

Preparation of Water-Based Alkyd/Acrylic Hybrid Resins

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ABSTRACT

Alkyd resins are amongst the most important and widely used resins in coating sectors. In this communication we report on preparation of alkyd resins emulsified by grafted acrylic resins on their fatty acid moieties. Both high-shear mechanical homogenizer and ultra-sonic sonicator were used step-wise to disperse the alkyd resin and acrylic based monomers in aqueous media. The resins are of nanometric particle size (~200nm) dispersed in water in the presence of polymerization emulsifying agent. The FT-IR spectroscopy revealed the differences in the spectrum of the base resins and hybrid resin. The extraction test revealed formation of better than 99% of grafted hybrid resin. The DSC test showed that the glass-transition temperatures of the hybrid resin are very lower than that of the base alkyd and acrylic polymers which re-confirm formation of chemically grafted hybrid resin. The molecular weight of the hybrid resin was also found to be a combination of those of the base resins. The polydispersity of the base resins is about 8, whereas that of the hybrid resin locates around 32 which is resulted from differences in the molecular weight of the base resins. The films of the resulting resins were fully dried after 8 hours at room temperature without any further loss in weight or tackiness. Prog. Color Colorants Coat. 4(2011), 15-25. © Institute for Color Science and Technology.

1. Introduction

Alkyd resins belong to an important family of resins which are as old as the modern paint and coating industry. These resins are polyesters that contain mono- and poly- functional acids and alcohols (Figure 1).

The coatings made of long-oil alkyd resins deliver properties such as ability to be air-dryable and good interactions with polar substrates such as wood and steel. In addition, the coatings containing alkyd resins have a relatively lower cost. The coatings of conventional alkyd resins with any oil content or acid value are solvent-based and usually diluted in an organic solvent such as

toluene, xylene and different oil cuts or a mixture of these solvents.

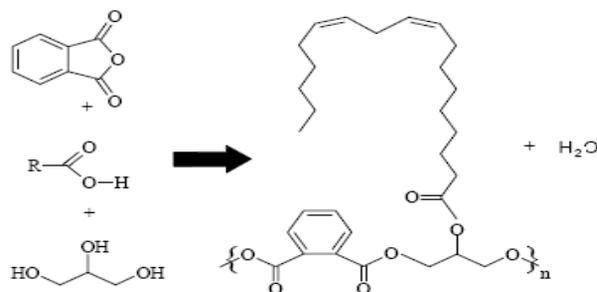


Figure 1: The general chemical structure of alkyd resins.

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During the process of coating, these solvents are released into the atmosphere and cause too many environmental problems. To overcome these problems, two procedures were developed. In the first approach, powder coatings were developed and the solvent was totally omitted from the coatings formulation. Of course, this technique has its own shortcomings. In the second approach, the organic solvent was replaced by water. To achieve this goal, there is a major obstacle. In fact, a standard alkyd resin is not miscible with water which opposes the feasibility of switching from white spirit to water.

Some authors tried to incorporate some water soluble monomers in the alkyd resin's structure [1]. Thereafter, in parallel to this, other technologies such as UV (radiation) cure coatings and high solid coatings were developed in the field of acrylic resin emulsions [2]. The technique of emulsion polymerization was used in preparation of acrylic emulsion. These are very stable emulsion with micro and nano scale particles of polymer in water medium [3]. Polymerization of stable acrylic emulsions in presence of an alkyd resin results in a hybrid resin which consists of two different oil and water soluble polymers. The resulting polymer forms a nano-size dispersion of hybrid resin in water medium. The technique of miniemulsion [4-8] was used to copolymerize methyl methacrylate, butyl acrylate and acrylic acid in the presence of alkyd resin [9]. It was reported that the resulting emulsion is stable and ^{13}C -NMR studies showed that 20-30% alkyd's double bonds are reacted. This confirms grafting of copolymer on alkyd resin. Characterization of the hybrid acrylic/alkyd resins showed that the alkyd's double bonds which were engaged in graft reaction are those located next to the acid groups [10]. It was also reported that the resulting hybrid resin has a broad distribution of molecular weight distribution and there also exist free alkyd and poly acrylate resins in the mixture. It was also found that the nucleation mechanism mostly proceeds via monomer droplet nucleation path. The sunflower unsaturated triglyceride was grafted by acrylates using a redox initiator system. The cryo-TEM technique showed formation of heterogeneous particles [11]. The AFM technique confirmed phase separation of acrylic phase from the oil phase upon drying [12]. In a report it was claimed that grafting reaction can be raised from less than 5% to higher than 70% by changing alkyd or urethane resins to polyester resin [13]. It was also found that the resulting resin has good stability and its film is

