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Effect of variousparameters onkineticsof formation of thepolyurea microcapsules by interfacial polycondensation.

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Abstract

Study of kinetics of formation of polyurea microcapsules by interfacial polycondensation is very essential to know the optimization of the process. Interfacial polycondensation is one of the effective methods used for the fast production of polymers at a smaller quantity. Interfacial polycondensation has been studied for various applications such as synthesis of polymers, production of thin film composite membrane, micro encapsulation, etc. In these reactions, the reactants are brought together at an interface of two immiscible phases. An Interfacial reaction provides the possibility of fast reactions with production of low molecular weight polymers under ambient conditions. This is an important technique in the formation of polyurea microcapsules. The formation of aqueous core polyurea microcapsules via interfacial polycondensation of a Toluene Diisocynate (TDI) in organic solvent and Ethylene Diamine (EDA) in water is studied. The formed microcapsules are insoluble in both the phases. Detailed kinetic information has been obtained by using a continuous pH measurement system. The polymer formed is thermoplastic and semi crystalline in nature which having melting point of about 295^0C. It is generally assumed that the reaction is second order and rate of reaction is diffusion controlled. The aim of this work was to study kinetics of the reaction and to determine the optimum conditions which are useful for the formation and enhancing properties of microcapsules by optimizing various parameters such as stirring speed, solvent proportion, monomer ratio, surfactant concentration and pH of the aqueous phase. Crystallinity of polyurea microcapsules were studied by X ray Diffraction (XRD) method.

Keywords: Interfacial polycondensation, microcapsules, optimization, kinetics, Crystallinity.

Introduction

The polyurea microcapsules formation was affected by many variables such as composition of organic and aqueous phases, partition coefficient of aqueous phase monomer, rate of stirring, surfactant concentration and the mole ratio of the reactants. The experimental data available at present is not sufficient to clear the whole picture of interfacial polycondensation technique. Berezkin and Khokhlov (2006) mentioned the need for a systematic experimental study of interfacial polycondensation reaction mechanism for the effective development of this technique. The present experimental study is inspired by the few lacunas that we observed in the literature. The effect of the solvent used for the monomers has been mentioned in the literature (Morgan, 1965) but more quantitative information of solvent effect on reaction kinetics has not appeared in the literature.

The objective of this research work was to study the various aspects of interfacial polycondensation as well as to study the effects of various parameters on an interfacial polycondensation reaction between toluene diisocynate and ethylene diamine. The aim of this work was to determine the optimum conditions which are useful for formation and enhance properties of microcapsules by optimizing various parameters such as pH of aqueous phase, stirring rate, reaction time, solvent proportion, monomer ratio, surfactant concentration and phase volume ratio. Characterization of the chemical structure and properties of microcapsules prepared by the method of interfacial polycondensation was the objective of this research work. The objective of this research work was to outline the kinetics and thermodynamics aspects of interfacial polycondensation and to study effect of various parameters on the kinetics of interfacial polycondensation process. Therefore a detailed and systematic experimental study has been carried out to understand various aspects of interfacial polycondensation technique.

Effect of monomer mole ratio on kinetics of reaction

For many polymerizations reactions, it has been found that there should be an optimum ratio of concentration

of reactant in the organic phase to the concentration of reactant in the aqueous phase for the production of the high molecular weight polymer. This may result from favourable changes in the diffusion rates and location of the polymerization zone. The optimum ratio is affected by the properties of the reactants, the organic solvent and agitation. For smooth operation in a stirred interfacial polycondensation, the polymer should be 5% or less on the basis of combined weights of water and organic solvent. At concentrations of 10% and above, all the liquid may be absorbed by the swollen polymer so that the mass cannot be stirred. This can lead to incomplete polycondensation and formation of low molecular weight polymer. For every pair of reactants in a given solvent, there are optimum polymerization conditions which are expressed as a ratio of the monomers of the reactants in their respective phases.

