resin.

Polymerization of miniemulsions of alkyd resins dissolved in acrylic monomers has the potential of achieving both goals at the same time [2–6]. Polymerization of acrylic monomers in the presence of alkyd resin yields graft copolymers due to both radical addition to the alkyd carbon–carbon double bonds and abstraction of the allylic hydrogens of the alkyd [7]. Overall, the addition process is energetically favored over abstraction [8]. Therefore, the

formation of the graft copolymer is often accompanied by an important reduction of the unsaturated groups of the alkyd resin [4], which results in the adverse deterioration of the auto-oxidative properties of the alkyd, i.e., in weaker mechanical properties of the film.

This effect is enhanced by the requirements imposed by the miniemulsification process and the characteristics of the polymers. In order to achieve intimate contact between the alkyd resin and the acrylic polymer, small droplets are needed, which can only be prepared maintaining the viscosity of the organic phase (solution of alkyd in the monomer) below a certain threshold [9]. For a given content of alkyd in the miniemulsions, this means that the molecular weight of the alkyd is limited. Therefore, in practice, relative short alkyd resins are used. As the acrylic chains produced in the polymerization are much longer than the alkyd chains, statistics leads to a system in which most of the acrylic chains have some alkyd chains grafted, whereas it is difficult to achieve the incorporation of a high fraction of the alkyd chains without reducing the content of unsaturated groups of the alkyd below the level in which the formation of the network by curing is compromised [6].

Attempts to improve the grafting of the alkyd resin on the acrylic polymer in waterborne systems without causing a substantial reduction of the alkyd double bonds have been reported. Thus, Goikoetxea et al. [6] observed that the type of initiator strongly affected the mechanism of grafting between the alkyd and the acrylic phase. Thus, hydrophobic oxygen-centered radicals produced from tert-butyl hydroperoxide/ascorbic acid in the

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Table 1

Summary of the hybrid alkyd/acrylic latexes.

Latex	Alkyd resin	Surfactant	d_a (nm)	d_p (nm)	Conversion (%)	RDG (%)	RDB (%)	Gel (%)	Mw (g/mol)
L1	S293 ^a	Surfmer ^c	180	186	96	16	5	1	160000
L2	FS293 ^b	Surfmer ^c	187	179	98	33	7	29	215000
L3	FS293 ^b	Dowfax ^d	138	137	95	44	6.5	25	223000
L4	S1630 ^a	Surfmer ^c	186	187	96	6	2	1	236000
L5	FS1630 ^b	Surfmer ^c	170	178	97	31	8	1	420000
L6	FS1630 ^b	Dowfax ^c	144	139	97	45	3	0	385000

^a Non-functionalized resin.^b Functionalized resin.^c Reactions carried out at 90 °C.^d Reaction carried out at 70 °C.

aqueous phase, that can enter directly into the particles, promoted the formation of graft copolymer through hydrogen abstraction from the alkyd resin. This allowed the formation of a relatively high fraction of graft copolymers with a modest reduction of the double bonds of the alkyd resins.

The grafting mechanism promoted by the oxygen-centered radicals may be the reason for the improvement in the homogeneity of PMMA/sunflower oil hybrid particles observed by Van Hamersveld et al. [10] when hydroperoxide initiators were used. However, neither the extent of the alkyd grafting nor the fraction of the unreacted double bonds were reported.

In an attempt to compensate the problems caused by the reduction of the alkyd double bonds occurring during polymerization, Shoaf et al. [5] used allyl methacrylate in the acrylic formulation. They found that the allylic bonds contribute to the curing of the film. However, avoiding the reaction of the allylic

bonds during polymerization and storage, and triggering its reaction upon film formation may be difficult.

In this work, a novel strategy to improve compatibility between the alkyd resin and acrylic copolymer in high solids content aqueous hybrid dispersions without affecting alkyd double bonds is explored. The strategy is based on the use of an auto-oxidatively crosslinkable alkyd resin that, in addition to the characteristic unsaturations located along the alkyd backbone, contains terminal double bonds.

