

Research Article

# Biobased Alkyd Acrylic Hybrid Core Shell Approach

Beyhan Erdoğan<sup>1\*</sup>, Özgür Şeni<sup>2</sup>

<sup>1</sup> DYO Paint Factory, İzmir, Türkiye Orcid ID: <https://orcid.org/0000-0001-8427-4209>, E-mail: [beyhan.erdogan@dyo.com.tr](mailto:beyhan.erdogan@dyo.com.tr)

<sup>2</sup> DYO Paint Factory, İzmir, Türkiye Orcid ID: <https://orcid.org/0009-0005-2115-963X>, E-mail: [ozgur.sen@dyo.com.tr](mailto:ozgur.sen@dyo.com.tr)

\* Correspondence: [beyhan.erdogan@dyo.com.tr](mailto:beyhan.erdogan@dyo.com.tr)

(First received October 11, 2023 and in final form December 19, 2023)

**Reference:** Erdoğan, B., Şen, Ö. Biobased Alkyd Acrylic Hybrid Core Shell Approach. The European Journal of Research and Development, 3(4), 218-228.

## Abstract

*The main objective of this work was to synthesize bio based alkyd-acrylic hybrid emulsion by using core shell approach. Step by step growing polymerization was used for the preparation of the bio-based alkyd resin. Bio-based sebacic acid was used in the synthesis. In the core shell approach; shell part contains a acrylic polymer, core part contains bio based alkyd emulsion, which was synthesized by phase inversion. The acrylic shell was synthesized in the presence of the alkyd resin by the emulsion polymerization method.*

**Keywords:** Bio based alkyd, acrylic, emulsion, core shell, polymerization

## 1. Introduction

Alkyd resins have been widely used in paint and coating industry because of its superior performance (good aging, greater weather resistance, high heat resistance, outstanding gloss, etc.). Conventional alkyd resins are produced by the esterification of polyhydric alcohols and dibasic acids and through modification with oil and fatty acids in 200-240°C [1,2,3,4]. During the synthesis, petroleum-based materials are commonly used. Due to the current state of sustainability concerns, more sustainable and eco-friendlier biobased materials is growing interest in alkyd synthesis compared to petroleum derived materials.

Conventional alkyd resins dominate the paint and coating market, but due to their organic solvent application, increasing attention is given to waterborne resins in the market because they are low VOC, non-toxic, non-flammable and do not pollute the air. Waterborne hybrid system are one of the important class of materials with superior properties which come from the synergistic combination of acrylic polymers and alkyd emulsion prepared by phase inversion process. Waterborne hybrid systems merge the

positive properties of alkyd emulsion and acrylic polymer [1-8]. The alkyd emulsion has advantages coming from the alkyd chemistry such as good flow and leveling, superior substrate wetting properties, good adhesion and good gloss development. Despite these advantages, drying time for alkyd emulsions is too long. Acrylic polymers have excellent water and weather resistance properties and mechanical properties because of having main polymer chain carbon-carbon bonds. Although there are advantages of acrylic polymers, they exhibit poor substrate wetting and leveling properties. Hybrid systems merge the advantages of alkyd emulsion and acrylic polymers. Fast drying properties of hybrid system come from the acrylic part, whereas high gloss and good penetration come from the alkyd part. One of the techniques for the formation of water borne hybrid system is the mechanical mixing of an acrylic polymer and an alkyd emulsion. In this method, the alkyd resin is slowly added into the acrylic polymer under mechanical mixing. The main drawback of the method is the phase separation between acrylic polymer and alkyd emulsion during storage due to inhomogeneity of the phases. The other technique is the emulsion polymerization which provides an effective processing method to synthesize homogeneous hybrid system [4-7,12] In this method, the acrylic phase is synthesized in the presence of the alkyd resin. Core shell approach which is an effective route for achieving homogeneous hybrid system is prepared by emulsion polymerization. The core and shell combines through chemical bond integration of certain active groups on the surface of core part or groups that are produced during the formation of shell constituent [4-7,12].

The objective of the study is to synthesize waterborne hybrid system by using core shell approach. In the core shell approach, core part contains bio based alkyd emulsion, which was synthesized by phase inversion. Biobased alkyd resin was synthesized by replacing aromatic diacids and anhydrides with biobased organic acids. Bio-based sebacic acid was used for this purpose. In the core shell approach, shell part contains acrylic polymer which was synthesized in the presence of biobased alkyd resin by the emulsion polymerization method.

