

Comparative study of the behavior of carboxymethyl cellulose-g-poly(*N*-isopropylacrylamide) copolymers and their equivalent physical blends

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Abstract

A comparative study of the behavior of carboxymethyl cellulose and poly(*N*-isopropylacrylamide) (PNIPAM) as graft copolymers and physical blends, in solution and in solid state was accomplished by viscometry, turbidimetry, IR spectroscopy, X-ray diffraction, thermogravimetry, and enzymatic degradation. Both in diluted and concentrated solutions, the graft copolymers exhibited a thermothickening effect, while the corresponding mixtures of the two components exhibited an Arrhenius behavior. Solid phase investigations showed morphological differences between graft copolymers and their equivalent physical blends. The enzymatic degradation behavior is essentially similar both for copolymers and blends (enzymatic degradation activity has similar values) although a slight increased enzymatic activity was noticed for the graft copolymers in comparison with the blends.

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1. Introduction

Designing new materials with improved or tailored properties is one of the main goals of the chemists. Two common ways are mainly used to get a material with improved or new properties: chemical synthesis or blending. Chemical synthesis is an unlimited method to get new substances with well-defined properties but it is often time consuming and not seldom costly. On the other side blending is a well-known, efficient way to prepare new materials with improved properties [1].

In one of our previous papers [2] we have synthesized new graft copolymers with a hydrophilic backbone, carboxymethyl cellulose (CMC) and hydrophobic side chains, poly(*N*-isopropylacrylamide), (PNIPAM). This kind of copolymers are included in the class of the so-called "smart" materials, comprised of polymers and copolymers with special structures and architectures, that are responsive to internal or external stimuli. This field is relatively recent and represents an actual concern of many research groups, especially from pharmaceutical field, due to their potential controlled release capabilities [3].

Generally, at heating in semi-dilute aqueous solution, some graft copolymers with hydrophobic side chains on a hydrophilic backbone present a substantial viscosity increase, thermothickening or gelling properties (thermothickening is a special behaviour, presented by some

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systems, where the viscosity increases as temperature increases) [4,5], in comparison with most of fluids that are characterized by the well-known Arrhenius thermothinning behavior (i.e. the viscosity decreases as temperature increases).

In most of cases where thermothickening properties are observed in aqueous solutions, polymers with lower critical solution temperature (LCST) behavior i.e. polyethylene oxide (PEO) and oligomers of polypropyleneoxide, poly(*N*-isopropylacrylamide) (PNIPAM) and nonionic cellulose ethers are involved. These thermosensitive polymers, due to a delicate balance between hydrophilic and hydrophobic interactions, separate out from water upon heating, although they are well soluble at low temperature.

CMC is a chemically modified cellulose derivative with good water solubility, broadly used due to its low cost, biodegradability and lack of toxicity. Food industry, cosmetics, pharmaceuticals, suspension agents, tablet excipients, viscosity increasing agents, formulation agents for controlled release of drugs and pesticides, paper and paper products, adhesives, and ceramics provide a small compilation of the numerous applications where CMC is used in the acid or in the sodium salt form [6,7].

The reversibility of the phase transition of PNIPAM, occurring at an easily accessible temperature (LCST of PNIPAM is ~ 33 °C) [8,9] close to the body temperature, is of great interest for uses in biomedical applications, like isolation and purification of biologically active substances [10,11].

The purpose of the present paper is to investigate the differences in behavior and properties of the graft copolymers of CMC with PNIPAM and their equivalent physical blends.

2. Experimental section

2.1. Materials

CMC, purchased from Polyscience Inc., was purified by dialysis and freeze-drying. Its average viscometric molecular weight, determined in a 0.2 M NaCl aqueous solution, at 25 °C, with the relation: $[\eta] = 43 \times 10^{-3} [M_w]^{0.74}$ [12] was of 82,000 daltons. The content of the carboxyl groups evaluated by an acid–base titration was 0.78 carboxyl groups per anhydroglucose unit [2].