hard enough to be considered for coating applications. Some patents also appeared in which the same technique of miniemulsion polymerization was used [14, 15]. The mechanism of grafting in miniemulsion polymerization technique was studied and it was found that hydrophilic monomers face obstacles to enter reaction zones whereas hydrophobic monomers can't pass through the aqueous phase to reach to the reactive chains [16]. Meanwhile, monomers such as methyl methacrylate (MMA) are sterically hindered to polymerize and their grafting tendency decreases. Alkyd resin was suspended in an acrylic emulsion [17] and the interfacial, viscosity and solid content effects were studied. It was reported that mixture preparation procedure affects the liquid particle structure (O/W or W/O/W). A copolymer of 15 to 40wt% of n-butyl acrylate and maleic anhydride was polymerization-grafted on modified palm oil and a water-reducible acrylic-alkyd resin was formed [18]. It was reported that the resulting resin has excellent water and acid resistance as well as good alkali resistance. A silicone version of acrylate-alkyd resin was also synthesized and non-pigmented film showed a very high resistance which was suitable for exterior coating applications [19]. The molecular structure of acrylic alkyd hybrid resins obtained from miniemulsion technique was characterized using different analytical technique [20]. It was found that the technique of extraction is accurate only in the case of high grafting rates to determine the percentage of the bonded alkyd. The effect of miniemulsion polymerization parameters such as resin hydrophobicity and the kind of initiator on the resin architecture and particle morphology was investigated [21]. It was concluded that the final resin mainly contains acrylic resins with some moiety of alkyd and a minority of alkyd with acrylic grafting. It is claimed that the hydrolytic stability of waterborne alkyd resins is relatively low which results in a short shelf life [22]. This shortcoming of this family of resins has been overcome via introducing polyacid acrylic copolymer in the structure of the resin. The limited conversion is a technical challenge in the miniemulsion polymerization during preparation of alkyd-acrylic hybrid resins [23]. This obstacle was removed using post-polymerization technique to minimize the amount of unreacted residual monomers. This process affected the structure and morphology of the resulting hybrid resin. The technique of emulsion polymerization was used to prepare 46% solid content with 97% conversion of MMA and BA monomers on unsaturated alkyd resin [24]. Accelerated

and mechanical storage stability tests showed that the resulting resins are long enough stable. It was also found that the resin has a good penetration into the wooden substrates. It is known that in preparation of hybrid alkyd resins, the unsaturated content of the base alkyd resin decreases due to the way grafting happens [25]. This in turn results in a reduction in the ability of the hybrid resin to be cured. In a new approach, an alkyd resin containing methacrylic groups was prepared at first and in the next step a system of monomer was grafted on the modified alkyd resin without any risk of unsaturation reduction. A technique similar to that of [1, 26] was also reported in [27] via grafting maleic anhydride and fumaric acid on rubber seed oil. The resulting resin found to be water reducible.

In this paper we report a novel technique for dispersing a mixture of alkyd resin and components of emulsion polymerization using ultrasound and high-shear mixer and preparation of a hybrid alkyd/acrylic resin having nanometric particles using KPS initiator. The stability, molecular distribution and film formation of the resins were reported.

2. Experimental

2.1. Materials

A phthalic anhydride and soya fatty acid based alkyd resin with an acid value in the range of 10-15 mgKOH/g and 98% solid content was obtained from Kimia-e-Qom Paint and Resin company. All monomers were technical grade. Reagents and initiators were purchased from Merck (Germany).

2.2. Procedures

The alkyd resin and the mixture of monomers and emulsifier were dispersed in water using an ultrasound disperser and a homogenizer (high-shear) mixer in a plastic beaker thermo-bathed in water. After preparation of the reaction mixture, it was transferred into a reaction kettle (Figure 2) and the initiator mixture was added drop wise into the reactor at 75°C along with mixing under a nitrogen blanket. During the reaction, the conversion factor was determined via successive sampling.

To characterize the particle size of polymerized particles, particle size analyzer Model MasterSizer 2000 (Malvern) was employed. Also, to observe the morphology of the particles, transmission electron microscope (TEM) model EM 208-100KV from Philips Company was used.



Figure 2: The reaction vessel and its peripheral.

The molecular weight distribution of the samples were determined on a gel permeation chromatograph (Agilent, GPC 110, Germany) using columns PL gel 10mm (10^3 , 10^4 and 10^5 Å in series). The flow rate was fixed at 1 ml/min and all measurements were carried out at 30°C. The employed detector analyzed materials based on their refractive index (RI) and the instrument was calibrated using standard polystyrene. The thermal properties of the resins were analyzed on a Perkin-Elmer differential scanning calorimeter (DSC, Pyris 6) at 10°C/min rate of heating.

