



Hydrophobic Waterborne Hybrid (Alkyd/Styrene Acrylic) Latexes

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1. INTRODUCTION

2. EXPERIMENTAL

3. EVALUATION OF ANALYSIS RESULTS

4. CONCLUSION

5. REFERENCES

6. ACKNOWLEDGMENT

- **Developing technology**
- **Increasing population**
- **Industrialization**



**Composite
Materials**

**Hybrid
Materials**

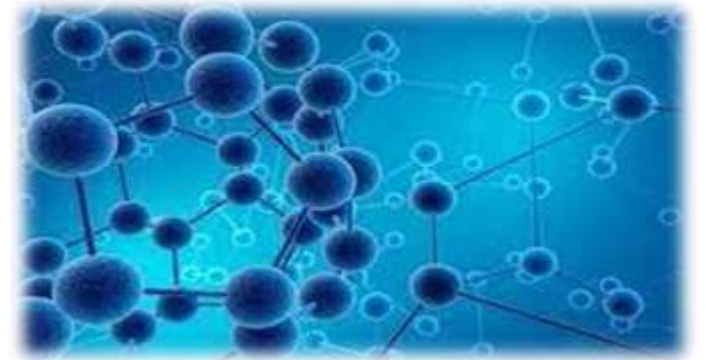


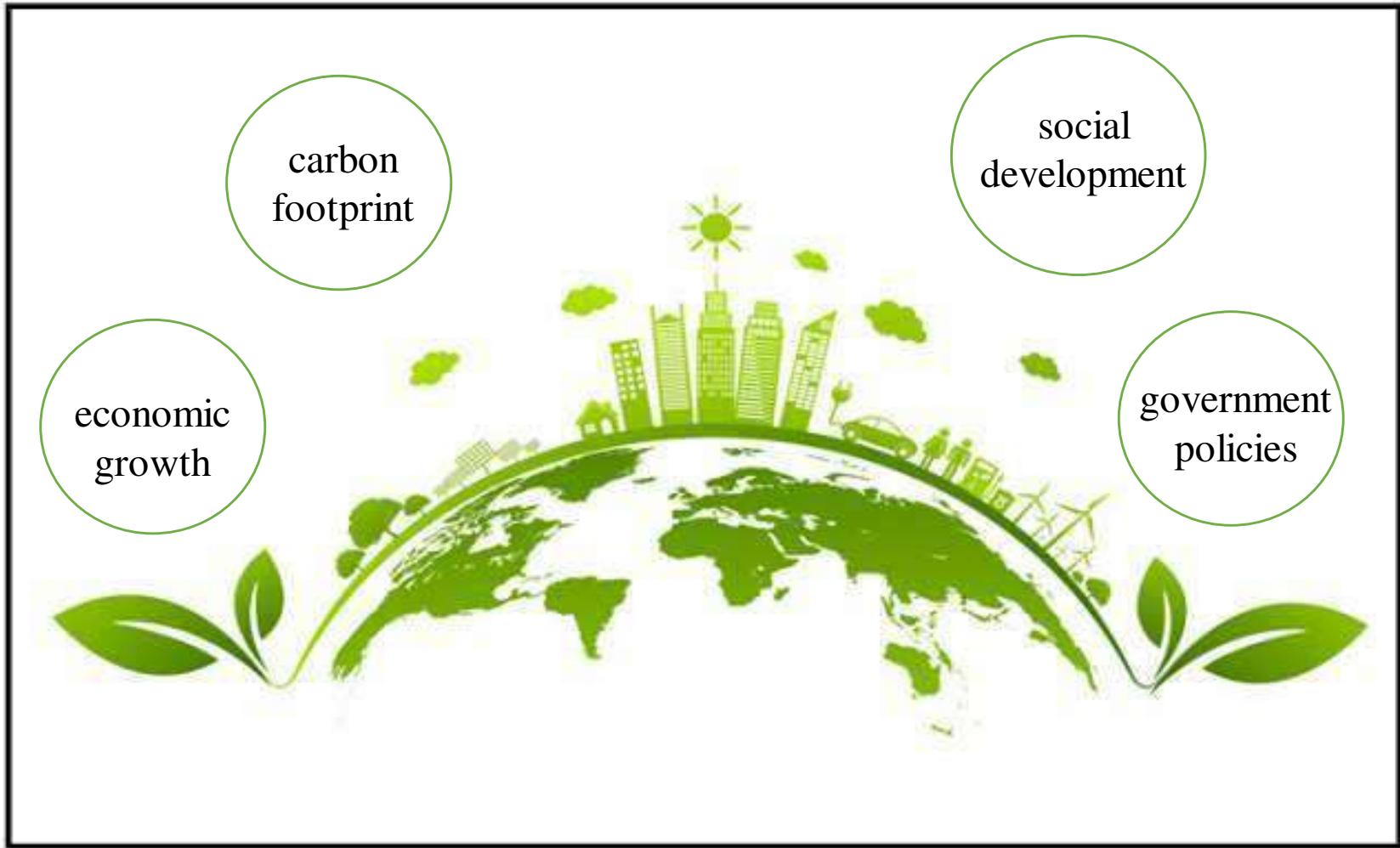
- **Material requirement**
- **Cost**

- **Disruption of supply-demand balance**
- **Shortage of raw materials**

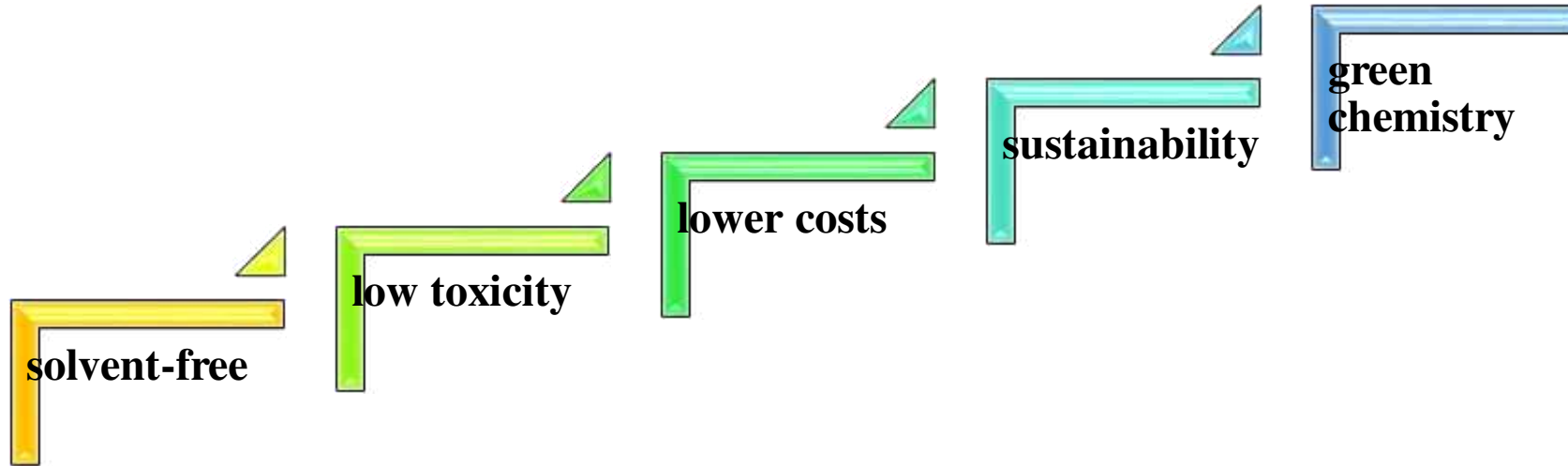


This technology offers the possibility of combinations of at least two different, normally incompatible materials, combining certain properties that cannot be achieved in a single polymer by either component alone.



