J. of the Korean Oil Chemists' Soc.,
Vol. 28, No. 1. March, 2011. 10~14

A study of Polymerization and Thermal Characteristics of Core-Shell Emulsion particles

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(Received December 17, 2010 ; Accepted January 8, 2011)

Abstract : Emulsion polymerization was carried out using RMA like MMA, EMA, BMA and Styrene(St.) as monomer for core-shell latex preparation. It was synthesized at 80℃ in the presence of anionic surfactant SLS. FT-IR, TGA and DSC analysis are used to confirm synthesized core-shell emulsion latexes and to investigate the thermal characteristics of them. From analysis of TGA and DSC, the differences of the decomposition rate and the activation energy are not so large. It considers that the pendent group is not affect of the thermal characteristics and stability on core-shell latexes, which is synthesized with RMA and Styrene.

Keywords : Thermal stability, Activation Energy, DSC, TGA

1. THEORY

Generally, the reaction rate of degradation is proportional to the concentration of the reactant [11].

$$\frac{dx}{dt} = kf(x) \quad (1)$$

Where x=conversion(-), t=time(min), k=rate constant(min^{-1}) and $f(x)$= the function of the conversion. Eq. (1) is expressed the rate of conversion dx/dt at constant temperature T as some functions of the reactant $f(x)$ and the rate constant k.

In the case of polymer degradation, it is usual to assume that the rate of conversion is proportional to the concentration of the material, which remains to react;

$$f(x) = (1-x)^n \quad (2)$$

where n=reaction order(-). This function is used in polymer degradation kinetics where a solid material is decomposing to give gaseous reaction products. Meanwhile, the temperature dependence of the rate constant is given by the Arrhenius expression:

$$k = Ae^{-E/RT} \quad (3)$$

where A=frequency factor(min-1), E=activation energy (Kcal/mol). The combination of the above three eqs. gives the following relationship:

$$\frac{dx}{dt} = A(1-x)^n e^{-E/RT} \quad (4)$$

If the temperature rises at a constant heating rate β, then based on the differentiation of Eq. (4)

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$$\frac{d^2x}{dt^2} = \frac{dx}{dt}\left(\frac{E\beta}{RT^2} - An(1-x)^{n-1}e^{-E/RT}\right) \quad (5)$$

The maximum rate occurs at temperature Tm as defined by setting Eq. (5) equal to zero.

$$\frac{E\beta}{RT_m^2} = An(1-x)^{n-1}e^{-E/RT} \quad (6)$$

The product $n(1-x)^{n-1}$ is independen to Eβ and nearly equal to unity ($n(1-x)^{n-1} \fallingdotseq 1$) for a first order reaction such that the following expression can be derived:

$$\frac{d\left(\ln\frac{\beta}{T_m^2}\right)}{d\left(\frac{1}{T_m}\right)} = -\frac{E}{R} \quad (7)$$

If Eq. (4) is changed to heat rate;

$$\frac{dH}{dt} = A\exp(1-x)^n e^{-E/RT}(1-H)^n \quad (8)$$

Reaction order could be able to assume to first order, then take logarithms;

$$\ln\frac{(dH/dT)}{(1-H)} = \ln A - E/RT \quad (9)$$

3. EXPERIMENT

3.1 Materials

In this study we have used Methyl methacrylate(MMA), Ethyl methacrylate (EMA) and Butyl methacrylate(BMA) for core and Potassium persulfate(PPS) are used as initiator. These were purchased from Junsei Co. Ltd.. Surfactant was used as Sodium lauryl sulfate(SLS). Deionized water was used for all reactions, that is solution preparation, polymer purification and so on.