3. Results and discussion

The composition of the different formulations is summarized in Table 1. Under the conditions during graft polymerization, the acrylic monomers are polymerized in the presence of soya-based alkyd resin. Under these conditions, both graft copolymer and homo-polymer of the existing monomers are formed. The resulting mixture is a stable milky emulsion and its properties will be discussed in the following paragraph.

In Figure 3 the conversion of the polymerization of different formulations is presented. As it is observed, the monomer to polymer conversion approaches completion (between 80 and 100%) for HA4 and HA9 formulations. This shape of conversion curve is in agreement with that of the typical addition polymerization conversion curve. Regarding the formulation and polymerization conditions, we observe that the concentration of cetyl alcohol can be reduced with changing the mixing condition.

Table 1: Composition of different formulations.

	A1	HA4	HA5	HA6	HA7	HA8	HA9	
Alkyd	0	187	187	187	187	187	187	
MMA(ml)	180	100	100	100	100	100	100	
BA (ml)	180	100	100	100	100	100	100	
AA (ml)	4	2.5	2.5	2.5	2.5	2.5	2.5	
SDS (g)	5.014	5	5	5	2	5	5	
KPS (g)	1	1	1	1	1	1	1	
H ₂ O (g)	461	430.5	430.5	430.5	421	430.5	430.5	
Cetyl alcohol	0	10	10	10	4	1	1	
Homogenizer rpm (duration, min)	--	--	7500 (60)	7500 (20)	---	7500 (10)	7500 (10)	9000 (2)
Ultrasound power (duration, min)	---	150 (20)		150 (20)	150 (20)	150 (10)	150 (10)	150 (2)

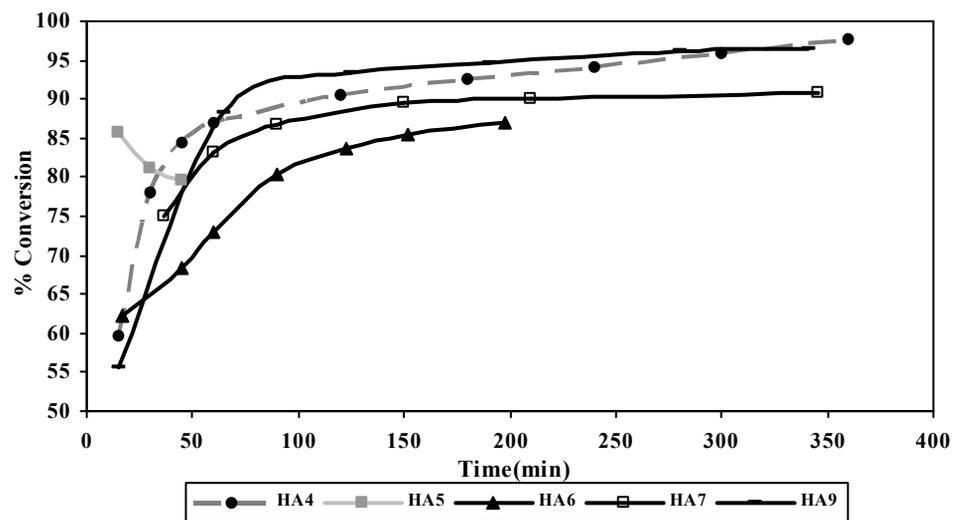
**Figure 3:** Conversion factors for different formulations.

Figure 3 indicates that for HA4 and HA9 formulations, the reaction almost completes after 100 minutes and longer polymerization times only are of very marginal effects on conversion percentage of the polymerization reaction. However, the HA7 formulation shows a lower conversion factor and it can be concluded that this formulation with a lesser SDS concentration is not suitable for complete conversion of monomer to polymer. The reason for this behavior is reflected in very essential effect of this agent. As a matter of fact, Figure 3

data can be used in optimization of polymerization process.

In Figure 4 the FT-IR spectrum of the hybrid resin is presented. Comparison between A1 resin and the base alkyd resin indicates that a hybrid structure is formed (either chemically or physically). In the same figure, the spectrum of the base alkyd resin is reported. The chemical structure of both alkyd resin and the acrylic resin are close and we observe only very small differences. However, the difference around 3000 cm^{-1} is

very clear. The spectrum of the hybrid resin is a combination of the starting resins which confirms the

existence of both structures, especially considering the peaks around 3000 and 1100 cm^{-1} .