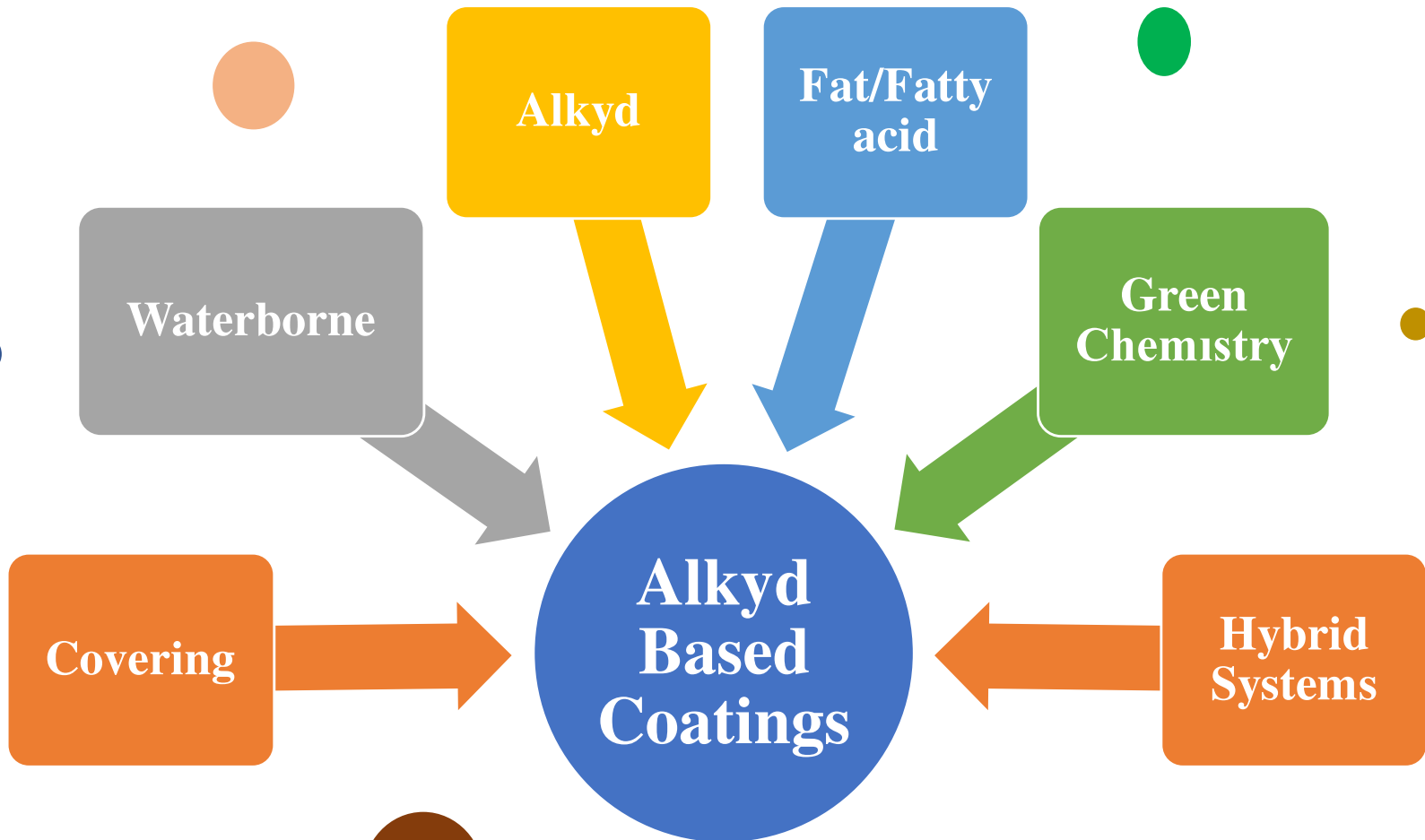


Waterborne Hybrid Materials





In recent years, waterborne formulations have dominated the architectural paint market due to their low VOC, odor and toxicity.





Waterborne hybrid (alkyd/styrene acrylic) emulsion polymers and exterior paint applications

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Received: 4 November 2022 / Revised: 31 January 2023 / Accepted: 1 February 2023
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Synthesis of Hydrophobic Waterborne Hybrid (Alkyd/Styrene Acrylic) Latexes

- *Alkyd resin synthesis*

Why hemp seed oil (HSO)?

	HSO
Chemical form	Triglyceride
Acid value (mg KOH/ g sample)	5,47
Iodine index(g I ₂ /100g)	160
Oil lenght (%)	60
Drying index	86
Class	Drying oils
Linoleik asit (%)	56
Oleic acid (%)	18

- *Alkyd resin synthesis*

Table 1. Formulation of alkyd resin synthesis

Alkyd synthesis	Functions	Suppliers
Pentaerythritol	Polyalcohol	Acros Organic Company, Belgium
Phthalic anhydride	Polybasic acid	Sigma Aldrich, USA
Xylene	Solvent (reflux)	Sigma Aldrich, USA
o-Phosphoric acid	Catalys	Fluka, Turkey
Lithium stearate	Catalyst	Sigma Aldrich, USA



Hemp



Hemp seed



Hemp seed oil

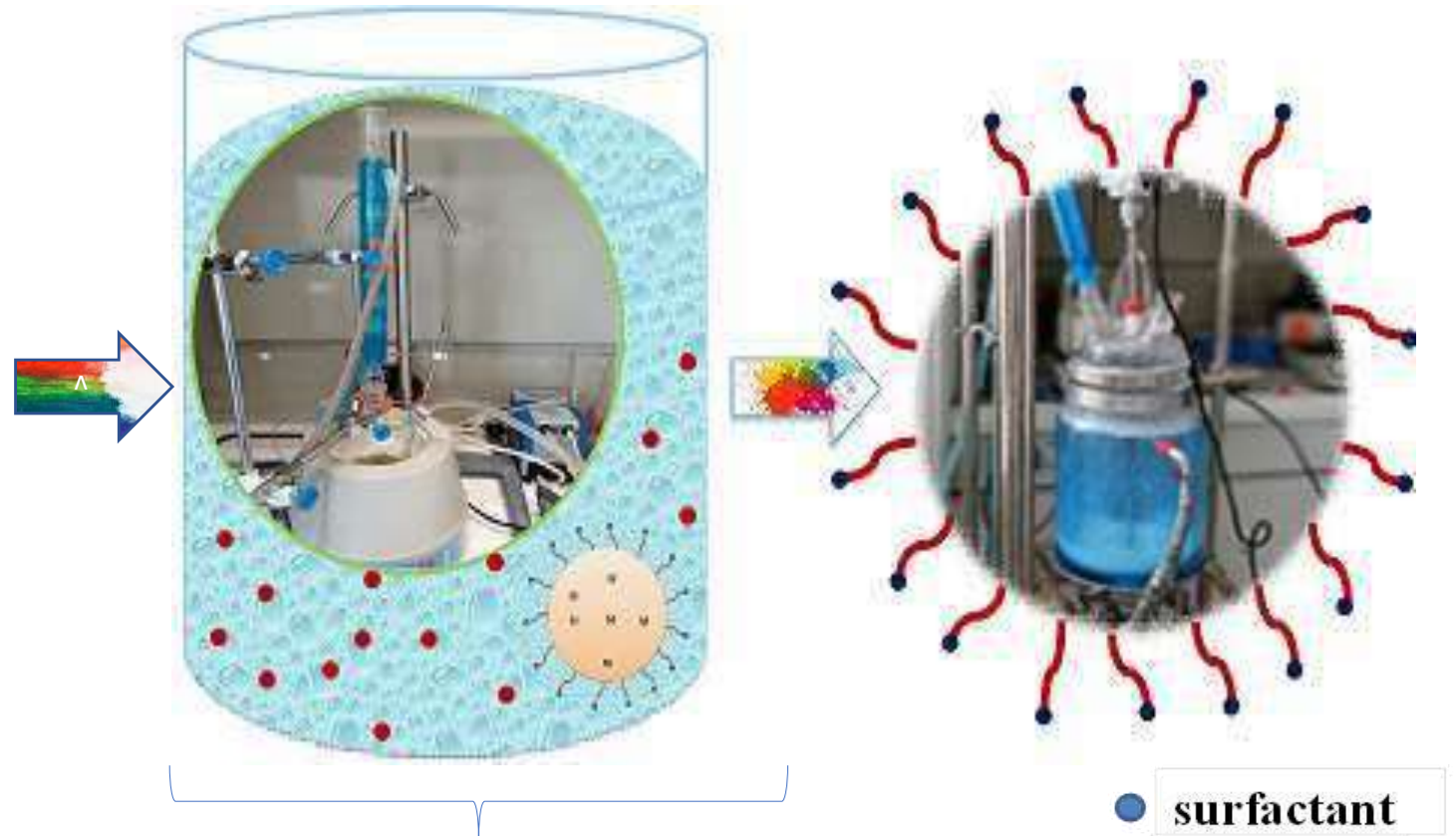


Monoglyceride (Alcolysis) Method

• *Synthesis of Hydrophobic Waterborne Hybrid (Alkyd/Styrene Acrylic) Latexes*

Table 2. Formulation of hydrophobic waterborne hybrid (alkyd/styrene acrylic) latexes

