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Thermal decomposition behaviour of ethyl cellulose grafted copolymers in homogeneous media

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The homogeneous grafting of both poly (ethylene glycol) allenyl methyl ether macromonomer (PEGA39), and 2-acrylamido-2-methylpropane sulphonic acid (AMPS) onto ethyl cellulose (EC) was carried out in benzene and benzene: ethanol (1 : 1 v/v ratio) solvent systems, respectively. The thermal decomposition behaviour of the grafted products, ethyl cellulose and homopolymers was investigated using TGA and DTG thermal methods. The thermal stability of the grafted products EC-g-PEGA39 are increased by increasing the macromonomer content, whereas the decomposition temperatures of the grafted products with AMPS (EC-g-AMPS) are decreased remarkably in most cases compared to those of ethyl cellulose and PAMPS. The activation energies of the decompositions are determined and related to the thermal stabilities of the various polymers. © *2000 Kluwer Academic Publishers*

1. Introduction

Modifications to impart more desirable properties to natural macromolecules by chemical methods are very important to make them suitable for particular applications. Grafting has received a considerable attention for the modification of natural polymers. The effect of fine structure on the thermal properties of cellulose has been investigated by many authors [1–6]. It has been found that the thermal stability of cellulose depends mainly on its crystallinity [1, 6]. Furthermore, it has mentioned that the thermal behaviour of vinyl monomer grafted cellulose depends on the kind of monomer grafted [7–10]. Heterogeneous grafting onto cellulose proceeds mainly in its amorphous regions [11, 12] whilst in a homogeneous medium all the cellulose chains dissolved molecularly can participate in grafting. Nishioka *et al.* [13–17] studied the homogeneous grafting of vinyl monomer onto cellulose under various conditions and the grafted products are used as membrane materials.

The homogeneous grafting of methyl methacrylate, acrylonitrile and 4-vinyl pyridine onto ethyl cellulose have been studied, and high grafting yields are obtained [18–20]. Recently we investigated the graft copolymeization of poly (ethyleneglycol) allenyl methyl ether ($M_n = 390$), and AMPS onto ethyl cellulose in homogeneous media, and at various conditions. Characterization and evaluation of the grafted products have been also performed [21, 22]. The present study reports the thermal decomposition behaviour of ethyl cellulose, PEGA39, PAMPS, and the grafted products onto ethyl cellulose with different amounts of PEGA39 and PAMPS. The difference in the thermal stabilities was associated with the estimated values of the decomposition activation energies.

2. Experimental

2.1. Materials

Ethyl cellulose (EC, BDH) with a degree of substitution between 2.42 and 2.53. 2-Acrylamido-2-methylpropanesulphonic acid (AMPS, Merck). Poly (ethylene glycol) allenyl methyl ether ($M_n = 390$, PEGA39), were prepared as described in a previous paper [23]. The other chemical reagents and solvents, were of analytical pure grade and used without further purification.

2.2. Grafting and sample preparation

The homogeneous grafting of PEGA39 and AMPS onto ethyl cellulose in benzene and in benzene: ethanol (1 : 1 v/v ratio) solvent systems respectively, were performed according to methods previously mentioned [21, 22]. Homopolymers of PEGA39 and AMPS were done as described before [23, 24]. The homopolymer formed simultaneously during the grafting processes, are expected to be dissolved in the precipitating water medium. The grafting efficiency (GE%), grafting percentage (GP%), and weight percentage (WC%) of the different samples are given in Table I, according to our pervious studies [21, 22].

2.3. Thermal methods of analysis

Thermal gravimetric analysis (TGA), and derivative thermogravimetric analysis (DTG), were performed using a Shimadzu TGA-50H module. The thermal analyses were carried out from ambient temperature to 600 °C at a heating rate of 10 °C min^{-1}. The initial rates of the degradation of homopolymers, ethyl cellulose, and grafted polymers, were determined by means

TABLE I Synthesis and characterization of EC-g-PEGA39 and EC-g-AMPS copolymer samples