2. Experimental

2.1. Materials

Technical grade monomers, methyl methacrylate (MMA, Quimidroga), butyl acrylate (BA, Quimidroga), acrylic acid (AA,

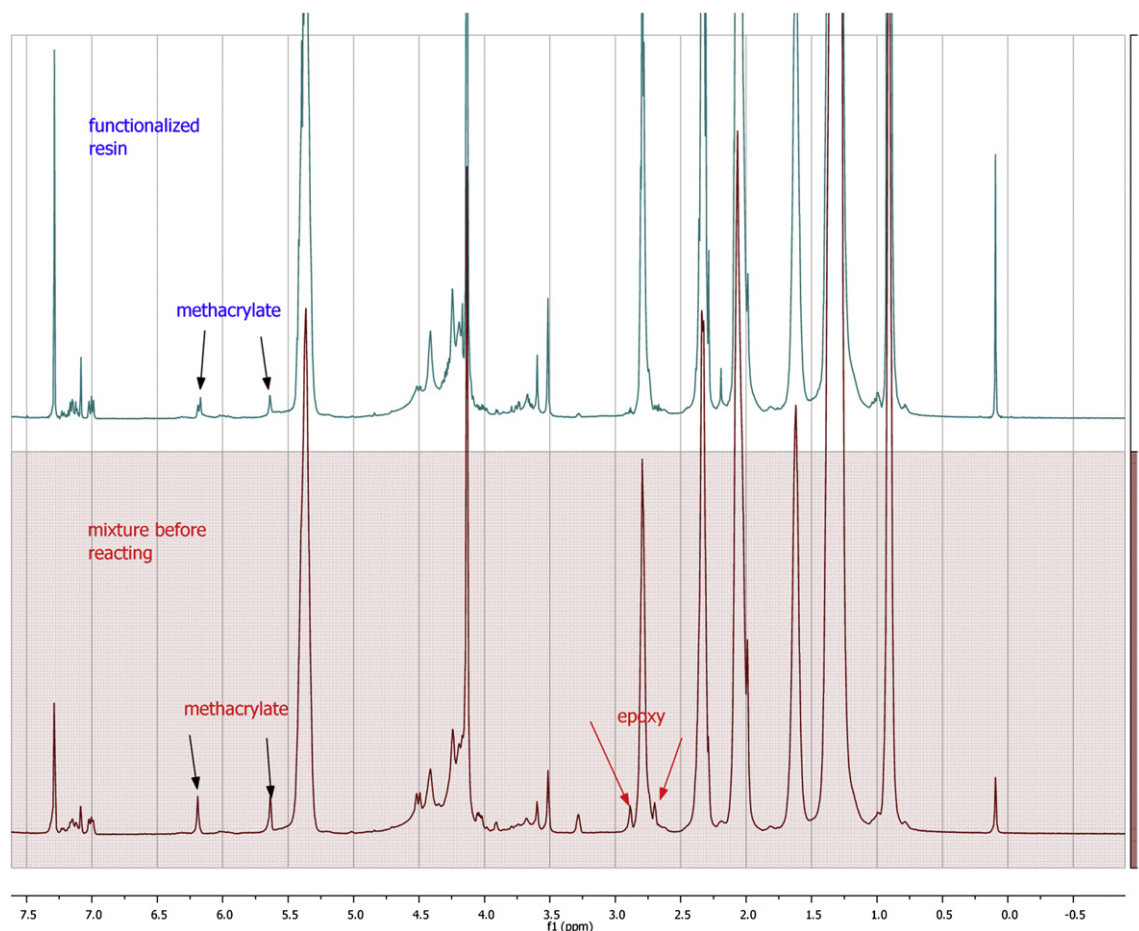


Fig. 1. ^1H NMR spectra of the S293 resin and GMA mixture before reacting and after functionalization.