N-isopropylacrylamide, (NIPAM, Aldrich), ammonium persulfate (APS, Serva) of analytical grade, 2-aminoethanethiol hydrochloride (AET, Aldrich), 1-(3-dimethylamino)propyl)-3-ethyl-carbodiimide hydrochloride (EDC, Aldrich), and LiNO₃ (Sigma) were used. Water was purified by means of a Seralpur Pro 90C apparatus combined with a USF Elga Laboratory unit.

Amino-terminated PNIPAM was prepared by radical polymerisation in aqueous solution by using the redox couple APS/AET as initiator, according to a method proposed by Durand and Hourdet [13]. The monomer was dissolved in water (0.1 mol in 80 ml of water), and the solution was deaerated with nitrogen bubbling. The temperature was adjusted at 29 °C by using a water bath. The initiators (1.1 mmol of APS and 2.2 mmol of AET·HCl) were dissolved separately in 10 ml of water and added after about 1 h to the monomer solution. The reaction time was 3 h. The product was purified by dialysis against water through a membrane (cut off ~ 12 000 Da, Sigma) and freeze-dried [2].

The graft copolymers of CMC with PNIPAM, CMC-g-PNIPAM, were prepared by grafting amino-terminated PNIPAM side chains onto a hydrophilic CMC backbone, through a coupling reaction between CMC and PNIPAM using EDC 1-3-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (98%) as condensing agent, according to the scheme presented in one of our previous papers [2].

The physical blends of CMC/PNIPAM, as powder samples, were prepared by atomization, with a BÜCHI 190 mini spray dryer, of the mixed aqueous solution of the partners, at a total polymer concentration of 0.2 g dl⁻¹, and the mixing ratios between partners equivalent with that from the graft copolymers.

The characteristics of the investigated samples are given in Table 1.

2.2. Methods

The comparative study of behavior of the graft copolymers and their corresponding blends was realized both in solution by turbidity, viscosity measurements and enzymatic degradation and in solid state by IR spectroscopy, X-ray diffraction, and thermogravimetry (TG).

Turbidimetry. The turbidity measurements of the CMC and PNIPAM systems were performed by visual observation and by means of a Hitachi spectrophotometer model U 2001, at a wavelength of 490 nm.

Viscometry. Viscosity measurements were carried out with an Ubbelohde type viscometer with dilution and suspended level. The viscometric behavior of the aqueous solutions of CMC, PNIPAM, CMC-g-PNIPAM 27 (or 47) and their corresponding blends, at a total polymer concentration of 0.2 g dl⁻¹, was investigated on a temperature range of 25–70 °C.

IR spectroscopy. IR spectra of the sample, in KBr tablets, were recorded on a Perkin–Elmer SPECORD M80 spectrophotometer.

Wide-angle X-ray scattering measurements were carried out using a Philips (PW 1050 model) powder diffractometer (CuNi-filtered radiation) equipped with a rotative sample holder device.

Table 1
Characteristics of the CMC, PNIPAM, CMC-g-PNIPAM copolymers and their corresponding blends

Sample	Symbol	Intrinsic viscosity (ml/g) ($t = 25\text{ }^{\circ}\text{C}$)	Reduced viscosity (ml/g) ($c = 0.2\text{ g/dl}$) ($t = 25\text{ }^{\circ}\text{C}$)	Average molecular weight (M_n)	Weight percent of NIPAM
Carboxymethyl cellulose	CMC	186	721.664	82,000	–
Poly(<i>N</i> -isopropyl acrylamide)	PNIPAM	32	34.958	43,000	–
Graft copolymers	CMC-g-PNIPAM 27	165	680	–	27
	CMC-g-PNIPAM 47	107	540.04	–	47
Blends	CMC/PNIPAM 27	–	624.4	–	27
	CMC/PNIPAM 47	–	552.9	–	47

Thermogravimetry. The thermogravimetric and differential thermogravimetric curves (TG/DTG) were recorded on a Paulik-Paulik-Erdey Derivatograph MOM Budapest, in a temperature range of 20–600 °C, at a heating rate of 12 °C/min, in 30 ml/min air flow and sample mass of 30 mg.