Polymer emulsion	Functions	Suppliers
Styrene (Sty)	Comonomer	Betek Boya, Turkey
Butyl acrylate (BA)	Comonomer	Betek Boya, Turkey
Acrylic acid (AA)	Comonomer	ZAG Kimya, Turkey
2,2,2-trifluoroethyl methacrylate (TFEMA)	Hydrophobic monomer	Sigma Aldrich, USA
Triethoxyvinyl silane (VTES)	Hydrophobic monomer	Acros Organic Company, Belgium
Span 80	Nonionic surfactant	Sigma Aldrich, USA
Exosel 073	Anionic surfactant	Betek Boya, Turkey
Hexadecane (HD)	Cosurfactant	Sigma Aldrich, USA
Potasyum Persulfate (KPS)	Initiator	Merck, Germany



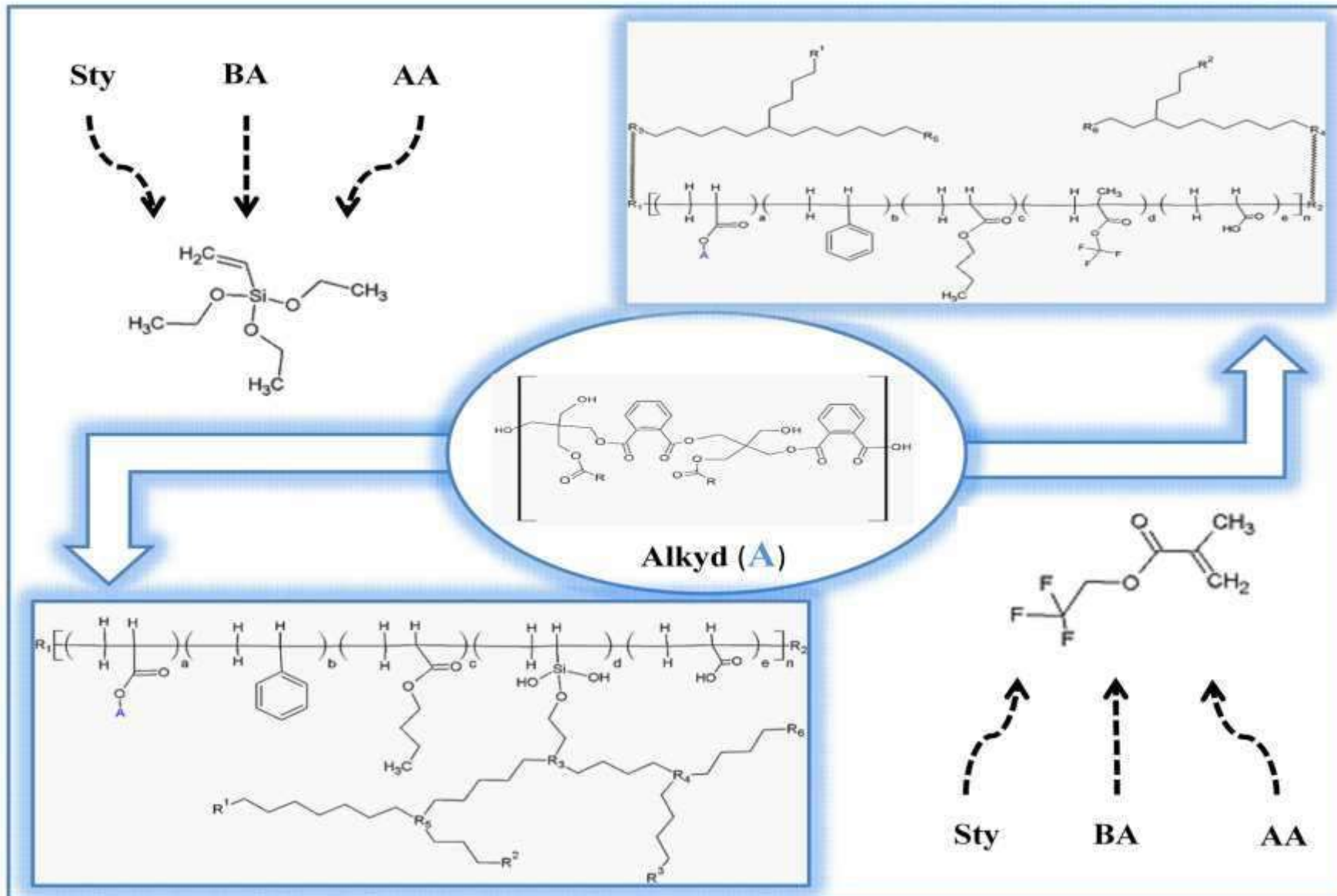
Mini-emulsion Polymerization (semi-batch)

	<i>A-3S</i>	<i>A-3F</i>	<i>A-6S</i>	<i>A-6F</i>	<i>K-3S</i>	<i>K-3F</i>	<i>K-6S</i>	<i>K-6F</i>
HSO based-Alkyd ^a	-	-	-	-	10	10	10	10
VTES ^a	3	-	6	-	3	-	6	-
TFEMA ^a	-	3	-	6	-	3	-	6
Sty ^a	47.5	47.5	46.0	46.0	42.5	42.5	41.0	41.0
BA ^a	47.5	47.5	46.0	46.0	42.5	42.5	41.0	41.0
AA ^a	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
HD ^a	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Span 80 ^a	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8
Exosel 073 ^a	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
DIW ^b	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0
Initiator-I								
KPS ^a	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Initiator-II								
KPS ^a	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Total (g)	200.0	200.0	200.0	200.0	200.0	200.0	200.0	200.0