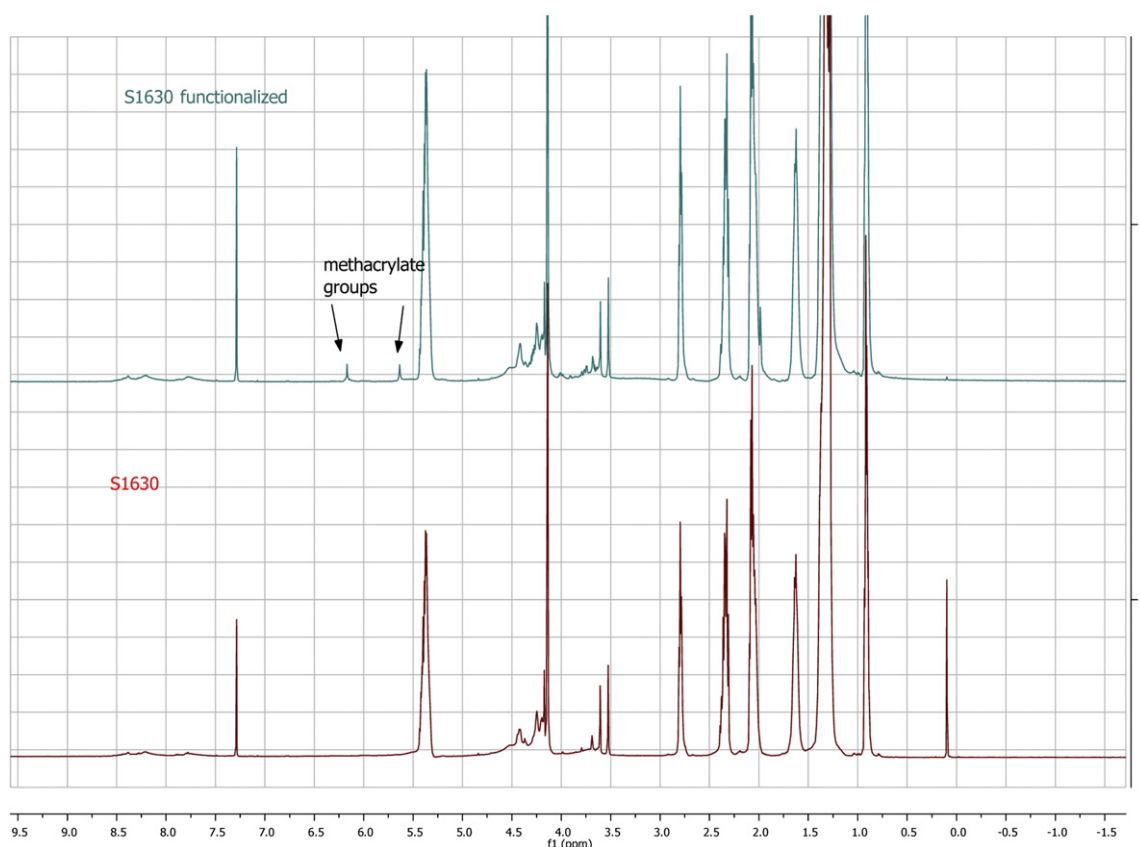


Fig. 2. ^1H NMR spectra of the S1630 resin before and after functionalization.

Aldrich), stearyl acrylate (SA, Aldrich) and glycidyl methacrylate (GMA, Aldrich) were used without purification. Two kinds of alkyd resins were used: SETAL 293 (S293, acid value 11 mg KOH/g) and the more hydrophilic SETAL 1630WP-292 (S1630, acid value 21.5 mg KOH/g) both supplied by Nuplex Resins. Both resins have similar iodine values that are proportional to the content of double bonds (S293:118 g/100 g; S1630:112 g/100 g). Dowfax 2A1 (alkyl-diphenyl oxide disulfonate, Dow Chemicals) and an anionic surfmer, supplied by Nuplex Resins, were used as surfactants. Ammonium persulfate (APS, Panreac) and sodium metabisulfite (SMB, Fluka) were used as redox initiators. GPC grade tetrahydrofuran (THF, Scharlau) was used as received. Distilled water was used throughout the work.

2.2. Synthesis of the methacrylate-functionalized alkyd resins

The functionalized alkyd resins were prepared by reacting the alkyd resins with GMA. The epoxide moiety of the GMA reacted with either the $-\text{COOH}$ or the $-\text{OH}$ groups of the alkyd resin, producing the methacrylate-functionalized resin.