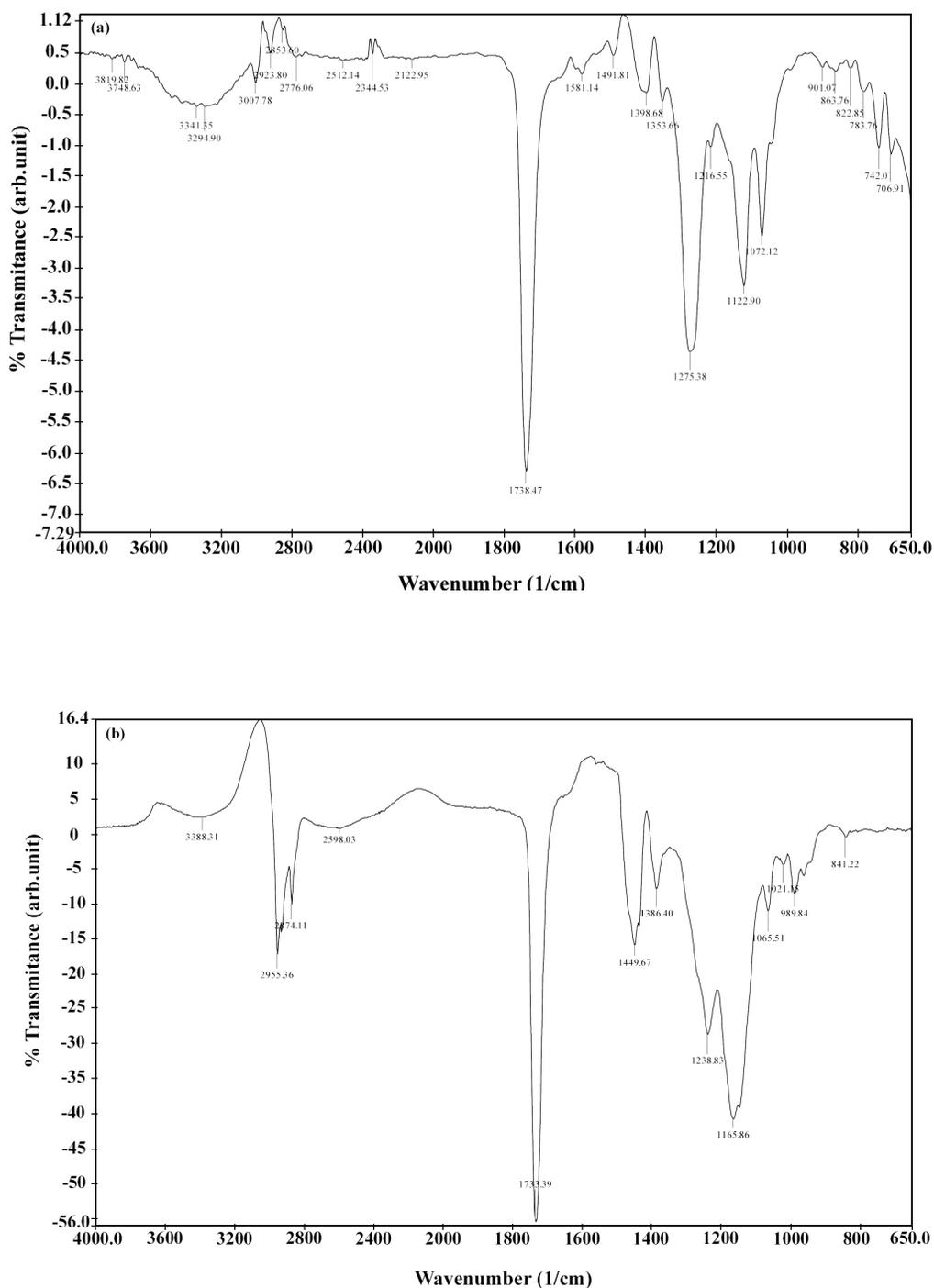


Figure 4: FT-IR spectrum of (a) the base alkyd resin, (b) acrylic resin (A1) and (c) the hybrid alkyd-acrylic resin (HA3).