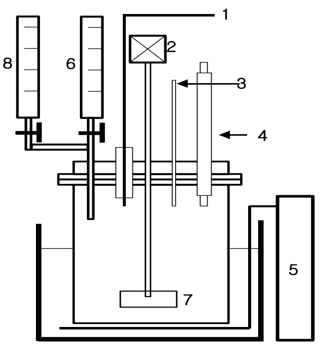
3.2 Polymerization

In core-shell latex polymerization, the pre-emulsion method which required minimized quantity of surfactant, has been used to increase the conversion rate and the stability of the core-shell particles, this receipt is shown in Table 1 and 2.

3.3 Analysis of thermal characteristics

FT-IR analysis was used for the purpose of confirming the synthesized structure of core-shell latex.

TGA and DSC analysis are conducted to investigate thermal stability of the core-shell latex. The thermal analysis was carried out about 5 mg of samples on aluminum cell in a nitrogen atmosphere. TGA was carried out at heating rate 10 ℃/min by recording the weight loss percentage and DSC analyzed at the various heating rate of 4,8,12,16,20 ℃/min.



1. N_2gaspurging 2. Motor 3. Thermometer
4. Condenser 5. Constant temperature bath
6. Initiator 7. Agitator 8. Monomer Tank

Fig. 1. Schematic diagram of experimental apparatus for polymerization.

Table 1. Recipe of core latex (at 80℃, 200rpm)

Ingredient	Amount(g)
De-ionized water	500
MMA, EMA, BAM	40
SLS	0.5
PPS	0.4

Table 2. Recipe of core-shell latex (at 80℃, 200rpm)

Ingredient	Amount(g)
De-ionized water	300
Styrene	10
Core latex	100
PPS	0.1

4. RESULT AND DICUSSION

4.1 FT-IR analysis

Fig. 2 is the FT-IR spectra on three kind of core-shell latexes. From this result, the intensity of characteristic absorption on stretching vibration of aromatic C-H(700㎝$^{-1}$) and stretching vibration C=O of carboxyl group (1730 ㎝$^{-1}$) are described.. (a),(b),(c) are indicated core latex of MMA, EMA, BMA. Also (d),(e),(f) are presented core-shell latex. From (d),(e),(f), typical Styrene FT-IR peak is shown in 700(㎝$^{-1}$).

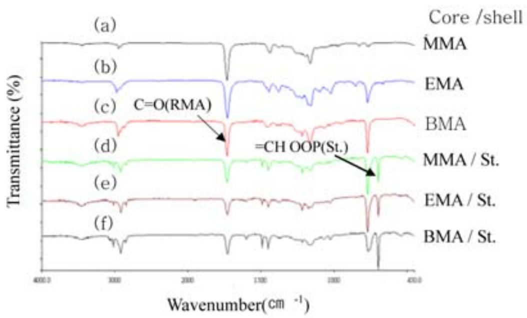


Fig. 2. FT-IR Spectrum of core-shell latex.

4.2 TGA analysis

TGA curves on the three different kind of core-shell latex are given to Fig. 3.

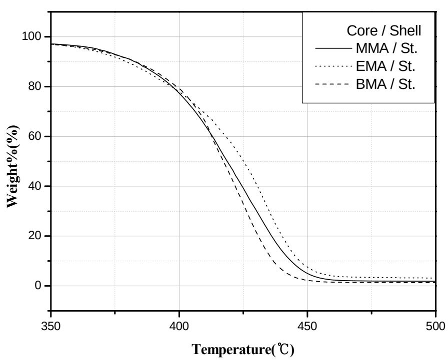


Fig. 3. TGA curves of core-shell latex (MMA/St., EMA/St., BMA/St.)

The degradation on initial temperature is similar to three kind of them at nearly 370℃ and the termination temperature is close to three sort of latexes at 450 ℃.

Actually in this figure, we could not exactly estimate that which one has better thermal stability.

4.3 DSC analysis

It is important to establish the degradation kinetics of latex in the thermal degradation process. Therefore, thermal analysis was performed widely. Kinetics studied have been widely used to comprehend the phenomena and the feature of polymer degradation with calculating kinetic parameters such as activation energy, etc.