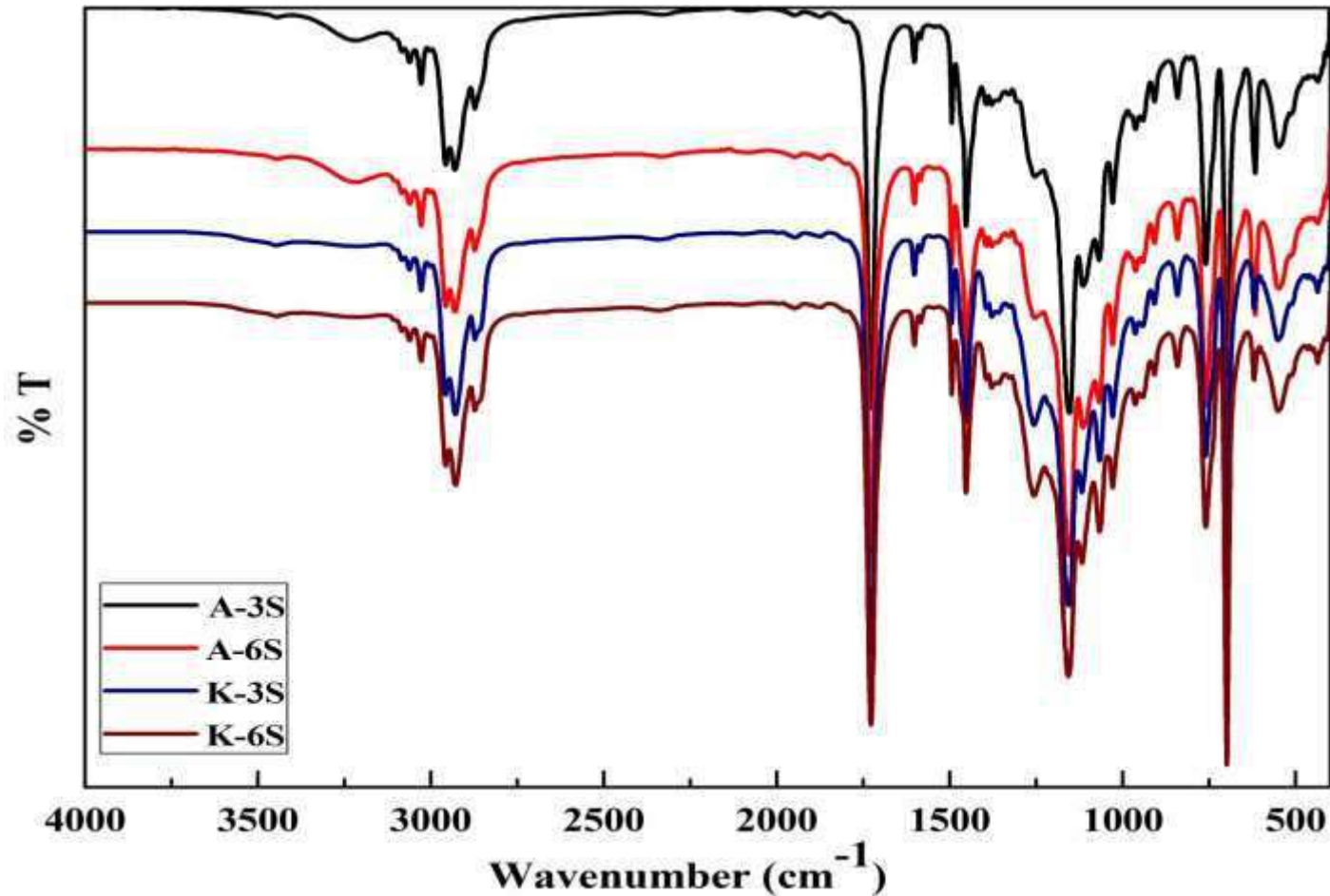
- **A-3S**; latex containinng 3% VTES
- **A-6S**; latex containinng 6% VTES
- **A-3F**; latex containinng 3% TFEMA
- **A-6F**; latex containinng 6% TFEMA
- **K-3S**; latex containinng alkyd and 3% VTES
- **K-6S**; latex containinng alkyd and 6% VTES
- **K-3F**; latex containinng alkyd and 3% TFEMA
- **K-6F**; latex containinng alkyd and 6% TFEMA

^a % of monomer amount,

^b 50% of total weight



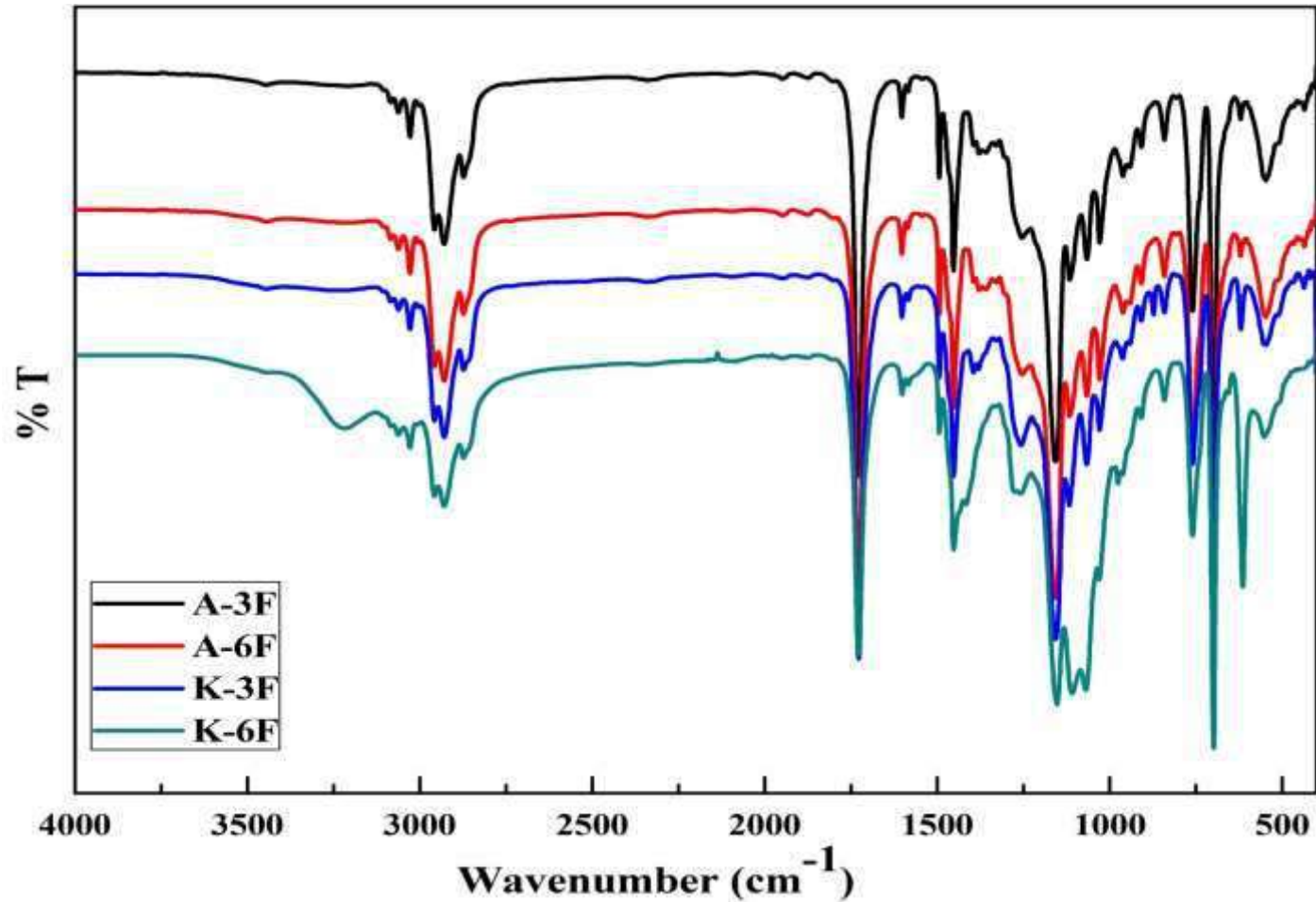
- *Tests and measurements*



cm ⁻¹	
3600-3300	-OH
3300-3000	=CH
3030	Ar-H
3000-2700	-C-H (-CH ₃ , -CH ₂ ve -CH groups)
1727	C=O
1675-1500	C=C (aliphatic/aromatic)
1150	C-O
750	ortho disubstituted benzene

Figure 1. FTIR spectra of VTES-containing waterborne hydrophobic hybrid (alkyd/styrene acrylic) latexes