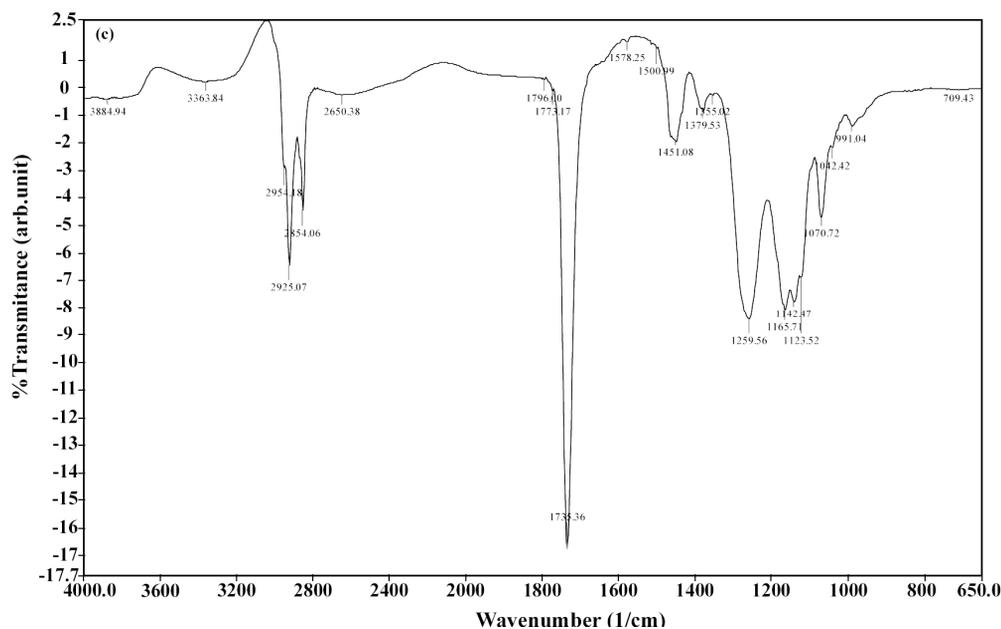


Figure 4: Continued.

However, it cannot be claimed that the hybrid resin is formed chemically but coexistence of both components are evident. Meanwhile, the extraction technique helps to prove chemical formation of the hybrid resin. To check this, we proceed as follows. To cross-check the grafting of acrylic resin on alkyd resin, we used the Soxhlet extraction test. At first we found that unlike alkyd resin, acrylic resin (A1) is fully soluble in diethyl ether. The extraction was performed for 14 hours and we obtained 99.98 wt% grafting which is consistent with high stability of the emulsions.

The differential scanning thermal analysis of the

resins is shown in Figure 5. The glass-transition temperature (T_g) of the alkyd and acrylic (A1) resins are about -19°C and 22°C , respectively. The thermal behavior of the hybrid resin is very different from that of the alkyd and acrylic resins. The resulting resin represents three major T_g s around -40°C , -3°C and 30°C . The low and high T_g s are attributed to the alkyd and acrylic resins, and the middle T_g assigned to hybrid grafted resin [10]. It can be concluded that hybrid species have more free-volume as compared with that of the pure alkyd and acrylic resins. This observation also confirms formation of the grafted structure.

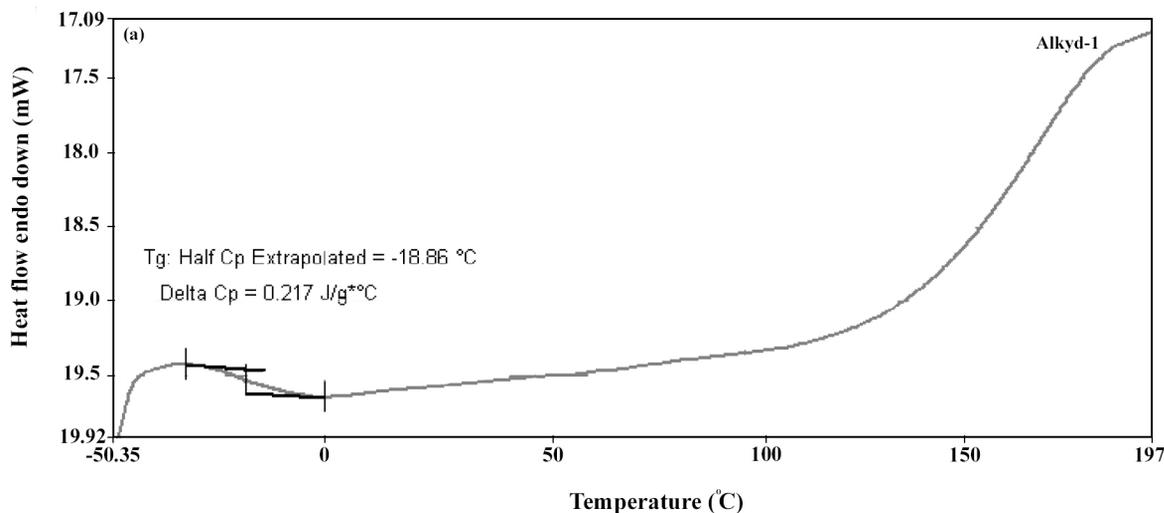


Figure 5: The DSC thermo-gram of (a) the base alkyd resin, (b) acrylic copolymer (A1) and (C) the hybrid resin (HA4).