	Synthesis mixture		Graft product			
Sample code	EC ($g/100\ \mu m^3$)	Monomer ($g/100\ \mu m^3$)	GP%	GE%	WC%	$[\eta]\ \mu m^3/g^c$
PEGA39 sample[a]						
EC-g-PEGA39 (I)	2	2	32	32	132	0.75
EC-g-PEGA39 (II)	2	3	36	22	136	0.62
EC-g-PEGA39 (III)	2	4	40	20	140	0.38
EC-g-PEGA39 (IV)	2	5	45	16	145	0.36
AMPS sample[b]						
EC-g-AMPS (I)	1	2	21	10	121	0.27
EC-g-AMPS (II)	2	2	17	17	117	0.37
EC-g-AMPS (III)	3	2	12	16	112	0.45
EC-g-AMPS (IV)	4	2	9	20	109	0.54

N.B. $1\ \mu m^3 \equiv 1 \times 10^{-6}\ m^3$.

[a] grafting time, 5 h. AIBN, 0.2 $g/100\ \mu m^3$. temp., 60 °C.

[b] grafting time 10 h, BPO, 0.2 $g/100\ \mu m^3$. temp., 60 °C.

[c] measured in benzene solvent at 25 °C.

of TGA at different intervals. The activation energies of the decomposition were obtained by application of the Arrhenius equation.

3. Results and discussion

3.1. EC-g-PEGA39 copolymers

The thermogravimetric analysis (TGA) curves of ethyl cellulose, PEGA39 and EC-g-PEGA39 copolymers are indicated in Fig. 1. The curves shows that the thermal stability of the grafted polymers lies in between those of the homopolymers, and the degradation is completed only in one step. The stabilities are enhanced by increasing the PEGA39 contents, and decreases in the order: PEGA39 > EC-g-PEGA39(IV) > EC-g-PEGA39 (III) > EC-g-PEGA39 (II) > EC-g-PEGA39 (I) > EC.

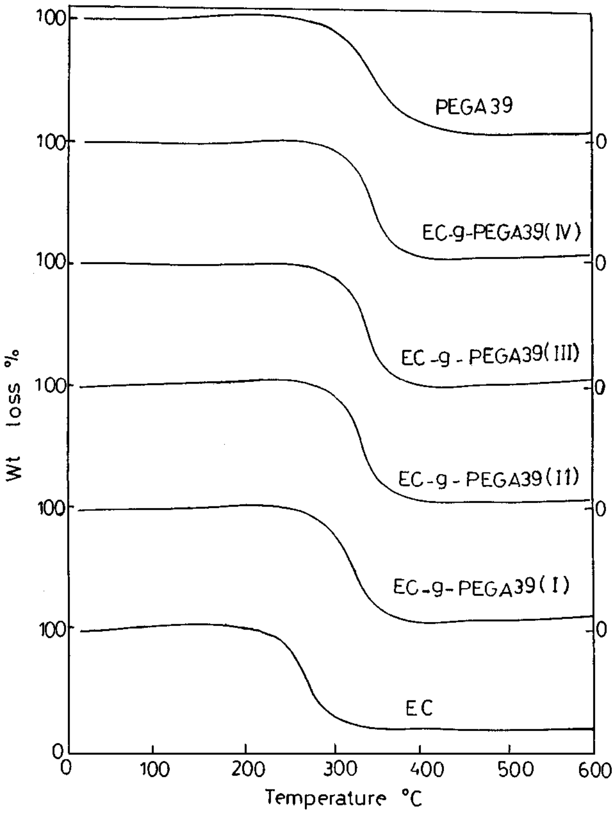

Figure 1 TGA curves of ethyl cellulose, PEGA39 and EC-g-PEGA39 coplymers.