Enzymatic degradation behavior was followed by Pettersson–Porath method [14,15]. This method determine cellulosic activity through color reaction with dinitrosalicilic acid. The Pettersson–Porath method used in this study is based on the determination of the reducing groups of the cello-oligosaccharide fragments, resulting from the reaction of the cellulosic substrate with the enzyme. By their reaction with dinitrosalicilic acid a yellow color was obtained. Specific absorption of UV spectra at 640 nm was used to determine the concentration of the reducing cello-oligosaccharide fragments. A calibration with freshly prepared glucose solutions in a concentration range varying from 0.1 to 1 g/100 ml was previously done.

Cellulase from *Trichoderma viride*, with an activity of 3 U/mg (CMC, pH=4.5 at 37 °C), purchased from Merck (Merk 2324) was used [16].

Cellulosic activity was calculated using the following relation:

$$U\text{ ml}^{-1}\text{ min}^{-1} = \frac{a \times 10^3}{2}$$

where a represents the glucose quantity corresponding to the extinction for each sample compared with the control (g/100 ml).

3. Results and discussion

Fig. 1 shows the variation of the cloud point temperature (CPT) of a 0.2 g dl⁻¹ aqueous solution of PNIPAM in the presence of the CMC. The results show

that CPT of the PNIPAM remains constant (36 °C) up to a CMC concentration of 0.2 g dl⁻¹, at the same value as that of the pure PNIPAM solution, and then it slightly decreases by further increasing of CMC concentration.

The presence of CMC in its sodium salt form contributes to an increase of the ionic strength of the solution and it is known that the depression of the LCST of PNIPAM by adding salts it has been observed [17]. That means that we could consider the CMC effect as a salt effect.

To evidence the presence of the interactions between CMC and PNIPAM in physical blends we have performed viscometric measurements, at 25 °C and a total polymer concentration of 0.2 g dl⁻¹. It is well known that the deviation of the experimental specific or reduced viscosity of a mixture of two polymers as a function of its composition, from an ideal value calculated in the idea of the lack of the interaction between the

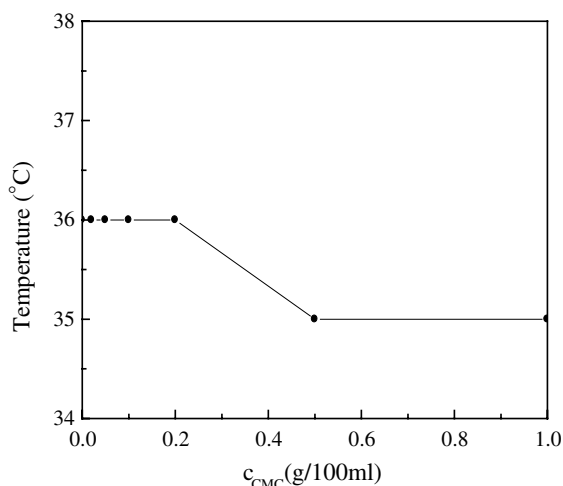


Fig. 1. Turbidimetric curve of CMC/PNIPAM blend (cloud point temperature versus concentration of CMC).

components is a broadly accepted criterion for the study of the compatibility or association of a mixture of two polymers. The ideal value of the reduced viscosity of the neutral polymers value is calculated as the weight average of the viscosities of the two constituents [18–21].

When one of the partners is a polyelectrolyte (i.e. CMC), whose viscosity increases by diluting (Fig. 2), a slightly modified formula for the ideal viscosity was proposed. It takes into consideration the contribution of the polyelectrolyte effect on the reduced viscosity of the polymer mixture [20].

$$(\eta_{sp}/c)_m = w_1(\eta_{sp,1}/c_1) + w_2(\eta_{sp,2}/c)$$

where w_1 and w_2 are the weight fractions of the two polymers. The reduced viscosity of CMC (a polyelectrolyte) was evaluated for its real concentration in the mixture (c_1), while for the reduced viscosity of PNIPAM (neutral polymer) was calculated at the total polymer concentration in solution (c).

