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BOOK OF
ABSTRACTS

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Computer Simulation Aided Synthesis of Sodium Acrylate/Acrylic Acid Superabsorbent Polymers

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Introduction:

In contrast to porous materials such as polyurethane sponges, superabsorbent polymers (SAPs) huge swelling capacity is driven by water dissolution into polymer structure. Absorption in porous materials is mainly described by the Darcy's law (flow in porous medium) while absorption in SAPs is dominated by a diffusion process quantified by the Fick´s law. The absorbent efficiency of these networks is further enhanced if the chains carry dissociated ionic functional groups, due to strong ionic solvation (ion-dipole interactions). These effects are not possible in nonionic hydrogels which have an absorption capacity resulting only of energetic and entropic effects, involved in the mix of the aqueous fluid with the hydrophilic groups present in polymer chains.[1] Differences between traditional absorbent materials and SAPs become clear when their end use properties are compared: water absorbency of a polyurethane sponge is around 10 g/g whereas SAPs are able to retain up to 1000 g/g of water relatively to dry weight.

Different classes of polymer gels exhibit superabsorbent behavior namely gels based on polyacrylamide, poly(ethylene oxide), poly(vinyl alcohol), starch/polyacrylonitrile (physical crosslinking), polypeptides (physical gelation - gelatin), polysaccharides such as cellulose and alginates (anionic) or chitosan (cationic). Even so, SAPs based on partially neutralized poly(acrylic acid) are those with better performance and also industrially more relevant.[1] End use properties of such sodium acrylate/acrylic acid SAPs are strongly dependent on the synthesis conditions used in their production and therefore the design of operation conditions allowing the improvement of the performance of these materials is s subject with industrial relevance.

This work reports experimental and theoretical studies concerning the synthesis, characterization and computer aided design of sodium acrylate/acrylic acid SAPs. Our aim is the development of a computational tool useful in the specification of operation conditions for the production of SAPs with tailored properties.

Experimental Part:

Synthesis of sodium acrylate/acrylic acid hydrogels was performed with a 2.5 L batch reactor of which a detailed description has been presented elsewhere.[2-3] Different polymerization runs were performed in aqueous solution and in inverse suspension, which is specially appropriated for gel production in batch reactor. Some runs were *in-line* monitored using an in-line FTIR-ATR probe. Samples collected at different polymerization times were characterized using SEC/RI/MALLS running with an aqueous eluent and also using gravimetric measurements. Kinetics of swelling of the produced SAPs was also measured. The following parameters were changed along the experimental program:

● Initial mole fraction (0.02 to 0.2%) and kind of crosslinker. Methylene bisacrylamide (MBAm, bifunctional) and Trimethylolpropane triacrylate (TMPTA, trifunctional) were used.

● Concentration of acrylic acid in the aqueous phase (15 to 50%) and degree of neutralization with NaOH (50 to 100%).

● Temperature of polymerization (from 20 to 50 °C), initial mole ratio initiator/monomer (0.05 to 0.5%) and kind of initiator. Thermal initiator 2,2'-Azobis(2-methylpropionamidine) dihydrochloride (V50) and the redox system ammonium persulfate (APS)/tetramethylethylenediamine (TEMED) were used.

● Different hydrophobic media (cyclohexane, toluene, paraffin) and suspension agents (Span 80, Span 60, ethylcellulose) were considered for the inverse suspension runs, using volumetric ratios

between oil phase and aqueous phase in the range 4 to 7. Thioglycolic acid was used as chain transfer agent (CTA) in the range 1 to 5% of the monomer concentration.

Computer Simulations:

A general kinetic approach[4] based on population balance equations of generating functions was used to predict some key properties of SAPs production. Dynamics of molecular weights before and also after gelation can thus be calculated. Weight fraction of gel was also predicted considering different operation conditions and kinetic parameters.
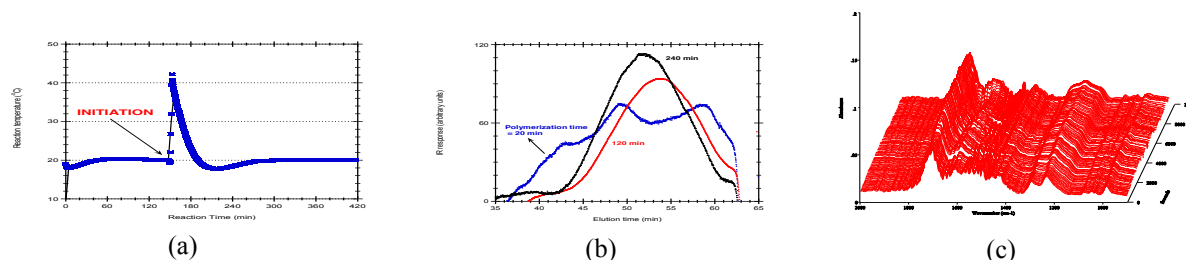
Results:

Figure 1: (a) Non-isothermal profile (temperature set-point = 20 °C) measured for inverse-suspension SAP production with initiation by APS/TEMED. (b) Aqueous SEC/RI/MALLS analysis of the sol fraction of SAP samples with different reaction time. (c) *In-line* FTIR-ATR monitoring of SAP production at 50 °C.
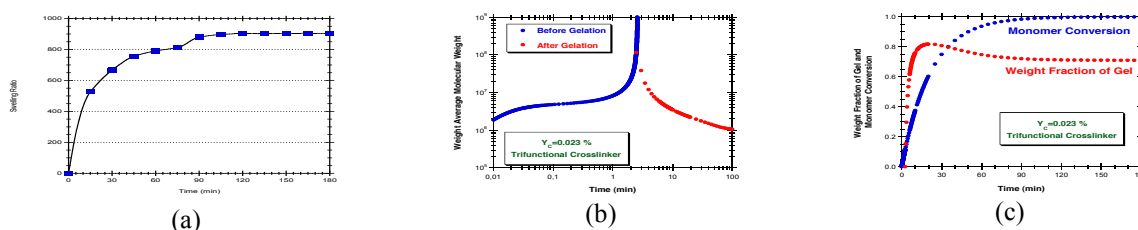

Figure 2: (a) Measured swelling kinetics of a produced SAP sample (equilibrium swelling ratio around 900 was observed). (b) and (c) Predicted dynamics during SAP synthesis of average molecular weights, gel fraction and monomer conversion. Predictions are possible both before and after gel point.

Conclusion:

The influence of the synthesis conditions on the end use properties of SAPs was experimentally observed. Initial proportion crosslinker/acrylic acid and degree of neutralization are examples of parameters with strong influence in the performance of these materials. The kinetic model developed is able to capture the main features of SAP production. Ongoing research should allow the prediction of elastic properties of this class of materials.

Acknowledgments:

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[4] M. R. P. F. N. Costa, R. C. S. Dias, An Improved General Kinetic Analysis of Non-linear Irreversible Polymerisations, Chem. Eng. Sci. 60 (2005) 423-446.