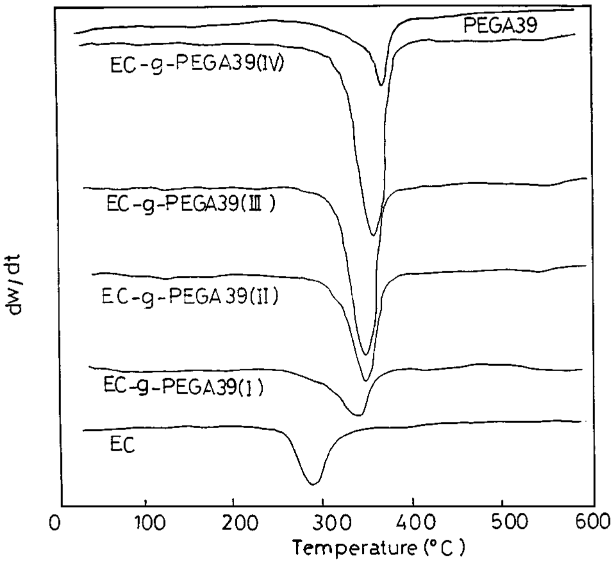

Figure 2 DTG curves of ethyl cellulose, PEGA39 and EC-g-PEGA39 copolymers.

The difference in the thermal decomposition behaviour of different samples can be seen more clearly from the derivative thermogravimetric (DTG) curves shown in Fig. 2. The decomposition rate of ethyl cellulose indicates the maximum value at 280 °C. This peak temperature (T_{DTG}) is used as a measure of the thermal stability. Relevant data are summarized in Table II. The data reveal that the thermal stability increases by increasing the macromonomer content within the grafted samples. Apparently the high molecular weight of the macromonomer and the intramolecular crosslinking reactions have a stabilizing effect [25].

The degradation rate constants of the homopolymer and the grafting polymers of EC-g-PEGA39, were determined from the TGA curves at the initial stages of decomposition. Then the calculations were performed by correlation of the percentage loss in mass as a function of time at different temperatures. The activation energies were determined from the temperature dependence of the rate of degradation as shown in Fig. 3.

TABLE II TGA and DTG data of EC, PEGA39 and EC-g-PEGA39 copolymers

Polymer sample	Volatilization temperature (°C)	T_{DTG} (°C)	Wt loss % at T_{DTG}	Residual wt % at 600 °C
Ethyl cellulose	175	280	44	15
EC-g-PEGA39 (I)	275	330	42	3
EC-g-PEGA39(II)	306	343	43	2
EC-g-PEGA39(III)	288	345	55	2
EC-g-PEGA39(IV)	307	354	50	1
PEGA39	150	360	54	6

TABLE III Activation energies of the thermal decomposition of EC-g-PEGA39 copolymers

Polymer sample	E_a (kJ/mol)
EC	14 ± 1
EC-g-PEGA 39(I)	23 ± 3
EC-g-PEGA 39(II)	27 ± 3
EC-g-PEGA 39(III)	32 ± 4
EC-g-PEGA 39(IV)	33 ± 4
PEGA39	34 ± 2

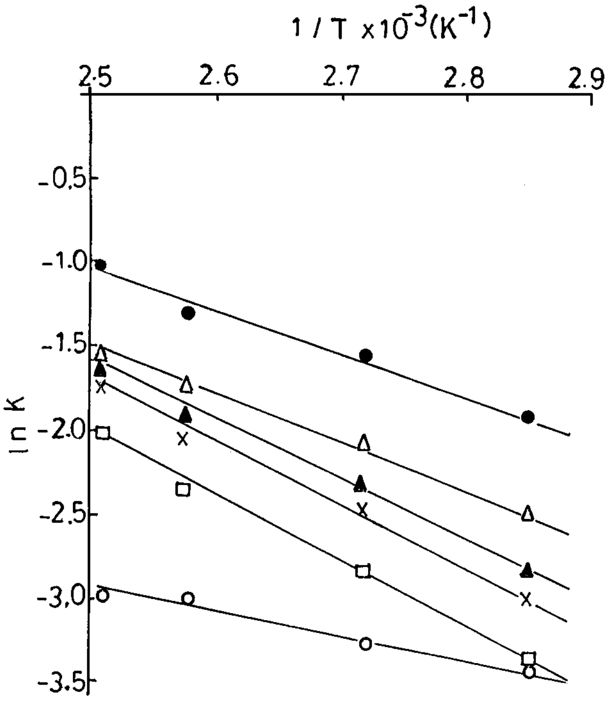

Figure 3 Arrhenius plots of the thermal decomposition rate constants (*k*) for EC,PEGA39, and EC-g-PEGA39 copolymers, (0) EC, (●) EC-g-PEGA39 (I), (△) EC-g-PEGA39(II), (▲) EC-g-PEGA39(III), (X) EC-g-PEGA39(IV), (□) PEGA39.