For an easier evidence of the interaction in a system, the ratio between the reduced viscosity of the mixture and the ideal one, $\eta_r = \eta_{exp,m}/\eta_{calc,m}$ is used. Any deviation of the η_r from the unity indicates the presence of the interactions in system. Values of η_r lower than unity indicate a compact structure of the sample, while values higher than unity evidence an expanded structure, known in the literature as “gel like” one [22].

Fig. 3 presents the variation of η_r versus the CMC weight fraction (w_{CMC}) in the mixture. The negative deviation of the η_r -composition (CMC wt.%) curve for a percent of CMC in the mixture lower than 30 wt.% indicates the existence of the interaction between components that lead to a compact structure. For a percent of CMC higher than 30 wt.% there is no deviation,

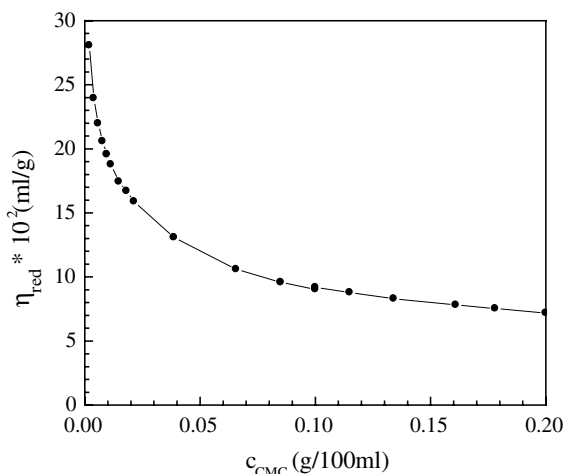


Fig. 2. Reduced viscosity of the CMC in water versus concentration of the solution at 25 °C.

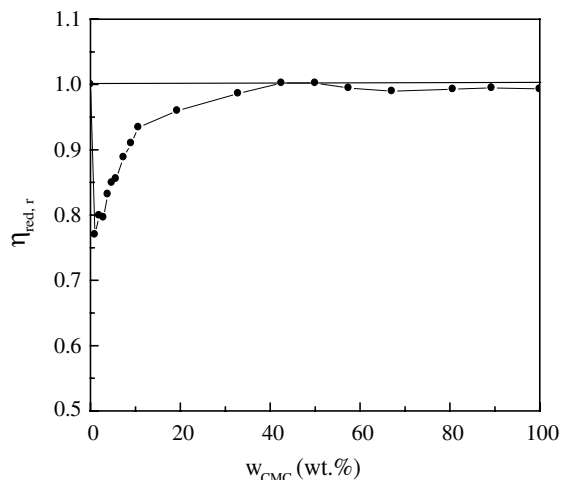


Fig. 3. Variation of the $\eta_{red,r}$ of the blend CMC/PNIPAM in water versus weight fraction of the CMC in the physical blend, at 25 °C. The polymer concentration is 0.2 g/dl.

which indicates that there are no interactions between components.

The *viscosity studies* also showed that the thermo-thickening phenomenon is typical only for the graft copolymers (Fig. 4), the blends having a normal rheological behavior (diminution of viscosity when temperature increases). The reduced viscosity of the graft copolymers decreases as temperature increases from 25 to 42 °C and then it increases (thermothickening behaviour). The reduced viscosity of the corresponding polymer blend decreases in the entire temperature range. The theoretical curve (open circles), constructed according to the additivity rule, show a slight decrease of the ideal viscosity of the blend with increasing temperature, from 470 ml/g at 27 °C until 400 ml/g at 70 °C. The thermo-thickening phenomenon occurs above 38–40 °C, when LCST of PNIPAM was exceeded. The reduced viscosity of CMC slightly decreases by increasing temperature, CMC being a hydrophilic polymer therefore not especially thermosensitive. On the contrary, the thermosensitive character of PNIPAM is revealed by an important decrease of the reduced viscosity when temperature approaches LCST, and the polymer chains collapse before phase separation takes place (Fig. 4 from [2]) [23–25].