Therefore, monomer ratio (R) plays vital role in rate of polycondensation reactions. Generally monomer ratio varies between 2 to 10. Table (1) shows operating variables used for preparation of polyurea microcapsules.

$$C_{AO} = \frac{n_L}{V_d}\frac{V_d}{V_c} \qquad \text{Continuous phase}$$

$$C_{BO} = \frac{n_L}{V_d}R \qquad \text{Dispersed phase}$$

Table 1: Operating variables used for preparation of polyurea microcapsules

Sample no.	R	V_d/V_c	N	Initial Rx. Rate
S19	2	0.25	0.035	$9.80*10^{-7}$
S49	4	0.25	0.026	$1.16*10^{-6}$
S50	6	0.25	0.035	$4.05*10^{-6}$
S51	8	0.25	0.0134	$5.76*10^{-7}$
S52	10	0.25	0.006	$1.25*10^{-7}$

The rates of reaction for two experiments on this basis, the experimental conditions are similar except the value of *R*, which is 4 for the sample S49 and 8 for the other sample S51. For *R* = 4, we would expect both monomers to be consumed completely, but the result in indicates that the amine is not completely consumed, the conversion at the end of the reaction being about 80 % where as for R = 10, conversion has reached to 95 % in five minutes.

Generally three types of oligomers were expected to form in polycondensation reaction depending on the end groups (oligomers in which both ends are amine, those in which both ends are isocyanate, and those in which one end is amine and the other isocyanate), the observed behaviour indicated a dominance of the isocyanate ended species. This would lead to an excess of isocyanate groups being reacted as compared to amine groups, and therefore a complete consumption of the diisocynate monomer took place before the diamine. This reaction is likely to be taken place on the organic side of the interface.

A differentiation equation (1) gives the following relation between the rate of consumption of monomer A and the concentration and the rate of decrease of pH (Wagh et al, 2009).

$$\left(\frac{1}{C_A}\right)\frac{dC_A}{dt} = 2.3026\, C\, \frac{dpH}{dt} \quad (1)$$

The initial part of the pH vs. time curves for the experiments are replotted, which shows the linear relationship. In experiment S49 conversion gone up to 80 %, and, in the case of S52, it reached up to 99 %. From the Equation (1) the overall proportionality of the rate to the concentration of A over a wide range of conversion. The two experiments were conducted with same initial concentrations of the ethylene diamine along with different diisocynate concentrations. The influence of the diisocynate concentration on the reaction rate is the indication of, reaction taking place to the organic side of the interface.

Effect of phase volume ratio on kinetics of reaction

As the phase volume ratio influences the interfacial area as well as the initial concentration of EDA, both of which are higher for the case of S54. The variation in the concentration of A during the experiment has an influence on the kinetics in this case. The final conversion achieved in higher values of V_d/V_c was nearly same. The interfacial nature of the reaction is clears from the considerable influence on the interfacial area.

Effect of N/V_d ratio on kinetics of reaction

The mole of limiting monomer restricts the amount of polymer that is formed and this ratio therefore determines the final film thickness. The experiments were conducted by keeping the other parameters same, but because of the difference in the number of mole of limiting monomer, it differs in the final thickness of the film. The smaller N/V_d exhibit a higher rate towards the end of reaction.

It is possible that diffusion limitations are responsible for lowering the rate in the case of the thicker film. Influence of the parameter N/V_d, which determines the final film thickness, on kinetics limitations become important only towards the end under these conditions. In other similar sets of experiments where the differences in N/V_d were smaller (say 30 - 40%), the kinetics were effectively reproduced over the entire range of pH.

Study of SEM micrograph of polyurea microcapsules

The microcapsules produced when sodium lignosulfonic acid was used as surfactant, we obtained more uniform size spherical microcapsules. Therefore some additional experimental runs have been taken with sodium lignosulfonic acid. Figure (1)shows the SEM micrographs of polyurea microcapsules formed by using sodium lignosulfonic acid as a surfactant with R= 8.0, V_d/V_c = 0.25 and N/V_d = 0.6 kmol/m^3.