The effective activation energies of the thermal decomposition of EC, PEGA39, and their grafted copolymers are listed in Table III. It has been found that the activation energies are in the same sequence as the stabilities of the homopolymer and the grafted polymer.

3.2. EC-g-AMPS copolymers

The decomposition behaviour of PAMPS homopolymer was described earliar in our laboratory [24, 26]. It degrades in two stages, the first starts around 182 °C with weight loss about 20%, and ends at 300 °C with weight loss 50%. The second stage follow the first and ends at about 400 °C with weight loss 80%. On the other hand the EC-g-AMPS copolymer exhibits only one degradation step in all cases, and the thermal stability of the grafted polymers is lower than that of the ethyl cellulose and PAMPS in most cases.

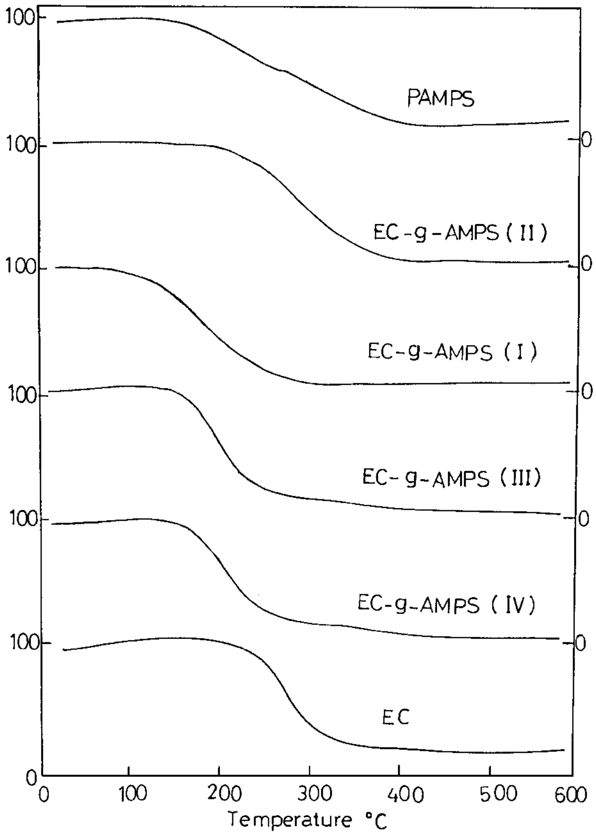

Figure 4 TGA curves of EC, PAMPS and EC-g-AMPS copolymers.

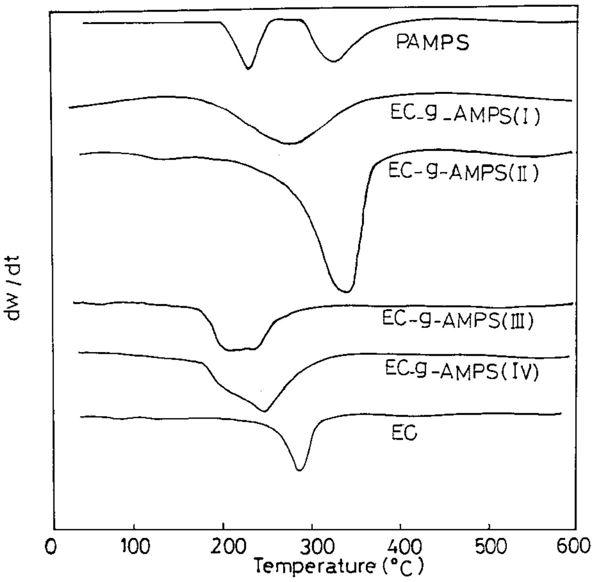

Figure 5 DTG curves of EC, PAMPS and EC-g-AMPS copolymers.

Fig. 4 shows the TGA curves of EC-g-AMPS in comparison with EC and PAMPS. The difference in thermal properties of the different samples can be seen more clearly from the derivative thermogravimetric curves indicated in Fig. 5.