The polymer chains are considerably expanded due to electrostatic repulsions between the carboxylate groups of the CMC backbone of the copolymer. Under these conditions, smooth interpolymer physical crosslinks through the PNIPAM side chains can be formed at high temperature. This could probably explain the gradual increase of the reduced viscosity of CMC-g-PNIPAM 27 for temperatures higher than 45 °C.

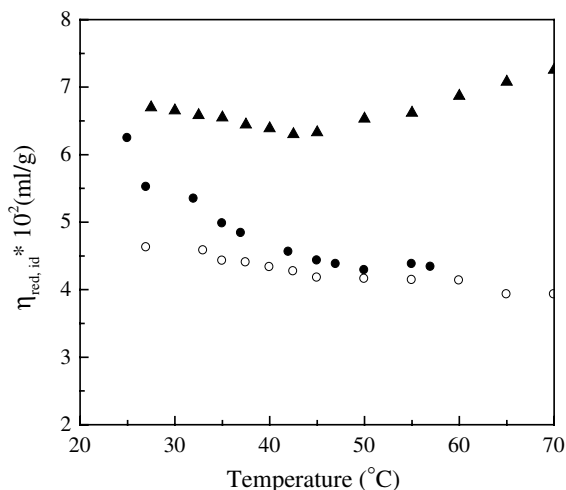


Fig. 4. Variation of the reduced viscosity of the graft copolymer CMC-g-PNIPAM 27 (▲) and variation of the reduced (●) and ideal (○) viscosity of the equivalent blend CMC/PNIPAM 27 as a function of temperature. The polymer concentration is 0.2 g/dl.

IR spectra of graft copolymers are completely different in the fingerprint region 1000–1700 cm⁻¹ from those of their equivalent physical mixtures.

In the IR spectra of the CMC we can notice the characteristic bands of COO⁻ at 1600, 1430 cm⁻¹, COOH groups at 900 and 1280 cm⁻¹, OH at 1430, 1340, 1170 cm⁻¹ and the ether groups at 1080, 1120 cm⁻¹. It is worth to remark that in the CMC a part of the carboxylic groups are in acid form and a part in ionic form. In the IR spectra of the PNIPAM could be observed the monosubstituted amide group at 3100, 1650, 1550, 1570, 1470, 1280 cm⁻¹, primary amine moieties at 1180, 1140, 1070 cm⁻¹ and isopropyl group at 2950, 1395, 1375, 1340, 1180, 1140 cm⁻¹.

In the IR spectra of the graft copolymers one can observe almost all the characteristic bands of both partners CMC (COO⁻ at 1600, 1430 cm⁻¹, acid groups 900, 1280 cm⁻¹, ether groups 1080, 1120 cm⁻¹ and OH groups: 1430, 1340 cm⁻¹) and PNIPAM (monosubstituted amide group at 1650, 1550, 1470, 1280 cm⁻¹, primary amine moieties at 1180, 1140, 1070 cm⁻¹ and isopropyl group at 2950, 1395, 1375, 1340, 1180, 1140 cm⁻¹), with the exception of the characteristic bands of primary amine from PNIPAM spectra, that vanished (bands 1180, 1140, decrease drastically). This indicates that the grafting reaction took place. The IR spectra of the two graft copolymers do not present significant differences in the shape being only slowly dependent on the content of the grafted polymer. This could be an indication that there are no physical interactions between the two partners of the copolymer.

In the fingerprint region, 1000–1700 cm⁻¹, the shape of the IR spectra of physical mixtures are completely different to that of their equivalent graft copolymers, depending in the same time on the mixing ratio of the components (Figs. 5 and 6). Generally we can notice the main characteristic bands of both components: COO⁻ at 1600, 1430 cm⁻¹, of COOH groups at 900 and 1280 cm⁻¹, of OH at 1430, 1340, 1170 cm⁻¹ and of the ether groups at 1080, 1120 cm⁻¹.

The absorption bands of the blends are larger and less clearly defined than that of grafted copolymers, because of complexity of structure and possible interactions between components.

X-rays diffractograms are presented in Fig. 7. It is known that the components of the systems are amorphous ones [26]. In comparison with the blends, that are completely amorphous independent on the mixing ratio of components, in graft copolymers, by increasing the content of PNIPAM, a certain degree of order is achieved (see the X-ray diffractogram of CMC-g-PNIPAM 47).