## 2. Materials and Methods

### Experimental

#### Biobased Alkyd Synthesis with Sebacic Acid

Laboratory-grade Tall oil fatty acid, phthalic anhydride, adipic acid, propylene glycol, trimethylol propane 1,6 hexandiol, and xylene were used in alkyd synthesis. Bio-based acid samples was purchased from Myriant Co. Synthesis studies were carried out using a 2000 mL 5-necked flask set-up. This balloon set-up consists of a motorized mixer; thermocouple, separator/condenser, nitrogen inlet and raw material charging parts. The reaction can be carried in a single step mixing all the reactants. Xylene was added by the

top of the condenser to fill the separator vertical inlet. The stirring was set at 50-100 rpm. The reactor was closed, and heated to 210 °C. The reaction was monitored by periodic determination of the acid number of the mixture until an acid number of about 5 was reached. At this point, heating was stopped and the mixture cooled to 100°C. During the reaction, the extracted water (lower phase) was periodically purged from the separator. Vacuum was then applied for evacuation of water from the reaction medium. After that reactor was cooled to 40-50°C. At this temperature, stirring was stopped and resin poured into a steel can.

Oil length of the synthesized alkyds were kept between %55-65 for facilitating the emulsification step in coating applications. Instead of phthalic anhydride, Sebacic acid was used at a maximum of 65% by weight. Since the synthesized alkyd polymers was emulsified, the acid number was kept low and the solids content was high. Synthesized products do not contain any co-solvents.

### **Biobased Alkyd Emulsion Synthesis**

The biobased alkyd resins were emulsified by phase inversion method. Bio-based alkyd was heated to 80 °C. Surfactant was added to bio-based alkyd resin under agitation. The surfactant was dissolved in the resin phase. The formation of water in oil (w/o) emulsion was completed by the addition of water to the resin phase. As more water was added the viscosity of the emulsion increased, and at a critical phase ratio, the emulsion inverted from the water-in-oil (w/o) emulsion to an oil-in-water (o/w) emulsion. The phase inversion was completed by the inversion from the water-in-oil (w/o) emulsion to an oil-in-water (o/w) emulsion. The combination of polymeric surfactant (nonionic surfactant) and dodecyl benzene sulfonic acid derived surfactant (anionic surfactant) were used in the synthesis.

### **Core Shell Hybrid System Synthesis**

The acrylic shell was synthesized in the presence of alkyd resin by the emulsion polymerization method. In the emulsion polymerization, methyl methacrylate, butyl acrylate and methacrylic acid were used as monomer, water were used as dispersion medium and ammonium per sulfate was used as initiator. Sulfosuccinic acid ester sodium salt and sodium lauryl ether sulphate were used as anionic surfactant, whereas nonylphenol ethoxylate was used as nonionic surfactant. In the polymerization, the reactor was charged with a solution of alkyd emulsion, water and nonionic surfactant. Reactor solution was heated up to 80 °C Emulsion part was prepared by mixing solution of acrylic monomers and anionic surfactants. Then, the catalyst of an aqueous solution of ammonium per sulfate (initiator) was added to reactor solution. After a period of 5

min, emulsion part was charged simultaneously with the catalyst of aqueous ammonium per sulfate solution during 2 h. Polymerization was carried out between 82 °C and 85 °C. In the synthesis, the combination of sodium lauryl ether sulphate (anionic surfactant) and nonylphenol ethoxylate (nonionic surfactant) were used.

### 3. Results and Discussion

Synthesis steps in the core shell approach were shown in Figure 1. The first step was the synthesis of sebacic acid modified biobased alkyd resin. Biobased alkyd emulsion synthesis was the second step. The third step was the core shell synthesis. In the synthesis, the acrylic shell was synthesized in the presence of the biobased alkyd resin in the core part by emulsion polymerization.