The DTG curves of EC shows a maximum at 280 °C while the PAMPS curves exhibit two broads peak at 240 °C and 325 °C corresponding to two gradual

TABLE IV TGA and DTG data for EC, PAMPS and EC-g-AMPS copolymers

Polymer sample	Volatilization temperature (°C)	T_{DTG} (°C)	Wt loss % at T_{DTG}	Residual wt % at 600 °C
EC	175	280	44	15
EC-g-AMPS (I)	191	265	48	2
EC-g-AMPS (II)	266	328	57	2
EC-g-AMPS (III)	165	218	31	1
EC-g-AMPS (IV)	172	236	35	1
PAMPS	182	240/325	65	18

decomposition regions. The peak temperature of EC-g-AMPS (II) is 328 °C indicating the higher thermal stability of the sample. Table IV summarizes the TGA and DTA data for the EC-g-AMPS polymers. The high thermal stability of EC-g-AMPS(II) could be attributed to high efficiency of grafting between EC and AMPS at these concentrations to give highly compatible impact polymers. A similar results was obtained by Nishioka *et al.* [17, 27], for the grafting of cellulose with acrylonitrile, methyl methacrylate and 2-hydroxyethyl methacrylate, the crystallinity of the polymers influences their thermal stability [28]. Presumably, the thermal stability of ethyl cellulose by the grafting of vinyl polymers depends on the partial influence on compatibility and crystallinity of the grafted products [29, 30].

The activation energies (E_a) of decomposition were calculated by using the Arrhenius equation, as indicated in Fig. 6. The determined activation energies of the thermal decomposition for the grafted AMPS onto ethyl cellulose, EC and PAMPS are summarized in Table V. Again the energies were in the same order as the thermal stabilities of PAMPS, ethyl cellulose, and EC-g-AMPS copolymers. Consequently it was suggested that the thermal analysis methods are useful to characterize the grafting onto ethyl cellulose.

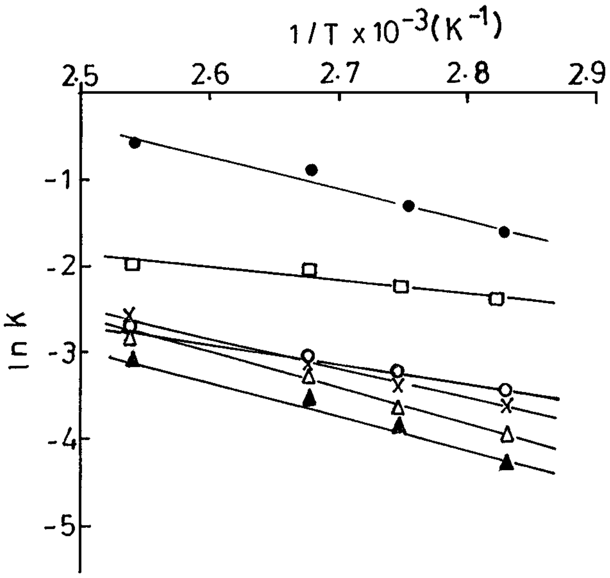

Figure 6 Arrhenius plots of the thermal decomposition rate constants for (*k*) EC, PAMPS and EC-g-AMPS copolymers, (0) EC, (●) EC-g-AMPS(I), (△) EC-g-AMPS(II), (▲) EC-g-AMPS(III), (X) EC-g-AMPS(IV), (□)PAMPS.

TABLE V Activation energies of thermal decomposition of EC, PAMPS and EC-g-AMPS copolymers

Polymer sample	E_a (kJ/mol)
EC	14 ± 1
EC-g-AMPS (I)	29 ± 1
EC-g-AMPS (II)	37 ± 3
EC-g-AMPS (III)	31 ± 3
EC-g-AMPS (IV)	27 ± 3
PAMPS	11 ± 1

4. Conclusion

Grafting of PEAGA39 macromonomer, and AMPS onto ethyl cellulose was performed homogeneously in benzene and benzene: ethanol (1 : 1 v/v ratio) respectively, with different centent. The TGA and DTG thermal curves show that the thermal properties of ethyl cellulose are enhanced by grafting with PEGA39 macromonomer, due to high molecular weight and the intrarmolecular crosslinking reaction. In the case of grafting of AMPS onto ethyl cellulose the stabilities decline in most cases and depend on the AMPS contents. The thermal stabilities of the different samples were confirmed by the corresponding determined activation energies. Accordingly it was suggested that the thermal decomposition measurement are useful method to characterize the grafted polymer containing ethyl cellulose as one component.