TG curves (Fig. 8) show a different thermo-oxidative behavior of the grafted copolymers compared with their corresponding physical blends.

Both components present a single thermogravimetric decomposition stage: CMC decomposes in the 200–310 °C (maxim at 260 °C) temperature range with a mass loss of 36 wt.%, while PNIPAM exhibits a degradative

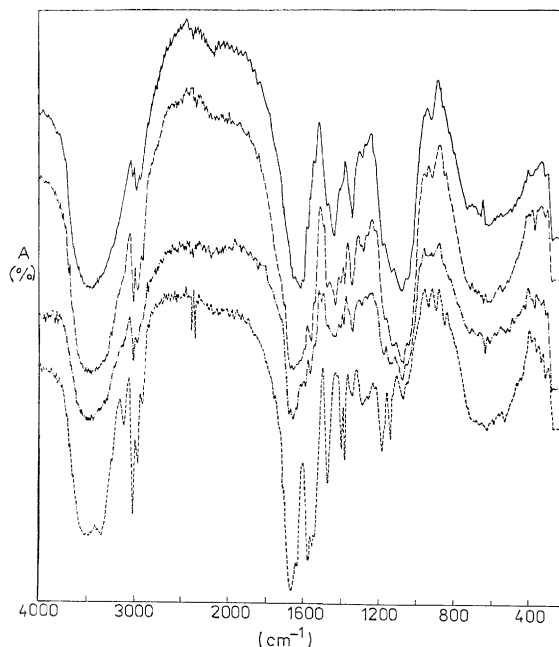


Fig. 5. IR spectra of the CMC (—), PNIPAM (---), CMC-g-PNIPAM 27 (-.-) and CMC/PNIPAM 27 blend (....).

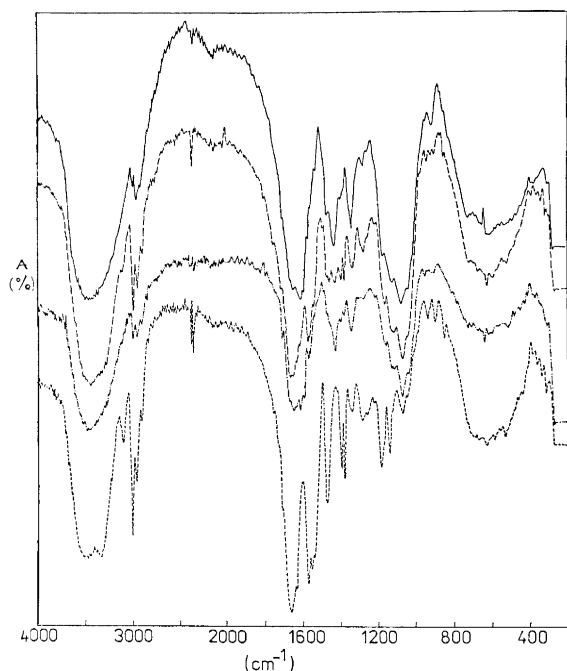


Fig. 6. IR spectra of the CMC (—), PNIPAM (---), CMC-g-PNIPAM 47 (-·-·) and CMC/PNIPAM 47 blend (- - -).

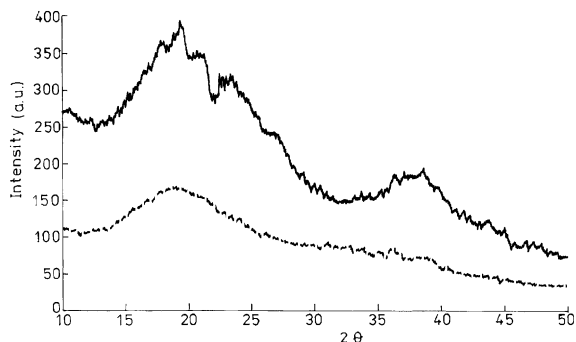


Fig. 7. X-ray diffractograms of the grafted copolymers CMC-g-PNIPAM 47 (—) and CMC-g-PNIPAM 27 (---).

step between 250 and 450 °C (maxim at 380 °C) with a mass loss of 63 wt.%.