The functionalization of the resins was carried out as follows: A equimolecular mixture of alkyd resin and GMA, containing

hydroquinone (1.5×10^{-4} mol hydroquinone/mol GMA), to avoid the homopolymerization of GMA, was charged to a reactor fitted with a reflux condenser and a stirrer. The mixture was heated to 150°C , under continuous stirring. After 2 h, the mixture was cooled to 130°C and more GMA (20%) was added. The mixture was heated to 160°C and maintained at this temperature for 1.5 h under stirring. Then, the reactor was allowed to cool to room temperature. The functionalized resins are denoted as FS293 and FS1630.

2.3. Miniemulsification

All miniemulsions contained 50% wt solids contents, 50% wbp (weight based on organic phase) of alkyd resin, 2.7% wbp of active surfactant, and NaHCO_3 at a concentration of 0.039 M in the water phase to control the miniemulsion viscosity [9]. The acrylic system was composed by BA/MMA/SA/AA (47.6/47.6/3.8/1 wt%). In order to produce the miniemulsions, the organic and the aqueous phases were mixed under magnetic stirring (10 min at 1000 rpm), and the resulted mixture was sonified with a Branson 450 equipment (15 min, power 9 and 80% duty cycle). Finally, the miniemulsion was further treated (6 cycles) in two-valves high-pressure homogenizer (Niro-Soavi, NS1001L PANDA) using 4.1×10^7 Pa in the first valve and 4.1×10^6 Pa in the second stage valve.

2.4. Synthesis of the Latexes

The latexes were synthesized in batch by miniemulsion polymerization at either 70°C or 90°C . Polymerizations were carried out in a 1 L glass reactor equipped with a reflux condenser, stirrer, sampling device, nitrogen inlet, and two feed inlet tubes. The redox initiator system used in all the cases was APS and SMB (1.6% wbm)

Table 2
Functionalized resins.

Resin	Acid value (mg KOH/g resin)		Iodine value (g/g resin)	
	Before functionalization	After functionalization	Before functionalization	After functionalization
S293	11	4.9	118	117.5
S1630	21.5	14.7	112	115

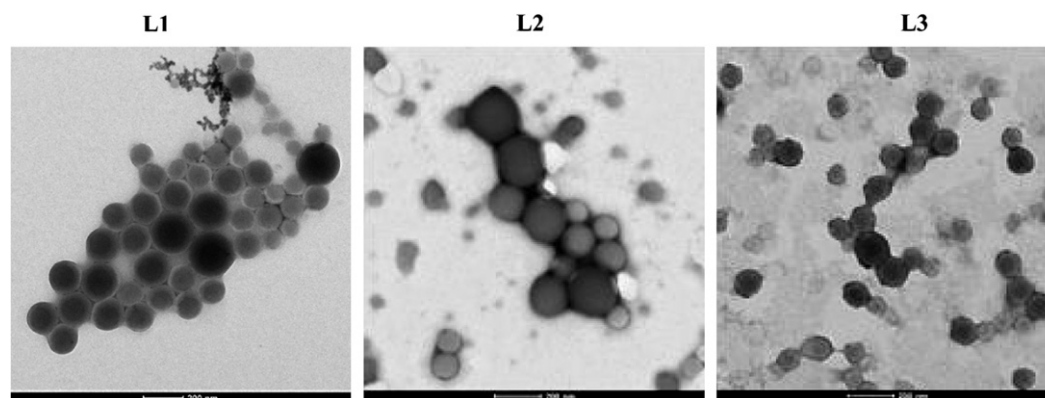


Fig. 3. Particle morphologies observed by TEM of the latexes produced with S293 (L1) and with the functionalized S293 resin (L2 and L3).

and they were fed separately during 4 h. Then the system was allowed to react in batch for one more hour. Table 1 summarizes the experiments performed.

2.5. Characterization

Droplet and particle size were determined by dynamic light scattering, using a Malvern Nanosizer. Conversion was measured by headspace gas chromatography. The analysis was performed with a Hewlett–Packard HP 7694E Headspace Sampler interfaced to a Hewlett–Packard HP 6890 GC system with electronic pneumatic control and a flame-ionization detector. Pentanol was used as the internal standard.