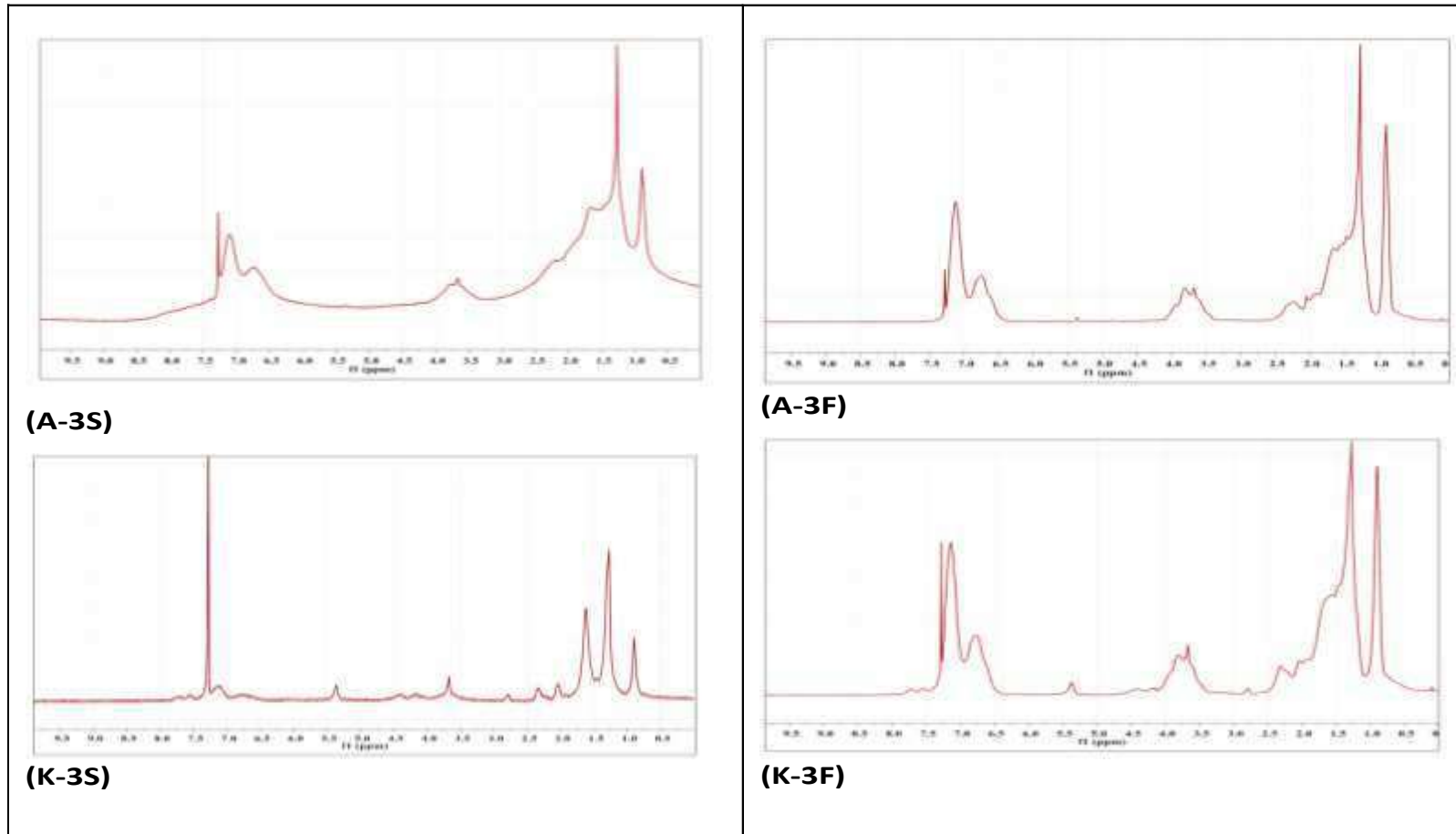
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Figure 2. FTIR spectra of TFEMA-containing waterborne hydrophobic hybrid (alkyd/styrene acrylic) latexes

- *Tests and measurements*



CHF; 4.70 ppm

Si-C; 1.50 ppm

Figure 3. ¹H-NMR spectra of waterborne hydrophobic hybrid (alkyd/styrene acrylic) latexes

- *Tests and measurements*

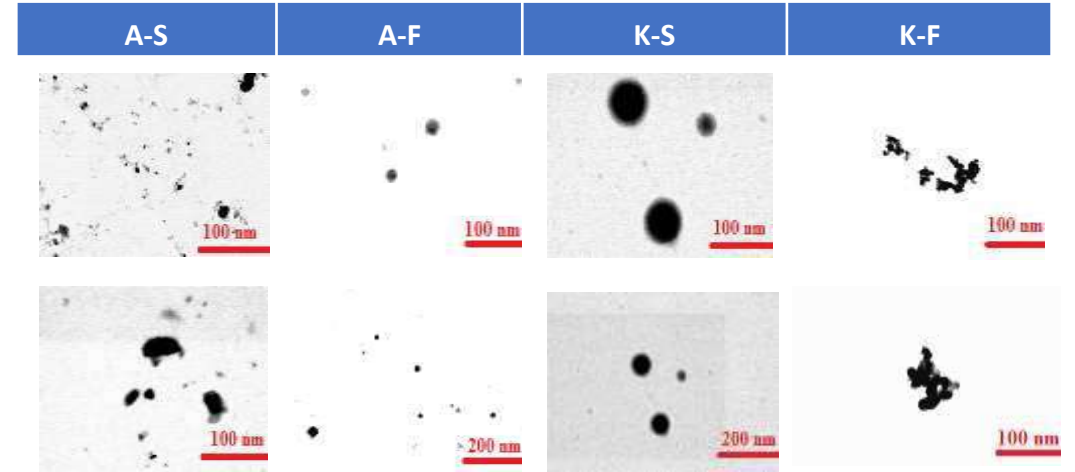
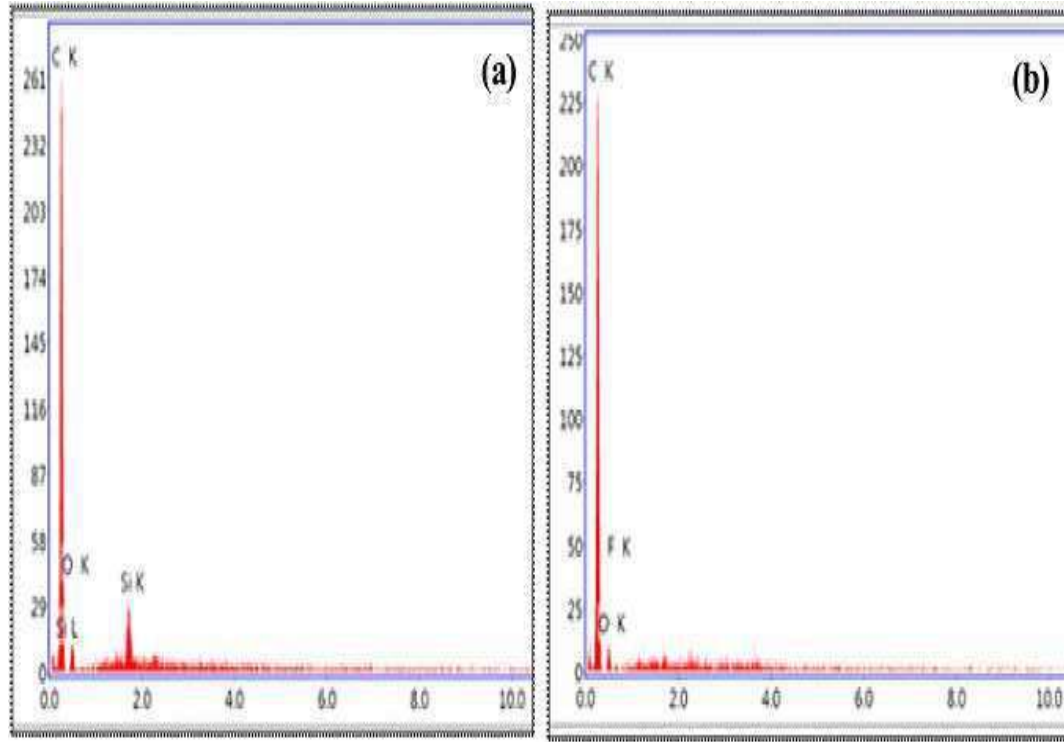


Figure 4. EDAX and STEM images of waterborne hydrophobic hybrid (alkyd/styrene acrylic) latex films containing VTES (a) ve TFEMA (b)

- *Tests and measurements*

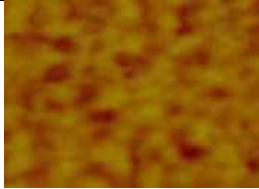
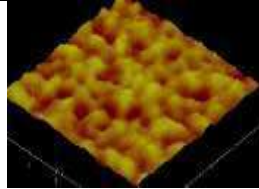
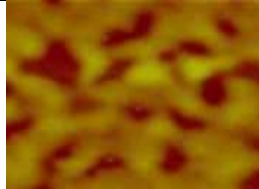
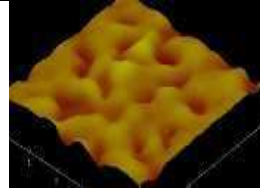
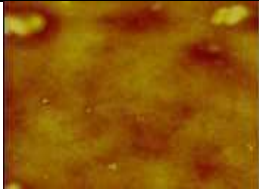
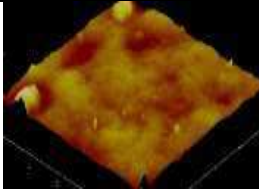