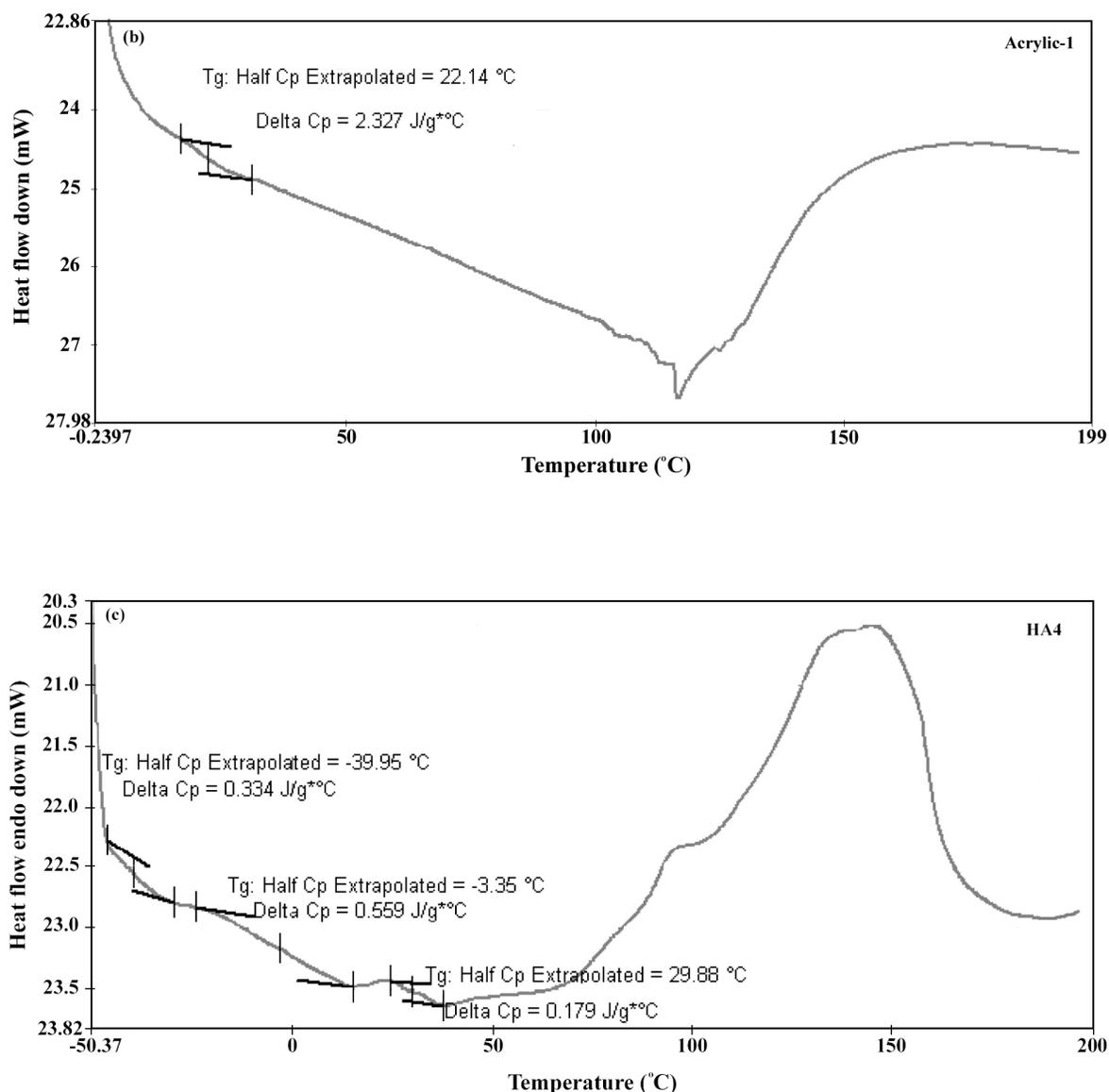


Figure 5: Continued.