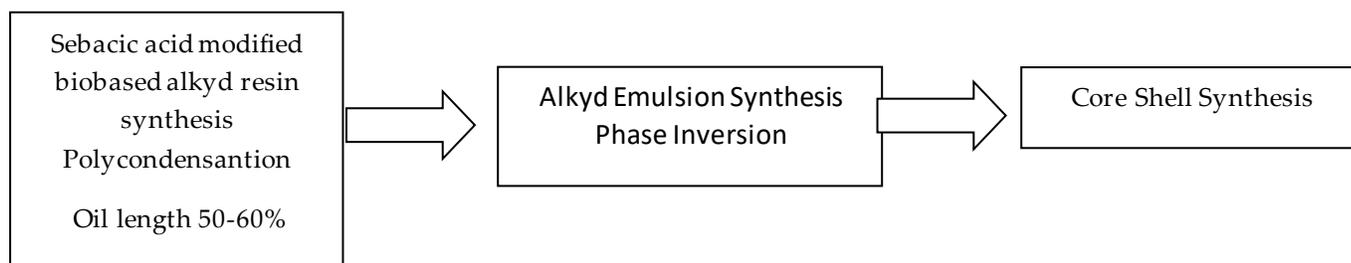


Figure 1. Synthesis steps in the core shell approach

In the first synthesis step, the effect of phthalic anhydride and bio-based sebacic acid on synthesis was examined by replacing them in certain proportions, and an attempt was made to increase the bio base content of the formula. Sebacic acid was used at a maximum of about 65% by weight instead of phthalic anhydride. Above this, the viscosity values were very high in the studies above and were not suitable for emulsification.

The synthesis results of biobased alkyd resin with sebacic acid was tabulated in Table 1. In the beginning of the study, targeted value of the biobased content of the alkyd resin was given as 35%. At the end of the study, the biobased content of the alkyd samples were higher than 49%. One of the project objectives has been achieved by exceeding the targeted value in biobased content.

Table 1. Technical Specifications of sebacic acid modified biobased alkyd resins

	F1		F2		F3		F4	
SEBACIC ACID	(%wt)	(%mole)	(%wt)	(%mole)	(%wt)	(%mole)	(%wt)	(%mole)

<b>Bio-based Sebacic Acid</b>	4,59	4,09	6,91	6,18	9,42	8,43	13,43	12,23
<b>Pthalic Anhydride</b>	16,73	20,38	14,07	17,20	13,05	12,30	7,18	8,93
<b>Other Rxn Substances</b>	78,68	75,533	79,02	76,623	77,53	79,273	79,39	78,84
<b>Bio-Based Content (%)</b>	49,83		51,41		52,31		57,15	
<b>Replacement of PA (wt%)</b>	21,5		32,92		48,36		65,16	
<b>Test Results (Sebacic )</b>								
<b>AN (mgKOH/g)</b>	10		9,5		9,0		10,5	
<b>Viscosity (p/25°C)</b>	178		190		230		700	
<b>% Solid Content (150°C - 2h)</b>	96,5		96,5		97,5		98	
<b>Final Hydroxyl Content (%OH)</b>	0,35		0,34		0,35		0,35	
<b>Conversion %</b>	96,5		96,5		97,5		98	
<b>Process Time (h)</b>	10		10,5		12		14	

In the next step, the biobased alkyd resins (F1, F2, F3, F4) were emulsified by phase inversion method. Literature studies indicated that alkyd resin with high viscosity had been found to be difficult to disperse during emulsification [9]. Due to the high viscosity of F4 alkyd, no phase change has been successfully achieved with the percentages of the anionic-nonionic surfactant pairs used in the emulsification of other bio-based alkyds. For this reason, F4 has been eliminated from the studies.

After emulsification studies were completed, the stability test results of biobased alkyd emulsion were evaluated. Literature studies revealed that the stability of the alkyd emulsion was significantly influenced by the alkyd oil length, acid value and hydroxyl number, type and amount of surfactant [10, 11,13]. The results indicated that two products with favorable stability were obtained with sebacic acid modified biobased alkyd resin, which were F2 and F3. Technical Specification sebacic acid modified biobased alkyd emulsion was given in Table 2. . In the beginning of the study, targeted solid content of the biobased alkyd resin was given as 50%. At the end of the study, solid content of the biobased alkyd resins were close to target solid value 48 %. The other project objectives has been achieved by synthesizing of the stable sebacic acid modified biobased alkd emulsion resins.

**Table 2.** Technical Specification sebacic acid modified biobased alkyd emulsion

Alkyd Emulsion Code	Alkyd Code	Surfactant amount % (wt alkyd)	Water amount (%)	Solid %	pH	Viscosity cps
AE2	F2	12	53	47.29	7.1	30
AE3	F3	12	53	47.80	7.6	60

\* surfactant type: combination of polymeric surfactant and dodecyl benzene sulfonic acid derived surfactant

Hybrids with different biobased alkyd–acrylic ratios were prepared. The effect of alkyd–acrylic ratios on the polymerization results and stability of the polymer were investigated. In the core shell approach; 50:50, 30:70, 20:80, 10:90 Alkyd-Acrylic ratios were studied and the results were evaluated. The effect of type and amount of surfactants on the polymerization rest were also evaluated. . A series of experiments was carried out by varying the amount of anionic surfactant 0.5-3% and 0.5-2 % nonionic surfactant. In the synthesis, the combination of sulfosuccinic acid ester sodium salt (anionic surfactant) and nonylphenol ethoxylate (nonionic surfactant) were studied and the results were tabulated in Table 3 and Table 4. The results were indicated that polymerization results were not succesful by using the combination of sulfosuccinic acid ester sodium salt (anionic surfactant) and nonylphenol ethoxylate (nonionic surfactant).