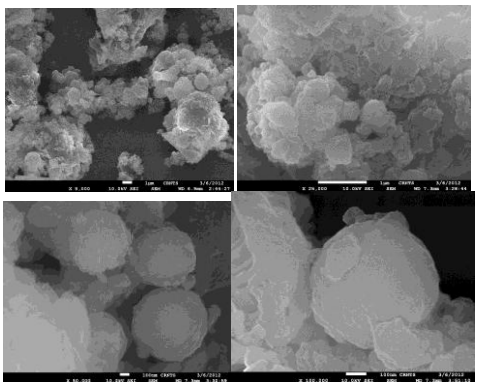

Figure1 : SEM micrograph of polyurea microcapsules

The size of microcapsules has been varied from 5 to 25 µm. Some reaction between the ethylene diamine and the surfactant was also possible and could contribute to the rigidity of the capsule wall. Capsules formed with surfactant Tween 85, where such rigidification of the capsule wall was not occurred also used for SEM study.

Study of intrinsic viscosity

It has been difficult to find molecular weight distributions of microcapsules due to the insolubility of polyurea in most of the solvents. Therefore the intrinsic viscosity (of solutions of polyurea in 98% sulphuric acid) has been taken as a measure of its molecular weight. The intrinsic viscosity values have been evaluated by the one point determination method. Viscosity of the polymer solutions is determined by the measurement of efflux time of the solution in an Ostwald–Fenske viscometer.

Intrinsic viscosities of polyurea solutions are determined under the conditions shown in Table (2). Figure (2) shows the effect of initial monomer mole ratio on the intrinsic viscosity of the polymer formed at different phase volume ratios for cyclohexane. It is found that at different values of phase volume ratio as the monomer mole ratio increased; there is an initial increase in molecular weight of the polymer. Once monomer ratio attains the maximum value of R somewhat greater than 1.0, it starts decreasing. These trends are similar to what has been reported in the literature (Wagh et al, 2009).

Table 2: Experimental conditions used for determining of intrinsic viscosity

Sr. No.	Experimental conditions	Details
1	Temperature	27^0C
2	Solvent	98% Sulphuric acid
3	Viscometer	Ostwald Fenske
4	Sample	20 ml
5	Volume concentration	0.5 g/dl
6	Efflux time for pure solvent	150 sec.

In the step polycondensation, a definite equivalence of functional groups is required to attain the high molecular weight and the latter decreases rapidly. In case of interfacial polycondensation one carry out the reaction in a thin zone of organic side of the interface, this situation is like a semi batch reactor. The aqueous phase monomer supplied continuously by diffusion to the reaction zone, which is in excess of the organic phase monomer.

Table 3 : Different value of V_d/V_c forIntrinsic viscosity for cyclohexane solvent

Sr. No.	R	V_d/V_c= 0.10	V_d/V_c= 0.25	V_d/V_c= 0.50
1	0.4	0.14	0.12	0.11
2	0.8	0.20	0.18	0.15
3	1.0	0.50	0.45	0.40
4	2.0	0.33	0.30	0.28
5	3.0	0.32	0.29	0.26
6	4.0	0.30	0.28	0.25
7	5.0	0.28	0.26	0.24

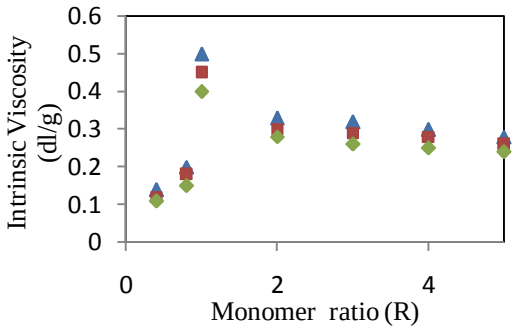

Figure 2 : Variation of intrinsic viscosity (molecular weight) for cyclohexane as solvent

Table (3) shows a comparison between the experiments with different values of (V_d/V_c) for cyclohexane as solvent. The parameter is seen to have a negligible influence on molecular weight. In summery therefore, it

appears that the mole ratio of monomers is the most important parameter to achieve high molecular weight.

