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Review

Effect of pH on the physico-mechanical properties and miscibility of methyl cellulose/poly(acrylic acid) blends

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ABSTRACT

The miscibility behavior and physico-mechanical properties between methyl cellulose (MC) of different molecular weights (4×10^4 and 8.3×10^4 g/mol) and poly(acrylic acid) (PAA) were studied by viscometry, differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), tensile strength and scanning electron microscopy (SEM) using water as a solvent. Various formulations were designed to investigate the effects of process variables such as pH on the physico-mechanical and miscibility properties of MC/PAA blends. The rheological features for the obtained blends are strongly dependent on the molecular weight of the MC used and pH. The viscosity measurements showed that all blends have non-Newtonian shear thinning (pseudoplastic) behavior. These blends have a single glass transition indicating that these blends are able to form a miscible phase due to the formation of hydrogen bonds between the hydroxyl group of MC and the carboxyl group of PAA. The MC/PAA blends exhibit good mechanical properties, thermal stability, characteristics of a MC–PAA polymer network. SEM of the blends showed no phase separation, when compared with the pure MC and PAA.

Contents

1. Introduction

Improving the properties of polymers can be achieved by chemical modifications or by a new novel architecture. Another possible approach to improve polymer properties, which has received much attention, is polymer blend since blending is a simple process. Polymer blend is an effective approach to develop new materials exhibiting combinations of properties that cannot be obtained by individual polymers. However, most polymer blends are immiscible with each other due to the absence of specific interactions. In general, to obtain a miscible blend system, it is usually necessary to ensure that favorable specific interaction exist

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between the two polymers, such as hydrogen bonding (Rakkappan & Anbalagan, 2009; Coleman, Guigley, & Painter, 1999; Vitaliy, Maria, Luigi, Zauresh, Grigoriy, & Rauash, 2003; Gina-Gabriela, John, Bernhard, & Cornelia, 2005). Therefore, various methods have been used to investigate interactions between polymers. Measurements of turbidity, pH and ionic strength as a function of weight ratio of the polymer in the media (Emine, Aylin, & Yoldaş, 2012; Neha, Seyedeh, & Kam, 2012; Sannino, Madaghiele, Lionetto, Schettino, & Maffezzoli, 2006), viscosity (Zhang, 1999), infrared spectroscopy, ^{13}C NMR, ^{1}H NMR, thermal analysis, p*K*a, powder X-ray diffraction (Anlar, Capan, Guven, Gogus, Dlakara, & Hincal, 1994; Lahaye, Inizan & Vigouroux, 1998; Roger & Jacqueline, 1998) were employed to evaluate interpolymer complexation. The properties of the blend such as T_g, T_m, modulus and crystallinity depend on the nature and physical state of the original polymer; and the processing methods in the added polymer (or additive); the interaction between polymers, the mixing ratio and the processing steps to which they are subjected (Sarawut, Sorada, Siriporn, Sunan & Tsutomu, 2008; Harry, Mukesh, & Paul, 1994).

In our laboratory, it is of particular interest to study interpolymer complexes via hydrogen bonding as an extension of our long-term studies on miscibility enhancement by introducing hydrogen bonding into polymer blends. Our previous work reported that complex formation between polyacrylic acid and poly (vinyl ether) of diethylene glycol (Zauresh, Grigoriy, Vitaliy, & Aibek, 2001) and poly(vinyl ether) of ethylene glycol (Nurkeeva, Grigoriy, Vitaliy, Victor, & Mangazbaeva, 2000) due to the presence of proton-accepting hydroxyl and ether groups in their elementary units (Zauresh, Grigoriy, Vitaliy, & Aibek, 2001). A number of studies have been reported on the subject. The general regularities of complex formation reactions between poly(carboxylic acids) and proton-accepting non-ionic polymers with formation of interaction polymer complexation via hydrogen bonding are summarized in several reviews (Jiang, Xiang, & Zhou, 1999; Nurkeeva, Mun, & Khutoryanskiy, 2001; Nurkeeva, Tyukova, Suvorova, Mun, Dzhusupbekova, & Khutoryanskiy, 2005).