References

1. A. BACH and M. LEWIN, *J. Polym. Sci. Polym. Chem. Ed.* **11** (1973) 3071.
2. A. BROIDO, A. C. JAVIER SON, A. C. OUANO and E. M. BARRALL, *J.Appl. Polym. Sci.* **17** (1973) 3627.
3. C. FAIRBRIDGE, R. A. ROSS and S. P. SOOD, *ibid.* **22** (1978) 497.
4. R. K. JAIN, K. LAL and H. L. BHATNAGER, *Macromol.Chem.* **183** (1982) 3003.
5. *Idem., J. Appl. Polym. Sci.* **33** (1987) 247.
6. M. E. CALAHORRA, M. CORTAZAR, J. I. EGUIAZABAL and M. GUZMAN, *ibid.* **37** (1989) 3305.
7. V. N. SHARMA and E. H. DARUWALLA, *ibid.* **21** (1977) 331.
8. S. N. BHATTACHRRYA and D. MALDAS, *ibid.* **30** (1985) 151.
9. M. J. FERNANDEZ, M. D. FERNANDE, I. COSINOS and G. M. GUZMAN, *ibid.* **39** (1990) 1101.
10. *Idem., ibid.* **39** (1990) 2219.
11. V. T. STANNETT and H. B. HOPFENBERG, "Cellulose and Cellulose Derivatives, Vol. V, Part V," edited by N. M. Bikales and L. Segal (Wiley, New York, N. Y., 1971) p. 907.
12. A. HEBEISH and J. T. GUTHRIE, "The Chemistry and Technology of Cellulosic Copolymers" (Springer-Verlag, Berlin-Heiderberg -New York,1981).
13. N. NISHIOKA and K. KOSAI, *Polym. J.* **13** (1981) 1125.
14. N. NISHIOKA, Y. MATSUMOTO, T. YUMEN, K. MONMAE and K. KOSAI, *ibid.* **8** (1986) 323.
15. N. NISHIOKA, K. WATASE, K. ARIMURA, K. KOSAI and M. UNO, *ibid.* **16** (1984) 867.
16. N. NISHIOK, M. UNO and M. KOSAI, *J. Appl. Polym. Sci* **41** (1990) 2857.
17. N. NISHIOKA, H. ONO and M. KARASUNO, *Polym. J.* **24** (1992) 301.
18. E. A. ABDEL-RAZIK, *Polym. Plast. Techn. Eng.* **36**(6) (1997) 891.
19. *Idem., Acta Polym.* **45** (1994) 50.
20. E. M. ABDEL-BARY, E. A. ABDEL-RAZIK, A. A. SARHAN and N. M. ABDEL-SALAM, *Polym. Plaset. Technol. Eng.* **35**(6) (1996) 947.

21. Y. A. AGGOUR and E. A. ABDEL-RAZIK, *Eur. Polym. J.*, in press.
22. Y. A. AGGOUR, *J. Polym. Mat*. **16** (1999) 1.
23. Y. A. AGGOUR, I. TOMITA and T. ENDO, *React. & Funct. Polym*. **28** (1995) 81.
24. Y. A. AGGOUR, *Acta Polym*. **44** (1993) 97.
25. *Idem., Polym. Degrad. Stab*. **51** (1996) 265.
26. *Idem., Polym. Degrad. Stab.* **44** (1994) 71.
27. N. NISHIOKA and N. YOSHIDA, *Polym J.* **24** (1992) 1009.
28. L. REICH and S. S. STIVALA, "Elements of Polymer Degradation" (McGraw-Hill, New York, N.Y., 1971).
29. S. SAVARD, D. LEVESQUE and R. E. PRUD'HOMME, *J. Appl. Polymer. Sci*. **23** (1979) 1943.
30. O. OLABISI, L. M. ROBESON and M. T. SHAW, "Polymer-Polymer Miscibility" (Academic Press, New York, N.Y., 1979).

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