Table (4) shows how the experimental variables that are related to the process variables. A variation in the interfacial area per unit volume and variation in the final film thickness could thus be achieved in the experimentation.

Table 4 : Relationship between the experimental variables and process variables

Sr. No.	Process parameters	Equation relating experimental variables
1	Interfacial area per unit dispersed volume	$6\left(\frac{Vd}{Vc}\right)dp\,[\,(\frac{Vd}{Vc})+\,1]$
2	Film thickness	$dp\alpha s(M_A+M_B)(\frac{N}{Vd})$ $/6\,\rho p$
3	Initial amine concentration	$\left(\frac{N}{Vd}\right)\left(\frac{Vd}{Vc}\right)\ (forR>1)$
4	Initial Diisocynate concentration	$\frac{\left(\frac{N}{Vd}\right)}{R}\qquad(forR>1)$

Kinetics of interfacial polycondensation reactions

The insights of the kinetics of interfacial polycondensation and polymer precipitation mechanism are essential in order to design processes for interfacial polycondensation. The fast kinetics and complexities of the process involving the interplay of several rates and equilibrium process make it difficult to study the reaction and explore the effect of kinetics on the properties of the polymer film or granular product form (Freger and Srebnik, 2003; Freger, 2005 and Dhumal et al, 2008). Generally interfacial polycondensation reaction has second order kinetics. Summary of literature on modeling of interfacial polycondensation processes are given in the Table (4).

Some of the factors affecting solute diffusion in polymers are chain mobility, chain entanglement, cross linking density, equilibrium degree of swelling, crystallinity, porosity and solubility of solute in polymer. On a microscopic level, solute diffusion through swollen polymer depends on the relative sizes of the diffusing species (Berezkin and Khokhlov, 2006; Sundeberg et al, 1990). Therefore morphological behavior is associated with reduced macromolecule chain mobility and barriers to solute diffusion are also associated with decrease solute diffusion coefficients (Dhumal et al, 2008).

Various steps taken place during reaction which are useful to study kinetics of the reaction, are as follows (Ji et al, 2001 and Dhumal et al, 2008),

1) The main chemical reaction between two monomers.
2) The reaction is heterogeneous and generally occurs near the interface.
3) The rate of polycondensation reaction is very fast.
4) Side reactions may takes place between monomer and solvent (hydrolysis may takes place).
5) As reaction proceeds and product get formed which decreases pH of the solution and at the end it remains constant.
6) Microcapsules get formed during the reaction which affects the rate of further polymerization and rate of transport of reactants.

Whenever polymer film formed of thickness δt, the rate of consumption of monomer A in the bulk aqueous phase is given by equation (1),
Subscript a, s, p and r sand respectively for aqueous phase, organic phase, polymer and reaction zone (Dhumal et al, 2008).

$$-\frac{dA_T}{dt}=\ k_{LA0}a_1\left(A_{0a}-A_{oap}\right)=\frac{D_{A0}a_1}{\delta t}\ (K_{A0ap}A_{0ap}-K_{A0sp}A_{0r})\quad(2)$$

Where,
k_{LA0} is the external mass transfer coefficient in the aqueous phase.
K is partition coefficient.

Solving the above equation we can obtain Equation (2),

$$A_{oap}=\frac{\left(k_{LA0}\delta t/\,D_{Ao}K_{A0ap}\right)A_{0a}+\ (K_{A0sp}/K_{A0ap})A_{0r}}{1+(k_{LA0}\delta t/\,D_{Ao}K_{A0ap})}$$

Hence,

$$-\frac{dA_T}{dt}=\ k_{eff}\,a_1\ (\,A_{0a}-K_{A0sp}A_{0r})$$

Where effective transport coefficient k_{eff} is given by,

$$k_{eff}\ =\frac{k_{LA0}}{1+(k_{LA0}\delta m\,/D_{A0K_{A0ap}}\,)\,\delta t/\delta m}$$