The thermal degradation of the grafted copolymer CMC-g-PNIPAM 47 occurs in two stages. The first TG stage referring mainly to degradation of the CMC main chain takes place in the 150–330 °C (maxim at 290 °C) temperature range, with a mass loss of 28 wt.%. The second TG stage, occurred in the 340–450 °C (max la 360 °C) temperature range with a mass loss of 35 wt.% which could be ascribed to the decomposition of the PNIPAM side chains. In the case of the graft copolymers, the first DTG peak is shifted to a higher temper-

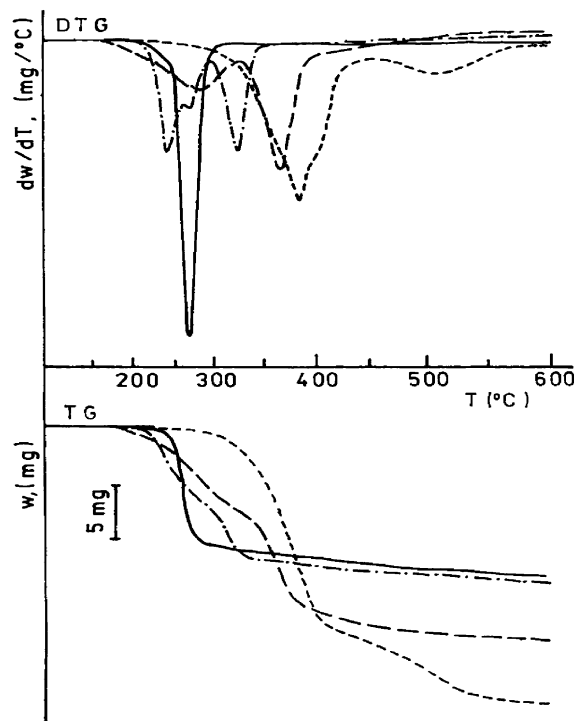


Fig. 8. TG/DTG curves of CMC (—), PNIPAM (---), their grafted copolymers CMC-g-PNIPAM 47 (-·-·) and CMC/PNIPAM 47 blend (- - -).

ature than that of CMC, while the second DTG peak is shifted to a lower temperature with respect to the corresponding peak of PNIPAM; these changes indicate an influence of the decomposition of one of the components on the decomposition of the other one. Therefore the graft copolymers are more thermally unstable than the homopolymers.

The TG/DTG curves of the physical mixtures are completely different to that of the components; this indicates interactions between components that could lead to a new structure. The TG/DTG curves of the mixtures present also two TG steps of decomposition. The first TG stage takes place in the 200–300 °C temperature range, and consists of two overlapped processes, one with the T_m at 240 °C and the other with the T_m at 270 °C. The total mass loss of the first TG step is of 26.7 wt.%. The second TG stage occurs in the 300–360 °C temperature range with a mass loss of 17.5 wt.%. Physical mixtures are more instable than the components and the corresponding graft copolymers; their TG/DTG curves are shifted to lower temperatures (Fig. 8).

Enzymatic degradation results do not indicate essential differences between the two sample types—graft copolymers and physical blends. It seems that the enzymatic degradation is more efficient for the graft copolymers [16] because the experimental values are a

little higher than the calculated ones. For CMC-g-PNIPAM 27 and 47 the enzymatic activity ratios between the experimental and calculated values were 1.4 and 1.5 respectively, while for the blends CMC/PNIPAM 27 and 47 the values were 1.2 and 1.3.

4. Conclusions

It has been established that the thermothickening effect is typical for grafted structures, which bring close enough grafted chains to form gels. The weak interactions also exist in the physical blends, both in solution and in solid state, but they are not strong enough to determine the changes in viscosity and enzymatic degradation evidenced for grafted copolymers. In the graft copolymers the self-association of grafted chains leads to thermothickening effect. The weak inter-associations are characteristic for PNIPAM-rich blends.

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