The resin degree of grafting (RDG), which is the ratio between the amount of alkyd resin grafted to the acrylic and the total amount of alkyd resin in the formulation, was determined using the method reported in ref [11]. The sol fraction of the latex was separated from the gel fraction using soxhlet extraction with THF. The non-soluble part was considered to be the gel fraction. The molecular weight was determined in a SEC equipment (LC-20AD Shimadzu pump, Waters Styragel HQ2, HQ4, HQ6 columns and two on-line detectors: differential refractometer (DR) and UV (Waters)). This allows to distinguish between the soluble acrylic polymer and the ungrafted alkyd resin [11]. The fraction of reacted double bonds of the resin (RDB) was determined by iodine titration based on the Wijs method [12]. This method was checked by comparison with the values obtained from ^1H NMR. It was found that the values obtained from both methods were within the relative error percentage of the Wijs method.

The morphology of the latex particles was determined by means of transmission electron microscopy, TEM, using a TECNAI G² 20 TWIN (200 kV, LaB6), after positively staining them with osmium tetroxide (OsO_4) and negatively staining them with phosphotungstic acid (PTA). This enhances the contrast between the alkyd (darker) and the acrylic (lighter) and the surfaces of the particles are contrasted [4].

3. Results and discussion

Figs. 1 and 2 show the ^1H NMRs of the reaction mixture before and after the functionalization for resins S293 and S1630, respectively. It can be seen that no epoxy groups from the GMA were left after the functionalization, namely, all the GMA reacted with the alkyd resin. On the other hand, the methacrylate double bond was available for the further reaction with the acrylic monomers. Table 2 presents the effect of functionalization on the acid and iodine values of the resins. It can be seen that carboxylic groups accounting for about 6–7 mg KOH/g resin reacted with the epoxy moiety of the GMA, and that the iodine value, which refers to the double bonds content, was not affected by the functionalization.

Table 1 shows the effect of the functionalization of the resin on the characteristics of the hybrids. It can be seen that for both the hydrophobic and the hydrophilic resins, functionalization led to higher values of the RDG without causing any increase of the consumption of the unsaturations of the alkyd backbone (similar low values of the RDB). The increase of the RDG was due to the incorporation of the alkyd to the growing acrylic chains through the reactive methacrylic group of the functionalized resin. The effect of the functionalization is particularly noticeable in the case of the

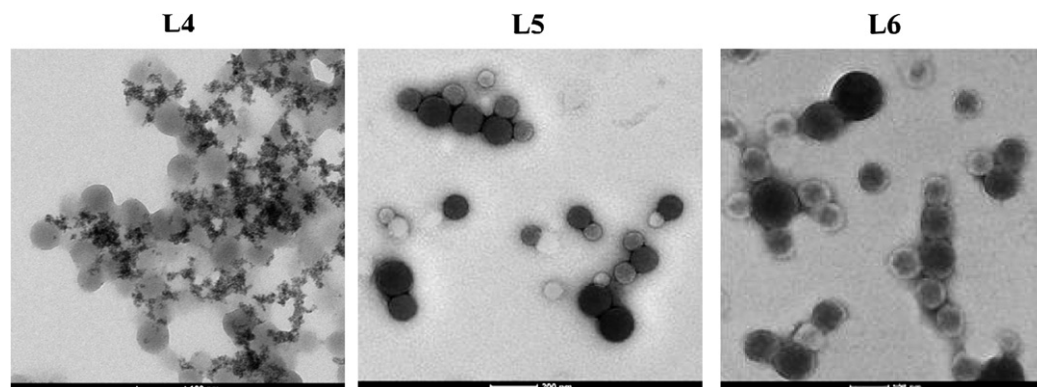


Fig. 4. Particle morphologies observed by TEM of the latexes produced with S1630 (L4) and with the functionalized S1630 resin (L5 and L6).

hydrophilic resin, which without functionalization is very difficult to graft to the acrylic polymer.

