Suspension polymerization of vinyl chloride: stabilization of "model o/w emulsions" by PVA

S. Hong[a], C. Labbe[a], G. Riess[a] and T. Lasuye[b]

[a] Ecole Nationale Supérieure de Chimie de Mulhouse, Laboratoire de Chimie Macromoléculaire (CNRS), 3 rue Alfred Werner, 68093 Mulhouse cedex

[b] LVM, Recherche de Synthèse, BP 49, Usine de Mazingarbe, 62160 Bully les Mines

PVC is mainly produced by suspension polymerization (85%) of Vinyl Chloride Monomer (VCM). In this method the monomer is dispersed in water and polymerized. The stability of the suspension is obtained by polymeric surfactants such as Poly (Vinyl Alcohol) –PVA- which characteristics influence greatly the quality of the resulting PVC (morphology, thermal stability…)

As VCM is carcinogen and highly volatile under normal pressure (boiling point at -13.4°C), an organic solvent, n-butyl chloride (BuCl), is used as VCM model liquid in this study.

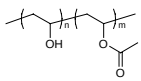
Objectives :
- characterization of PVA with different Degrees of Hydrolysis (DH)
- stability studies of PVA-water-"model liquid" emulsions

PVA characterization

PRODUCTS

Poly (Vinyl Alcohol)

(partially hydrolyzed Poly (Vinyl Acetate))

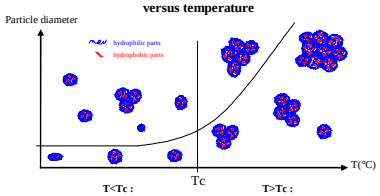


PVA	A	B	C	D
DH (% mol)	72	79	80	82
Cloud point (°C)	28.5 ± 1	45 ± 1	46 ± 1	61 ± 1
M_w (eq POE)	7 100	18 000	45 000	21 000
PI	2.1	4.0	4.1	4.2
T_g (°C)	61 ± 1	66 ± 1	66 ± 1	69 ± 1
Diameter range at 20 °C for 1% w/w PVA in water	20 – 40 nm			

** with Coulter N4+*

- at room temperature : micellar structure of PVA in aqueous solution
- above the cloud point: formation of aggregates

Schematic representation of PVA in aqueous solution versus temperature



T<Tc : **Micelles (15-50nm)** + very few aggregates

T>Tc : **Aggregates (>50nm)** + very few micelles

Studies of "model o/w emulsions" stabilized by PVA

EMULSION PREPARATION

Weight ratio:
- H_2O 75
- BuCl* 25

stabilized with 1% PVA/BuCl (w/w)

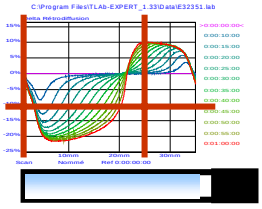
** density = 0.886g/cm³*

CHARACTERIZATION TECHNIQUES

- Stability studies (Turbiscan) ⇒ droplet migration rate and Stokes diameter with no stirring
- Particle size determination by :
  - laser scattering (Coulter LS230) ⇒ optical diameter on dilute emulsion
  - laser back scattering (Partec) ⇒ cord length on-line
  - optical microscopy

RESULTS

Turbiscan



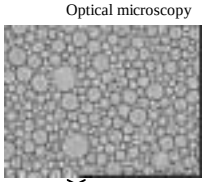
aqueous phase → emulsion

creaming

Room temperature

PVA	A	B	C	D	
DH (% mol)	72	79	80	82	
M_w (eq POE)	7 100	18 000	45 000	21 000	
Cloud point (°C)	28.5 ± 1	45 ± 1	46 ± 1	61 ± 1	
Creaming rate (µm/min)	450 ± 20	450 ± 20	770 ± 20	560 ± 20	Turbiscan
Stokes diameter (µm)	25 ± 0.5	25 ± 0.5	33 ± 0.5	28 ± 0.5	LabExpert
Optical diameter (µm)	17.0 ± 1.0	18.5 ± 1.0	23.5 ± 2.0	19.0 ± 1.0	Coulter LS230
Mean cord length (µm)	17.5 ± 1.5				Partec

Optical microscopy



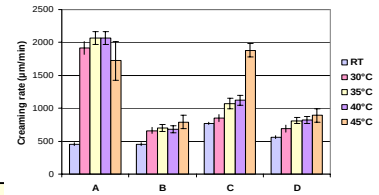
50µm

- good correlation on the droplet size between all the characterization techniques
- influence of DH : ↗ DH ⇒ ↗ droplet migration rate ⇒ ↘ emulsion stability
- influence of M_w : ↗ M_w ⇒ ↗ droplet migration rate ⇒ ↘ emulsion stability

Temperature studies with Turbiscan

- ↗ temperature ⇒ ↘ emulsion stability
- for T>Tc : ↗ temperature ⇒ ↘↘ emulsion stability (A)
- for T<Tc : influence of M_w more important than DH
  - at ~ DH : ↗ M_w ⇒ ↘ emulsion stability (B & C)
  - at ~ M_w : ↗ DH ⇒ low ↘ emulsion stability (B & D)
  - when : ↘ DH and ↗ M_w ⇒ ↘ emulsion stability (C & D)

Creaming rate in function of temperature



Conclusions

- Good correlation between the characterization techniques
- At room temperature, better stabilization for hydrophilic PVA with low DH and low M_w (efficiency : A = B > D > C)
- Temperature studies:
  - above the cloud point : formation of aggregates ⇒ ↘ stabilization efficiency (A)
  - below the cloud point : greater influence of M_w than DH (C & D)

References: *1. Aladjoff, I., Nilsson, H., Silvergren, C. and Tornell, B., Acta Chemica Scandinavica, 1982, A 36, p. 259-266 / 2. Aladjoff, I., Nilsson, H., Silvergren, C. and Tornell, B., Acta Chemica Scandinavica, 1982, A 36, p. 267-272 3. Chatzi E. G. and Kiparissides C., Chemical Engineering Science, 1994, 49 (24B), p. 5039-5052 / 4. Shiraishi M. and Toyoshima K., Br. Polym. J., 1973, 5, p. 419-432.*