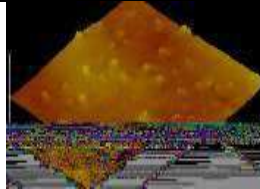
A-3S		A-3F	
Phase	Height (3D) (Rq= 12.163 nm, Ra= 9.621nm)	Phase	Height (3D) (Rq= 21.956 nm, Ra= 17.009nm)
			
K-3S		K-3F	
Phase	Height (3D) (Rq= 5.525 nm, Ra= 3.989 nm)	Phase	Height (3D) (Rq= 3.469 nm, Ra= 2.789 nm)
			

Figure 5. Phase contrast and topographic (5 $\mu\text{m} \times 5 \mu\text{m}$) AFM images of waterborne hydrophobic hybrid (alkyd/styrene acrylic) latexes

- *Tests and measurements*

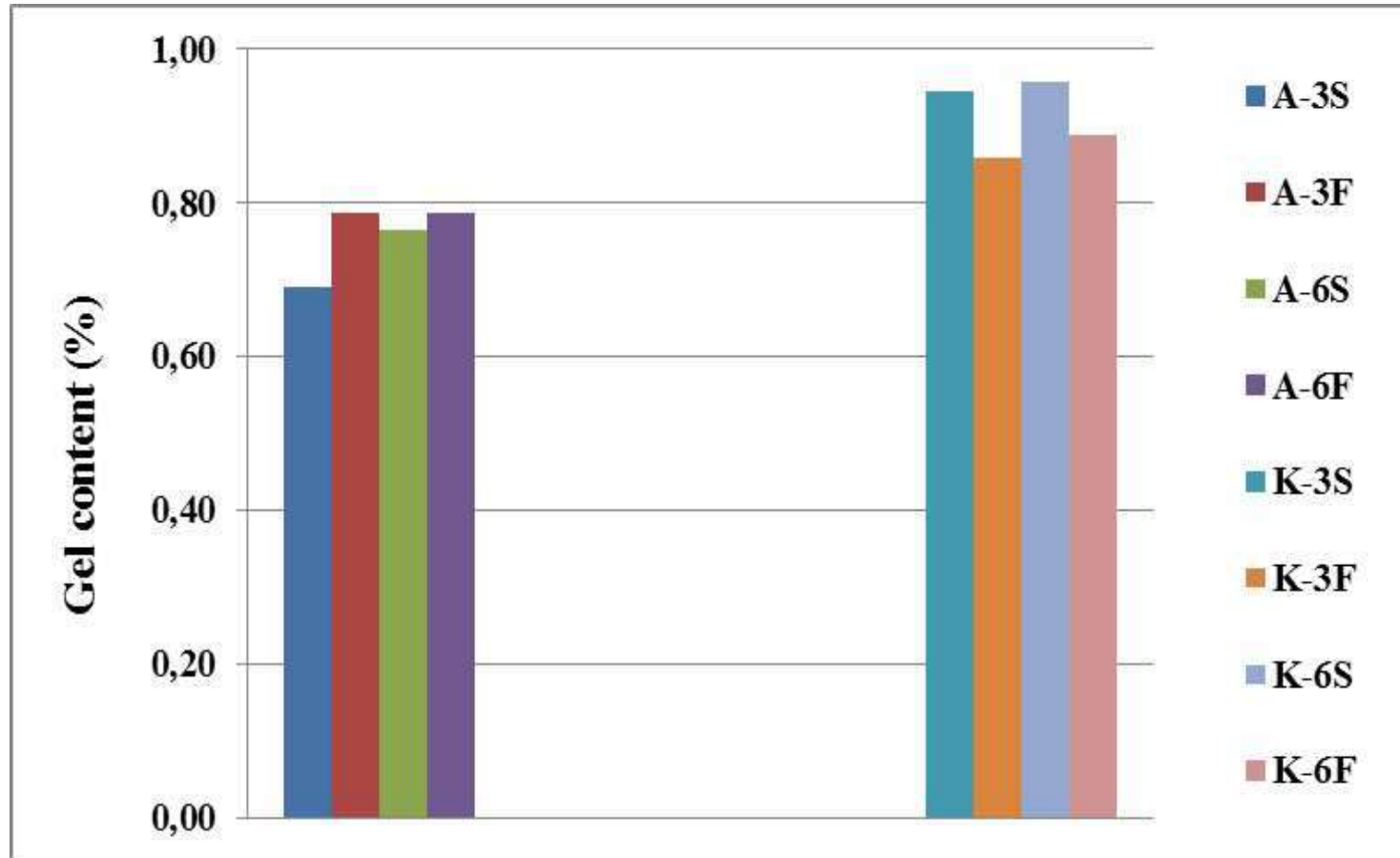


Figure 6. Gel content of waterborne hydrophobic hybrid (alkyd/styrene acrylic) latexes

- *Tests and measurements*

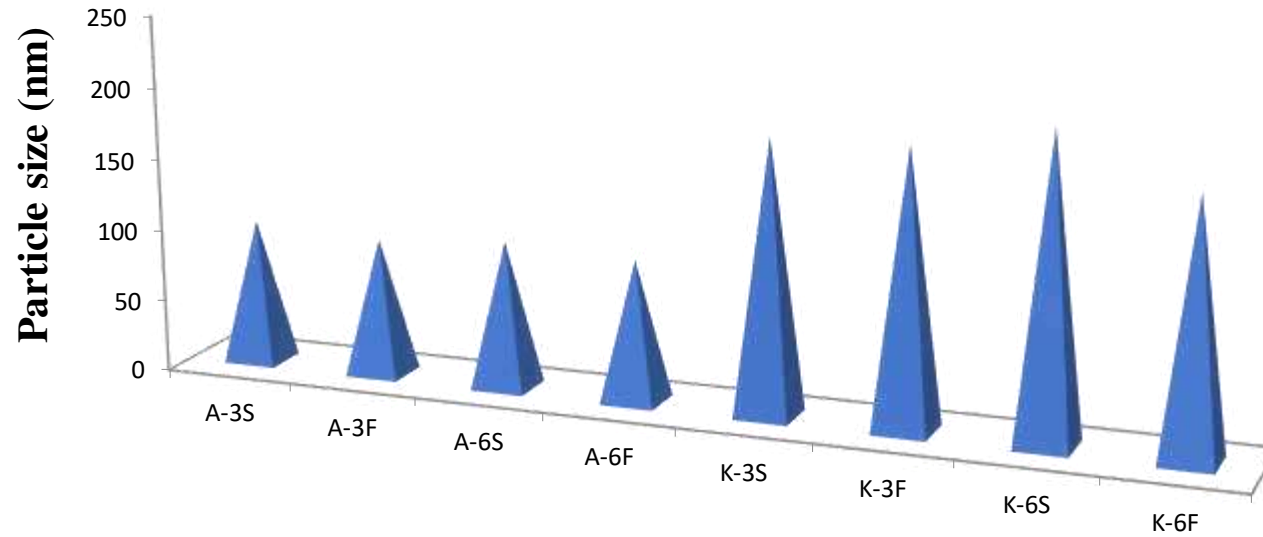


Figure 7. Particle size of waterborne hydrophobic hybrid (alkyd/styrene acrylic) latexes