In addition, the increase of the RDG was stronger when the particle size decreased (Latexes L2 vs L3 and L5 vs L6) because of the better contact between the alkyd resin and the growing acrylic chains. In order to discuss this point, let us consider a miniemulsion droplet, which is homogeneous because the alkyd resin is soluble in the acrylic monomers. Polymerization of the acrylic monomers leads to the formation of acrylic polymer that is incompatible with the alkyd resin and promotes phase separation. Once the phase separation occurs, the fraction of alkyd resin that is accessible to the acrylic growing chains is the one that is close to the alkyd/acrylic interface. Therefore, the accessibility increases with the interfacial surface area per unit volume, namely when the particle size decreases. A higher accessibility leads to the formation of more graft copolymer, which compatibilizes the resin and the acrylic polymers, further increasing the probability of grafting.

Table 1 also shows that functionalization led to higher molecular weights, which for the hydrophobic resin resulted in formation of gel. The increase was due to the fact that the functionalized resin may act as crosslinking agent because it contains both methacrylic double bonds and unsaturations in the alkyd backbone. The effect was stronger for the hydrophobic resin, likely because the hydrophilic resin was located at the outer part of the particle [6] and hence it was less accessible to the growing acrylic chains.

Fig. 3 presents the effect of the functionalization on the particle morphology for the hydrophobic resin. The non-functionalized S293 resin led to an alkyd rich core and an acrylic rich shell, which agreed with the equilibrium morphology predicted using the interfacial tensions between acrylic polymer, alkyd resin and water [6]. Particle morphology is ruled by both thermodynamics and kinetic factors, but low viscosity particles reach the equilibrium morphology [13–15]. In this case, the particles had a low internal viscosity because of the combined effect of the low molecular weight of the non-grafted alkyd resin, the relatively low molecular weight of the acrylic polymer and the fact that the process was carried in batch, namely, maximizing the concentration of monomer in the particles. Much more homogeneous particles were produced with the functionalized resin. The higher level of grafting found with the functionalized resin would decrease the interfacial tension between the acrylic and the free alkyd phase and facilitate the more intimate contact between them.

The effect of functionalization of the hydrophilic resin on particle morphology is presented in Fig. 4. It can be seen that the non-functionalized resin led to a segregated morphology, with most of the S1630 resin outside of the particles. Further, no alkyd resin was visible within the polymer particle. Since thermodynamic predicts hemispherical morphologies for this system [6], one could speculate that the hydrophilic resin was expelled from the polymer particles during sample preparation, which would be facilitated by the relatively low grafting degree of the alkyd. Resin functionalization drastically modified particle morphology. The latexes produced with the functionalized resin showed very homogeneous particles and some core-shell (the resin being in the core) structures. Therefore, it could be concluded that the incorporation of pendant methacrylic groups in the alkyd significantly improved the grafting reaction, enhancing the compatibility between the pure acrylic and free alkyd resin.

4. Conclusions

Grafting of alkyd resin and the acrylic polymer is needed to fully exploit the possibilities of these hybrids. However, in the current technology, grafting is accompanied by an important reduction of the unsaturated groups of the alkyd backbone, which adversely affects the curing of the film and its properties. This work presents a novel strategy that overcomes this limitation by achieving high degrees of compatibilization without any significant decrease of the degree of unsaturation of the alkyd resin. The strategy is based on the use of an auto-oxidatively crosslinkable alkyd resin that, in addition to the unsaturations located in the alkyd backbone, contains a methacrylic group inserted by reaction of the alkyd resin with glycidyl methacrylate. It was found that the alkyd unsaturation was not affected during the functionalization process. The waterborne hybrid dispersions prepared by miniemulsion polymerization using the functionalized alkyd resin showed a substantially higher degree of grafting of the resin to the acrylic polymer, without consuming unsaturations of the alkyd backbone. The incorporation of alkyd to the acrylic polymer was made through the methacrylate group of the alkyd. A consequence of the improved compatibility was that a more homogeneous particle morphology was obtained. The strategy works for hydrophobic alkyd resins mainly located in the core of the polymer particle, as well as for hydrophilic resins, which tend to be at the outer part of the particle.

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