Poly(4-vinyl phenol) (PVPh), which has a hydroxyl group at the para-position of the pendant phenyl ring, is capable of interacting with proton accepting functional groups in other polymers such as polymethacrylates (Weigui, Rongchun, Baohui, & Chen, 2013; Lee, Hsub, & Liou, 2006; Lin, Chen, Kuo, & Chang, 2006) [e.g., poly(methyl methacrylate) (PMMA), poly(ethylene methacrylate) (PEMA), poly(n-propyl methacrylate) (PnPMA)], and poly(ethylene oxide) (PEO)] or poly(vinyl alkyl ethers) (Belfiore, Pires, & Qic, 1991; Gestoso & Brisson, 2001) [e.g., poly(vinyl methyl ether) (PVME), poly(vinyl ethyl ether) (PVEE)] and poly(vinyl methyl ketone) (PVMK)]. In addition, PVPh can also form miscible blends with some aliphatic polyesters (Belfiore, Qin, Ueda, & Pires, 1993; Xing, Dong, An, Feng, Avella, & Martuscelli, 1997; Woo & Chiang, 2004) [e.g., poly(ε-caprolactone) (PCL), poly(ethylene succinate) (PES), poly(ethylene adipate) (PEA), and poly(β-hydroxybutyrate) (PHB)], or with some aromatic polyesters (Nurkeeva et al., 2000) [e.g., poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT) and poly(ethylene 2,6-naphthalenedicarboxylate) (PEN)].

Effects of change in complexation conditions such as pH, polymer molecular weight and solvent are also discussed. Depending on solution pH and PAA/PEO ratio the rheological properties of the polymer mixtures displayed a varying degree of association between carboxyl and ether groups (Xianke & Guojian, 2011). Also, it was observed that the higher the molecular weights of the proton-accepting polymers, the stronger the interaction became; this is in good agreement with the observations of many others (Halina & Aleksandra, 2006).

Wang, Chen, Chen, and Chun (2003) studied the effect of temperature, solvent and crosslinking of Hydroxypropyl methylcellulose (HPMC)/PAA on drug release. The H-bonding interaction of HPMC/PAA was found to be stronger in the blended films prepared from H_2O than that from H_2O/ethanol. However, the H-bonding effect between HPMC and PAA on drug release is indistinct. Karavas, Georgarakis, and Bikiaris (2006) prepared Polyvinylpyrrolidone (PVP)/HPMC blend with enhanced mucoadhesive properties for adjusting drug release in predictable pulsatile chronotherapeutics. Also, Blends of MC with PAA provide a promising set of materials for potential biomedical applications.

The present paper is a continuation of our work on the effect of pH on the physico-mechanical properties and miscibility of MC/PAA blends. We present some of the results of a viscometry, DSC, TGA, tensile strength, miscibility behavior and SEM study between methyl cellulose (MC) of different molecular weight (4×10^4 and 8.3×10^4 g/mol) and poly(acrylic acid) (PAA) at different pH.

2. Experimental

2.1. Materials

In our work, we used two samples of methylcellulose (MC): one of them, of molecular weight $M_1 = 4 \times 10^4$ g/mol, (viscosity of 2% aqueous solution at $\gamma = 1{,}7$ is 400 cps), the second one of $M_2 = 8.3 \times 10^4$ g/mol, (viscosity of 2% aqueous solution at $\gamma = 1{,}7$-1.9 is 4000 cps) purchased from Aldrich (USA). PAA (number average molecular weight 7.5×10^5 g mol^{-1}) was purchased from