- *Tests and measurements*

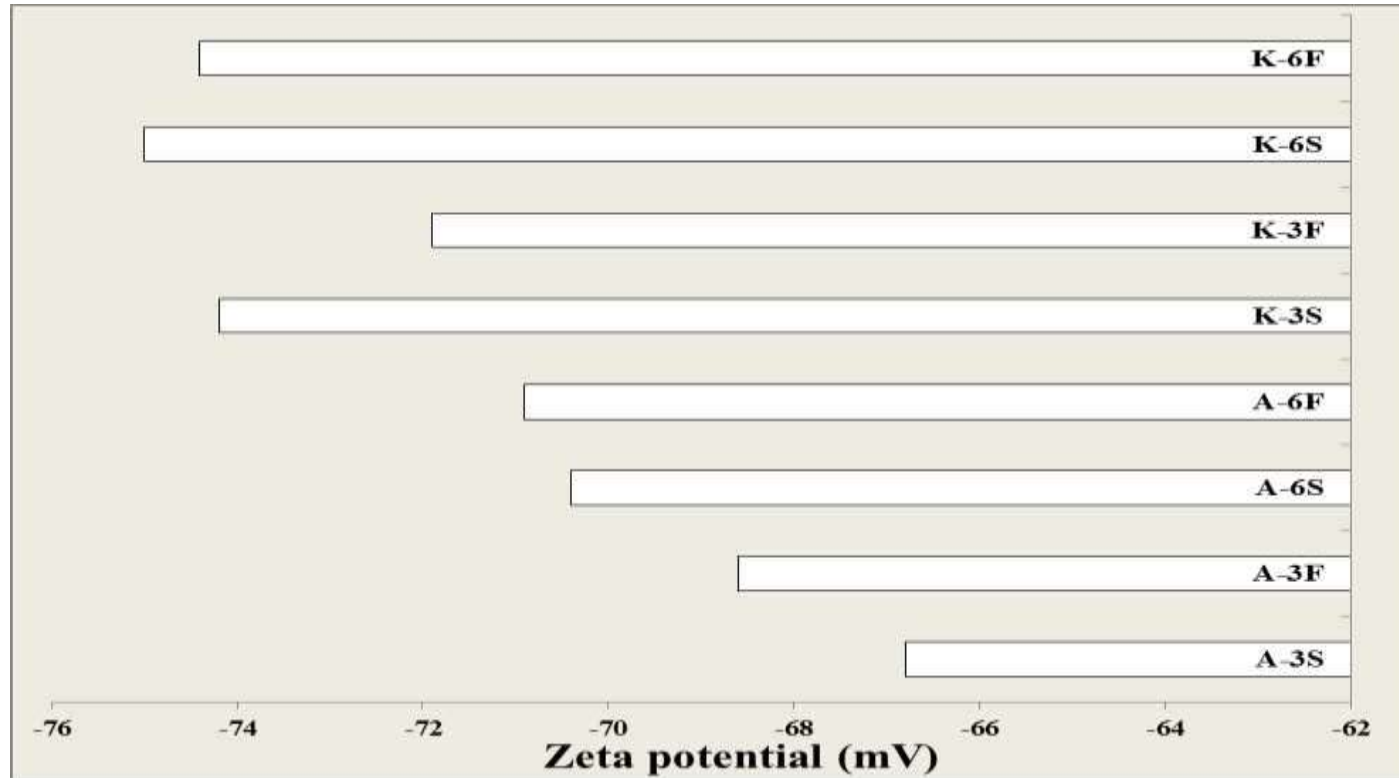


Figure 8. Zeta potential of waterborne hydrophobic hybrid (alkyd/styrene acrylic) polymer latexes

- *Tests and measurements*

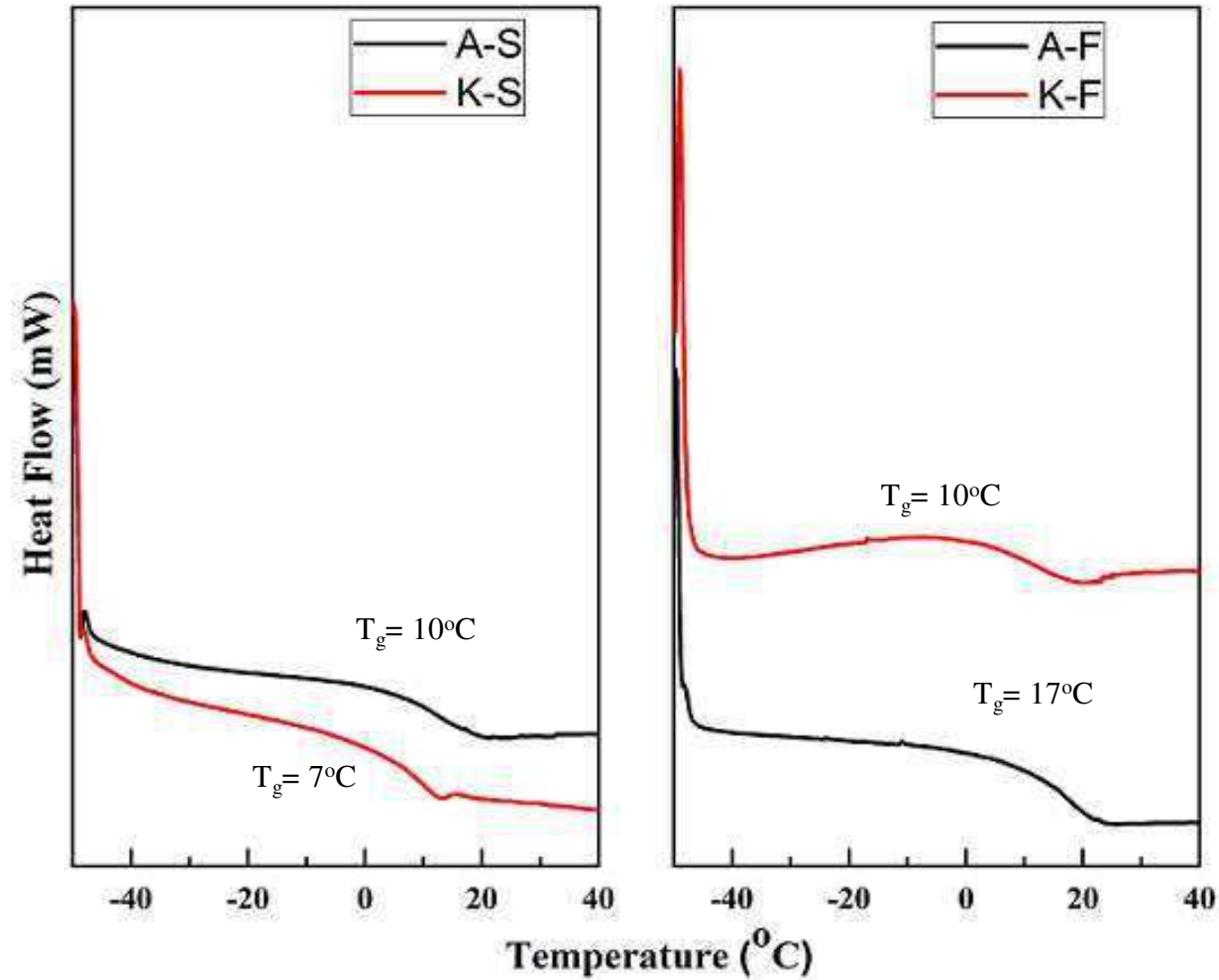


Figure 9. DSC curves of VTES and TFEMA-containing waterborne hydrophobic hybrid (alkyd/styrene acrylic) latexes