In Figures 6 to 8, the molecular weight distribution (MWD) of A1, base alkyd resin and hybrid resin (HA4) are presented. It can be seen that the MWD of the hybrid resin shows two peaks around 2000 and 1000000 g/mol which coincide to those of the base alkyd resin and A1 acrylic resin, respectively. The interesting point is the similarity of the base and hybrid resins. The height of peaks is different for hybrid and pure resins which can be considered as an indirect indication of physical mixture of the resins. The weight average (Mw) and number average (Mn) molecular weight of the resins along with the corresponding polydispersity index (PDI) are reported in Table 2. In case of the pure polymers, PDI stays around 8; however, due to the high-molecular

weight characteristic of acrylic copolymer (A1) which is typically resulted in addition polymerization reaction and low-molecular weight of alkyd resin which is usually resulted from poly-condensation reactions, the hybrid resin has a PDI slightly larger than 32.

Table 2: Molecular weight of the resins.

Resin	Mw (g/mol)	Mn(g/mol)	PDI
Alkyd	4.2039e4	4.8630e3	8.644
Acrylic (A1)	6.8236e5	9.1195e4	7.482
Hybrid (HA4)	2.7466e5	8.4917e3	32.344

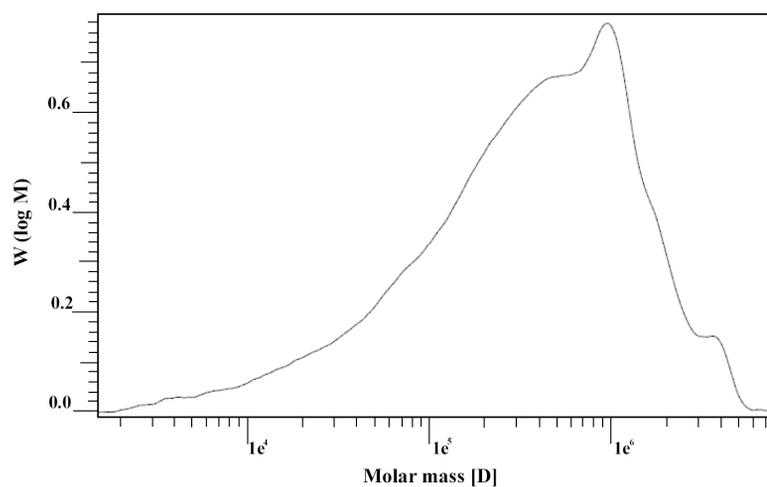


Figure 6: Molecular weight distribution of A1 resin.

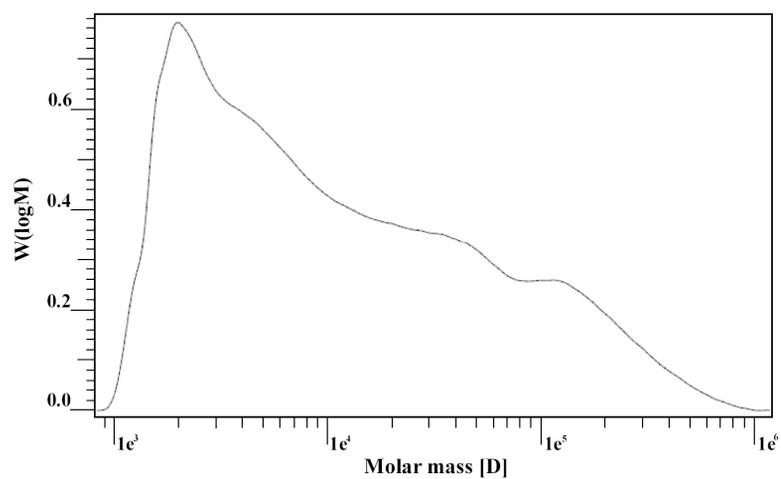


Figure 7: Molecular weight distribution of base alkyd resin.

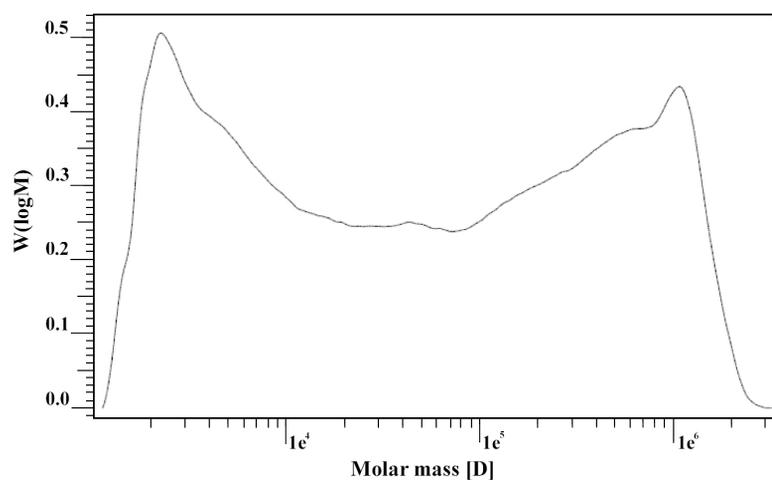


Figure 8: Molecular weight distribution of hybrid HA4 resin.