The consumption rate of monomer B in the bulk organic phase is given by,

$$-\frac{dB_{os}}{dt}=\ k_{LB0}a_1(\frac{V_a}{V_s-V_r})\,(\,B_{0s}-B_{0r})\quad(5)$$

The mass balance equation for the monomers in the reaction zone are given by,

$$\frac{d_{A0r}}{dt} = \frac{k_{eff}}{\varepsilon}\left(A_{0a} - K_{A0sa}A_{0r}\right) - \left(k_i A_{0r} B_{0r}\right) - k_{p1}A_{0r}\sum_{m=1}^{nmax} B_{mr} - k_{p2}A_{0r}\sum_{m=0}^{nmax} C_{mr} \quad (3)$$

$$\frac{d_{B0r}}{dt} = \frac{k_{LBO}}{\varepsilon}\left(B_{0s} - B_{0r}\right) - \left(k_i A_{0r} B_{0r}\right) - k_{p1}B_{0r}\sum_{m=1}^{nmax} A_{mr} - k_{p3}B_{0r}\sum_{m=0}^{nmax} C_{mr} \quad (4)$$

Phase separation and film formation

The events leading to phase separation and the mechanisms of phase separation considered in this work were described earlier with reference to the phase envelopes. In this work, the Flory–Huggins theory has been used to calculate binodal and spinodal curves for each oligomer at the temperature of reaction (Dhumalet at, 2008). The solution is assumed to be sufficiently dilute and interactions between oligomers are sufficiently small. The curves for each oligomer can be calculated as in a binary solution of those oligomers in the solvent. The oligomers solvent interaction parameter is estimated by the equation (5) as given below,

$$x = 0.34 + \frac{vs\ (\partial p - \partial s)^2}{RT} \quad (5)$$

Where ∂p and ∂s are the solubility parameters of an oligomer and solvent respectively. The ∂p values are calculated for each oligomeric species based on a group contribution method (Dhumal et al, 2008).

Phase separation by nucleation

The critical nucleus size of oligomers is calculated by Nucleation theory. *Ym*r is given in equation (6) as follows,

$$RCNYmr = \frac{-2\sigma Ymr}{\Delta f vYmr} \quad (6)$$

Where $\sigma Ymr$the interfacial energy between the nucleus and the surrounding lean is phase and $\Delta f vYmr$ is the free energy of coagulation per unit volume. Kamide et al. provide equations to calculate these quantities. The above equation shows larger nucleus size if the composition is closer to the binodal. Therefore, the probability of formation of large nuclei should be negligible (Dhumal et al, 2008). In order to account for this, disallow nucleation if the nucleus size as calculated above is more than the thickness of the reaction zone. Therefore to form critical nucleus is given in equation (7) as follows,

$$\frac{2RCNYmr}{\epsilon} \leq 1 \quad (7)$$

The rate at which the nucleated phase grows in volume is modelled as, where *k*m is a nucleation rate constant (assumed the same for all species).

Conclusion

Thus comprehensive modelling framework has been proposed for the interfacial polycondensation reaction used in the microencapsulation and in the manufacture of thin film composite membranes. The model incorporates the salient physicochemical processes involved in the diffusion of monomers, polymerization reactions, phase separation and formation of a coherent membrane. The model, with parameters obtained from kinetics and crystallinity values, it is able to predict the observed trends in the kinetics of the reaction, effect of parameters on crystallinity and also some important properties of the film such as molecular weight distribution and polydispersity.

Nomenclature

a -Interfacial area per unit volume (m^{-1})
C_A - EDA concentration (kmol/m^3)
C_B - TDI concentration (kmol/m^3)
h - Hydrogen ion concentration (kmol/ m^3)
M_A, M_B - Molecular weights of EDA and TDI (kg/kmol)
N - Number of moles of limiting monomer (kmol)
R - Monomer molar ratio
V - Volume (m^3)
X - Conversion
Xc - Crystallinity

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