- *Tests and measurements*

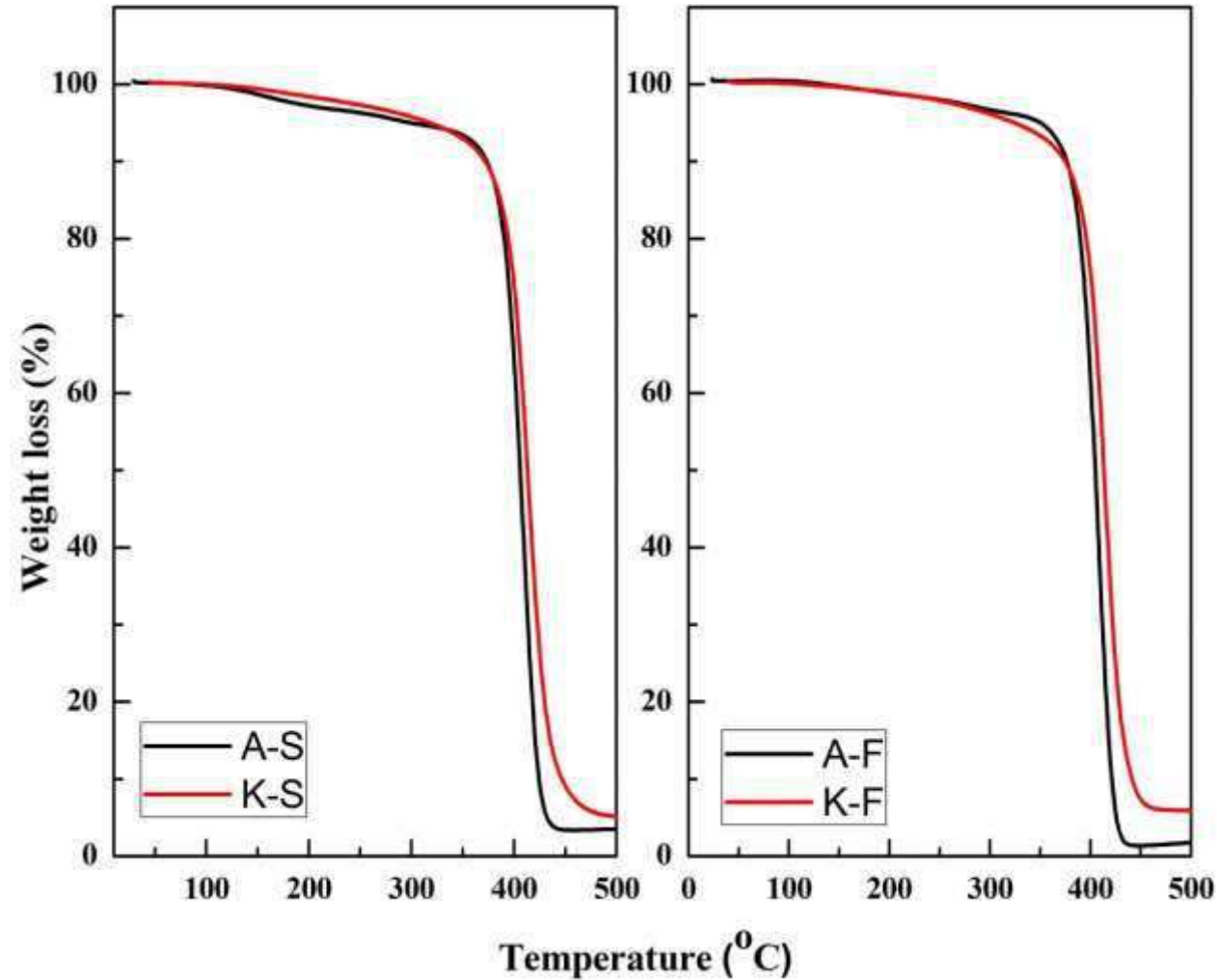


Figure 10. TGA curves of VTES and TFEMA-containing waterborne hydrophobic hybrid (alkyd/styrene acrylic) latexes

- *Tests and measurements*

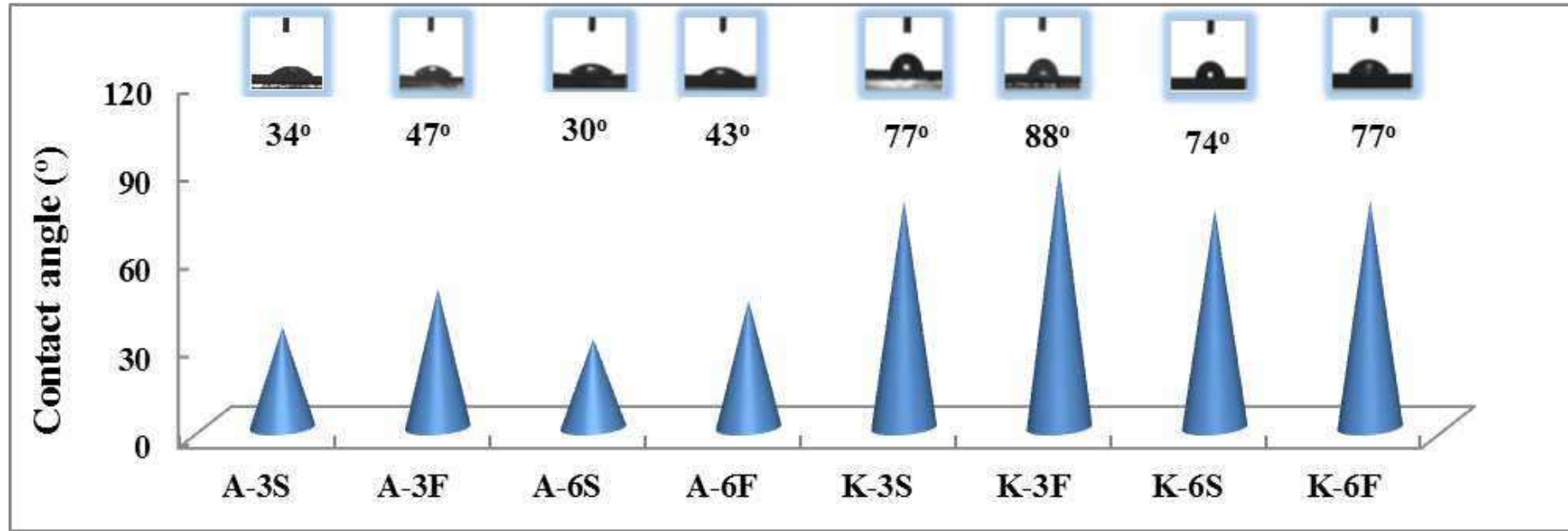


Figure 11. Static contact angle values of waterborne hydrophobic hybrid (alkyd/styrene acrylic) latexes containing VTES and TFEMA

The reaction was repeated for K-6S without AA. It has been observed that the contact angle of the obtained latex film increased (92°).

- *Tests and measurements*

Table 3. Physicochemical properties of hydrophobic hybrid latexes

Emulsion Properties	SC(%)	pH	Visc (cP) (20°C)	T_g (°C)
A-3S	49.70	8.18	105	10
A-3F	50.70	8.12	104	17
A-6S	50.02	8.24	108	
A-6F	49.86	8.30	107	
K-3S	49.03	8.24	116	7
K-3F	49.42	8.28	120	10
K-6S	50.72	8.20	132	
K-6F	50.24	8.18	136	

SC: solid content; Visc: viscosity; T_g: glass transition temperature

Conclusion

- In this study, monomers containing silane and fluorine groups were successfully incorporated into the waterborne hybrid (alkyd/styrene acrylic) polymer latex system. The effects of these fluorine and silane agents on the physical and chemical properties of the functional coating materials were discussed.
- The synthesized waterborne hybrid latexes and films were characterized by FT-IR, NMR, particle size, zeta potential, gel content, AFM, STEM, EDAX, TGA, DSC, and CA tests. The structures of waterborne hybrid (alkyd/styrene acrylic) polymer latex modified with VTES and TFEMA synthesized from FT-IR and NMR results were confirmed.
- The tests (AFM, STEM, EDAX, CA, DSC, and TGA) showed that, in addition to the alkyd content, silane and fluorine groups also contribute positively to the synthesized films. We saw more clearly the advantages of fluorine and silane groups, especially in polymer emulsions containing alkyd (K-S; K-F).
- As a result, it is expected to obtain composite materials with advantages and to expand the application range with the modification of silane and fluorine agents in addition to the copolymerization of three materials with high complementarity (alkyd-styrene-acrylate).
- It could be suggested that these synthesized alkyd-based hybrid latexes will increase their potential as protective coatings.

Conclusion

- In addition, it is thought that the use of plant sources such as hemp seed oil in the synthesis of alkyd-based hybrid latex, in terms of sustainability and environmental friendliness, will form the basis for more reliable and healthy coating applications in the future.

Acknowledgments

This study was supported by the Yozgat Bozok University Scientific Research Projects Unit with code 6602c-FEN/21-459. We would like to thank Betek Paint and Chemical Industry Inc and Dr. Mesut Eren and Özlem Yılmaz Adıgüzel for helping in the supply of monomers and performing some analysis.



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