The distribution of particle size of the synthesized resins is depicted in Figure 9. The particle size of the resins is mainly located around 200 nanometers. For some formulations a two-peak distribution is observed. This is evident that any change in mixing conditions and emulsifier concentration leads to a change in particle size distribution. However, the peak at 200 nm is always present for all formulations. TEM micrograph of the HA4 hybrid resin is shown in Figure 10. It is clearly observed that most particles are of a size of 200 nm. However, some larger particles are also present in the figure which may account for the tail of the curve at larger particle sizes.

The film formation the resins was also checked. A 70% solid content resin as mixed with 4 wt% of lead drier and a uniform film was resulted which was checked for drying and weight loss after 18 hours. A uniform

dried film of A1 to HA9 resins with a constant weight was left after this period of time. The final films had not any tacky surface.



Figure 10: Morphology of HA4 hybrid resin.

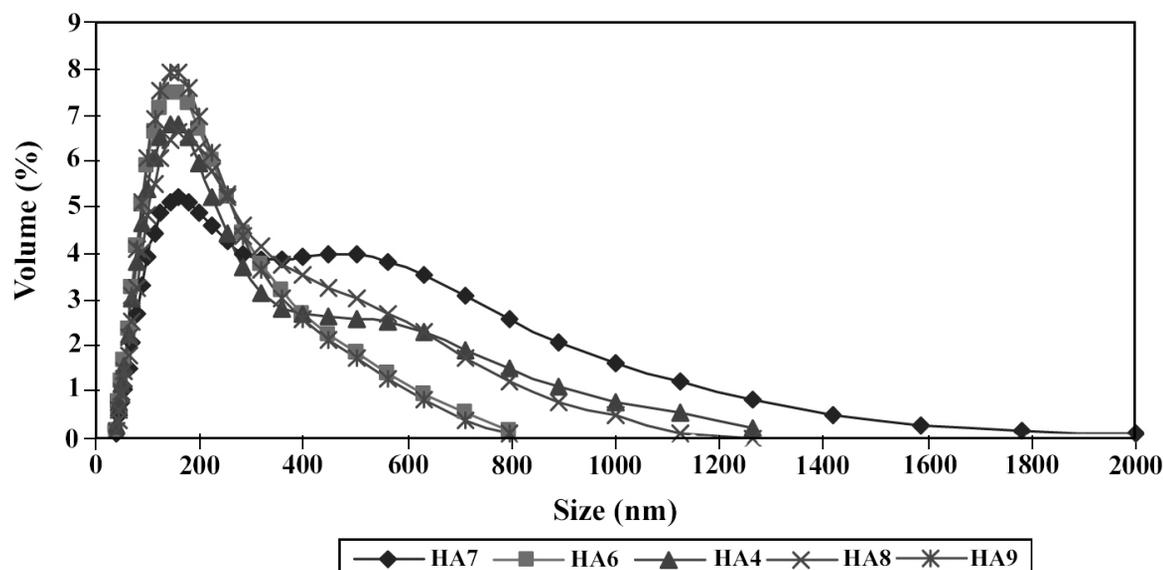


Figure 9: Particle size distribution of different hybrid resins.

4. Conclusions

The technique of mini-emulsion polymerization was used in preparation of stable water-based alkyd-acrylic hybrid resins. The resulting hybrid resins not only have many advantages of both alkyd and acrylic resins but also are water based resins. Both high shear mixer and ultrasonic disperser were used in dispersing alkyd resin and monomers in the polymerization medium (water) prior to initiation of polymerization. The polymerization

conversion was found to be higher than 80% and reached 94% for the optimum formulation. The FT-IR showed some differences between the base alkyd resins, acrylic copolymer and hybrid alkyd-acrylic resins. The extraction technique proved a graft reaction higher than 99% during polymerization. The DSC revealed about 20 degrees decrease in T_g for the components in the hybrid resins in comparison with that of the starting materials which may be another confirmation for the graft reaction.

The molecular weight distribution of the hybrid resin was found to be the combination of those of the base alkyd resins and acrylic copolymer. The polydispersity of the base resins was comparatively narrow and their PDI was found to be around 8, whereas that of the hybrid resin

was increased to 32. The particle size of hybrid resin was checked using two techniques and was found to be around 200nm. The films of all hybrid waterborne resins dried after 18 hours had no further weight lost and tackiness.

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