**Table 3.** Hybrid biobased AE2 alkyd emulsion–acrylic synthesis results

Alkyd: Acrylic Ratio	%anionic surfactant	%nonionic surfactant	Polimerization results
50:50	2	-	X
	2	0.9	X
	3	1.5	X
30:70	2	0.9	X
	3	0.9	X
	3	0.9 (0.6 E+0.3 R)	X
	3	1.5	X

20:80	2	0.9	X
	3	0.9	X
	3	1.5	X
10:90	2	0.9	X
	3	0.9	X
	3	1.5	X

\*the combination of sulfosuccinic acid ester sodium salt (anionic surfactant) and nonylphenol ethoxylate (nonionic surfactant) \*X: Polimerization results were not succesful.

**Table 4.** Hybrid biobased AE3 alkyd emulsion–acrylic synthesis results

Alkyd: Acrylic Ratio	%anionic surfactant	%nonionic surfactant	Polimerization results
50:50	2	-	X
	2	0.9	X
	3	1.5	X
30:70	2	0.9	X
	3	0.9	X
	3	0.9 (0.6 E+0.3 R)	X
	3	1.5	X
20:80	2	0.9	X
	3	0.9	X
	3	1.5	X
10:90	2	0.9	X
	3	0.9	X
	3	1.5	X

\*the combination of sulfosuccinic acid ester sodium salt (anionic surfactant) and nonylphenol ethoxylate (nonionic surfactant)

\*X: Polimerization results were not succesful.

For this reason, the another combination of sodium lauryl ether sulphate (anionic surfactant) and nonylphenol ethoxylate (nonionic surfactant) were used in the synthesis

studies. The results were tabulated in Table 5 and Table 6. The results indicated that combination of sodium lauryl ether sulphate (anionic surfactant) and nonylphenol ethoxylate (nonionic surfactant) were suitable in the hybrid biobased alkyd acrylic synthesis. The results also showed that hybrids with alkyd–acrylic ratio of 10:90, 20:80 and 30:70 were successfully synthesized at specific surfactant percentage.

**Table 5.** Hybrid biobased AE2 alkyd emulsion–acrylic synthesis results

Alkyd: Acrylic Ratio	%anionic surfactant	%nonionic surfactant	Polimerization results
50:50	2	-	X
	2	0.9	X
	3	0.9	X
30:70	3	0.9	X
	4	0.9	X
	3	1.5	X
	3	2	OK
20:80	3	0.9	OK
10:90	3	0.9	OK

\*the combination of sodium lauryl ether sulphate (anionic surfactant) and nonylphenol ethoxylate (nonionic surfactant)

\*X: Polimerization results were not succesful.

**Table 6.** Hybrid biobased AE3 alkyd emulsion–acrylic synthesis results

Alkyd: Acrylic Ratio	%anionic surfactant	%nonionic surfactant	Polimerization results
50:50	2	-	X
	2	0.9	X

	3	0.9	X
30:70	3	0.9	X
	4	0.9	X
	3	1.5	X
	3	2	OK
20:80	3	0.9	OK
10:90	3	0.9	OK

\*the combination of sodium lauryl ether sulphate (anionic surfactant) and nonylphenol ethoxylate (nonionic surfactant)

\*X: Polymerization results were not succesful.

The core shell samples which were succesfully emulsified were coded as C1, C2, C3, C4, C5 and C6. Technical specifications of the samples were given in Table 7. The stability results indicated that all core shell samples were stable.

*Table 7 . Technical specifications of the core shell samples*

Sample Code	Biobased Alkyd Emulsion Code	Alkyd/ Acrylic Ratio	Monomer Composition	Solid (%)	pH	Viscosity cps
CS1	AE2	30:70	50 MMA:50 BA	44.7	8.0	90
CS2	AE2	20:80	50 MMA:50 BA	44.3	9.1	160
CS3	AE2	10:90	50 MMA:50 BA	43.7	8.2	50
CS4	AE3	30:70	50 MMA:50 BA	45.0	7.4	200
CS5	AE3	20:80	50 MMA:50 BA	44.0	7.5	60
CS6	AE3	10:90	50 MMA:50 BA	43.0	7.5	60

The crystalline morphologies of the core shell samples were investigated by Carl Zeiss 300VP Scanning Electron Microscope (SEM). The results were given in Table 8. The results revealed that random spherical aggregates were observed.