The Kissinger's method allows calculation of activation energy from one point (maximum on DSC curves) at several heating rates. The activation energy was obtained from the slope of a plot as ($ln\beta/Tm^2$) versus ($1/Tm$). The Fig. 4 is shown a plot of Kissinger's method on core-shell latex of RMA/St. The slope was indicated 15.0(EMA), 13.3(MMA), 13.3(BMA), thus the activation energy was shown in Table 3.

In contrast to above mentioned, DSC method is expressed each axial like $ln(dH/dT)/(1-H)$ and $1/T$, therefore the activation energy was obtained from slope of them. The application of DSC method is plotted in Fig. 5 which is EMA/St. core-shell latex at heating rate 4, 8, 12, 16, 20℃/min. The slope was indicated 22.3(EMA), 39.6(MMA), 29.6(BMA), thus the activation energy was also shown in Table 3.

4.4 Comparison of activation energy

The activation energy of three different kind on core-shell latexes, which obtained by Kissinger's and DSC method are given to Table 3, and also this Table says the effectiveness of the pendant group on core material. The result of analysis on core-shell latexes have similarity of activation energy level in both method as 26.36, 26.39, 29.82 kcal/mol and 59.0, 59.32, 59.48 kcal/mol. EMA/St. latex has the highest energy and then MMA/St., the lowest to BMA/St. latex. Moreover, the two methods have a little bit differences on activation energy, however they have same trend.

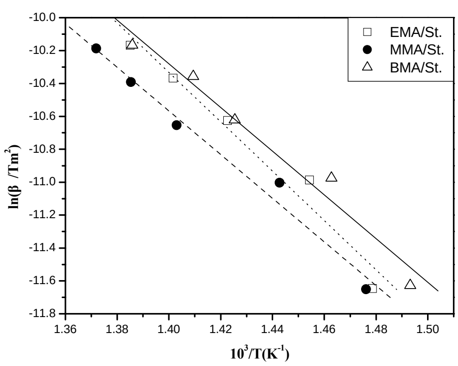


Fig. 4. Application of Kissinger's method to core-shell latex (MMA/St., EMA/St., BMA/St.)

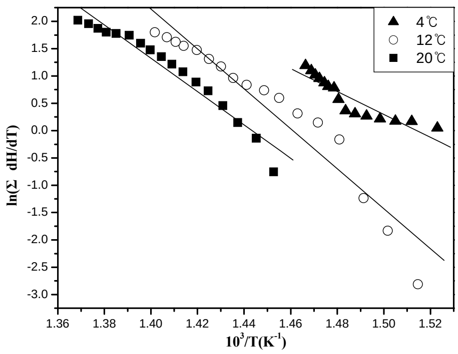


Fig. 5. Application of DSC method to EMA/St. core-shell latex.

Table 3. The comparison of activation energies (kcal/mol) by pendant group

Energy Method \ Activation Analysis		MMA /St.	EMA /St.	BMA /St.
Kissinger		26.4	29.8	26.4
DSC	4℃	33.6	44.3	27.8
	8℃	52.1	62.5	56.7
	12℃	78.7	78.7	76.3
	16℃	70.3	60.9	68.7
	20℃	61.9	58.9	65.5
	Average	59.3	59.5	59.0

5. RESULT

Emulsion polymerization which were using RMA and St. as monomer were carried out at 80℃ in the presence of anionic surfactant SLS.

The activation energies of three different core-shell latex (BMA/St., MMA/St., EMA/St.) were found 26.36, 26.39, 29.82 kcal/mol and 59.0, 59.32, 59.48 kcal/mol in case of Kissinger's and DSC method.

From results of TGA and DSC analysis, the differences of the decomposition rate and the activation energy are not so bog. It considers that the pendent group is not affect of the thermal characteristics and stability on core-shell latexes, which is synthesized with RMA and Styrene.

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