The particle sizes of the samples were determined by using Malvern Nano ZS 90 Zetasizer. The results indicated that the particle sizes of CS1-CS3 were in the range of 5-8 nm, whereas the particle sizes of CS4-CS6 were in the range of 2-5 nm.

*Table 8. Characterization of the Core Shell Samples*

Sample Code	Particle size (nm)	SEM morphological results
CS1	7.73	Random spherical aggregates
CS2	6.01	Random spherical aggregates
CS3	5.05	Random spherical aggregates
CS4	5.15	More ordered random spherical aggregates
CS5	4.43	More ordered random spherical aggregates
CS6	2.19	More ordered random spherical aggregates

As a summary,

- Bio based alkyd-acrylic hybrid emulsion by using core shell approach were synthesized.
- Hybrids with alkyd-acrylic ratios of 10:90, 20:80 and 30:70 were successfully synthesized by using F2 and F3 biobased alkyd emulsion.
- It was found that; alkyd to acrylic ratio, type of the surfactant and the surfactant percentage had the important effects on the emulsion polymerization results
- The stability test results indicated that all core shell samples were stable.
- The particle sizes of the core shell samples were in the range of 2-8 nm
- SEM morphological results indicated that random spherical aggregates were observed.

#### 4. Acknowledge

The authors are grateful to The Scientific and Technological Research Council of Turkey (TUBİTAK) We are grateful for the financial support provided by funding bodies within ERA-NET with co-funds from the European Commission ProWood project. We would like to thank to the ProWood consortium members their discussions and contributions in whole project.

## References

- [1] Ifijen, H. I., Maliki, M., Ifeanyi, J. O., Aghedo, O.N., Ohiocheoya, EçB., Review on Solvents Based Alkyd Resins and Water Borne Alkyd Resins: Impacts of Modification on Their Coating Properties, *Chemistry Africa*, 2022, 5, 211–225.
- [2] Yousefi, A. A., Pishvaei, M., Yousefi, A., Preparation of Water -Based Alkyd/Acrylic Hybrid Resins, *The Progress in Color, Colorants and Coatings (PCCC)*, 2011, 4, 15-25.
- [3] Elrebii, M., Mabrouk, A.B., Boufi, S., Synthesis and properties of hybrid alkyd–acrylic dispersions and their use in VOC-free waterborne coatings, *Progress in Organic Coatings*, 2014, 77, 757-764.
- [4] Elrebii, M., Kamounb, A., Boufi, S., Waterborne hybrid alkyd–acrylic dispersion: Optimization of the composition using mixture experimental designs, *Progress in Organic Coatings*, 2015, 87, 222–231.
- [5] Guyot, A., Landfester, K., Schorkc, F.J., Wang, C., Hybrid polymer latexes, *Progress in Polymer Science*, 2007, 32, 1439-1461.
- [6] Heiskanen, N., Jämsä, S, Paajanen, L., Koskimies, S., Synthesis and performance of alkyd–acrylic hybrid binders, *Progress in Organic Coatings*, 2010, 67, 329-338.
- [7] Nabuurs, T., Bajjards, R.A., German, A.L, Alkyd-acrylic hybrid systems for use as binders in waterborne paints, *Progress in Organic Coatings*, 1996, 27, 163-17
- [8] Weissenborn, P.K., Motiejauskaite, A., Emulsification, drying and film formation of alkyd emulsions, *Progress in Organic Coatings*, 2000, 40, 253-266.
- [9] Watson, D.J., Mackley, M.R., The rheology of aqueous emulsions prepared by direct emulsification and phase inversion from a high viscosity alkyd resin, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2002, 196, 121–134.
- [10] Östberg, G., Hulden, M., Bergenstahl, B., Holmberg, K., Alkyd emulsions, *Progress in Organic Coatings*, 1994, 24, 281-297.
- [11] Östberg, G., Bergenstahl, B., Hulden, M., Influence of emulsifier on the formation of alkyd emulsions, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 1995, 94, 161-171.
- [12] Kivitt, P.J.J., Aramendia, E., Cabrera, A.A., Rios, L. Water-Based Coatings Based on Mixtures of Acrylic Dispersions and Alkyd Emulsions, 2009, *Macromolecular Symposia*, 283–284, 290–299.
- [13] Karlsson, O.J., Deriss, M.J., Morphologies and droplet sizes of alkyd–acrylic hybrids with high solids content, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2004, 245, 115–125.