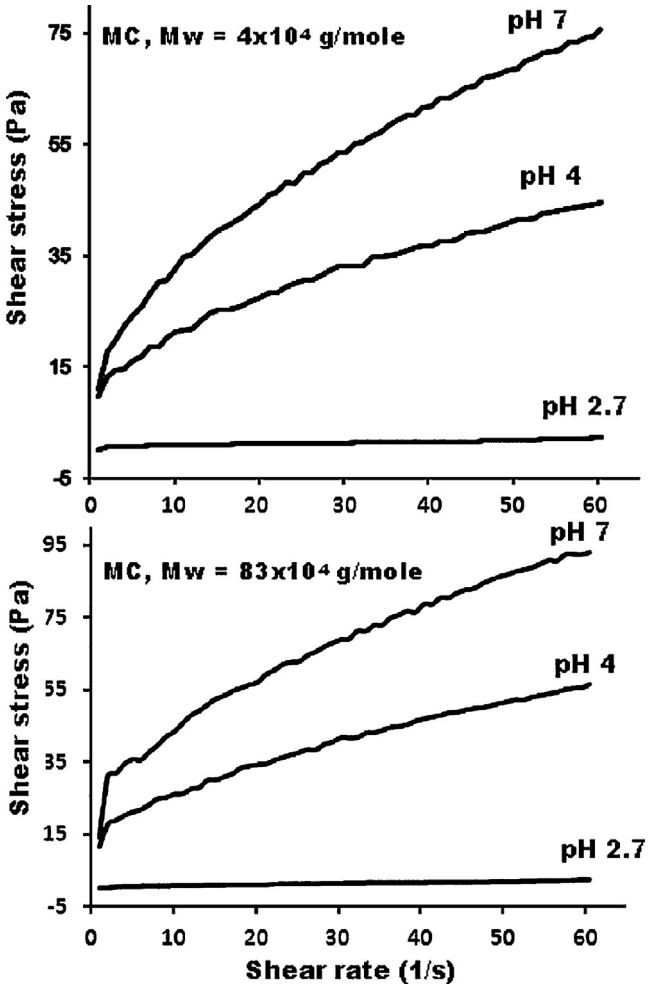

Fig. 1. Relationship between the shear stress and shear rate of MC/PAA blends (1/4) mol.% with different molecular weight of MC and pH.

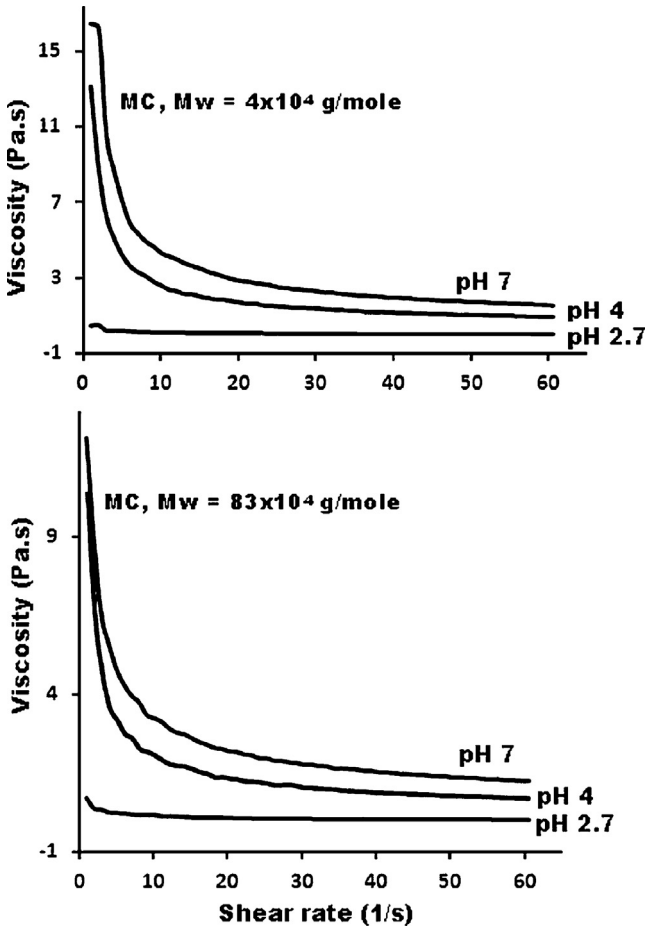

Fig. 2. Relationship between viscosity and shear rate of MC/PAA blends (1/4) mol.% with different molecular weight of MC and pH.

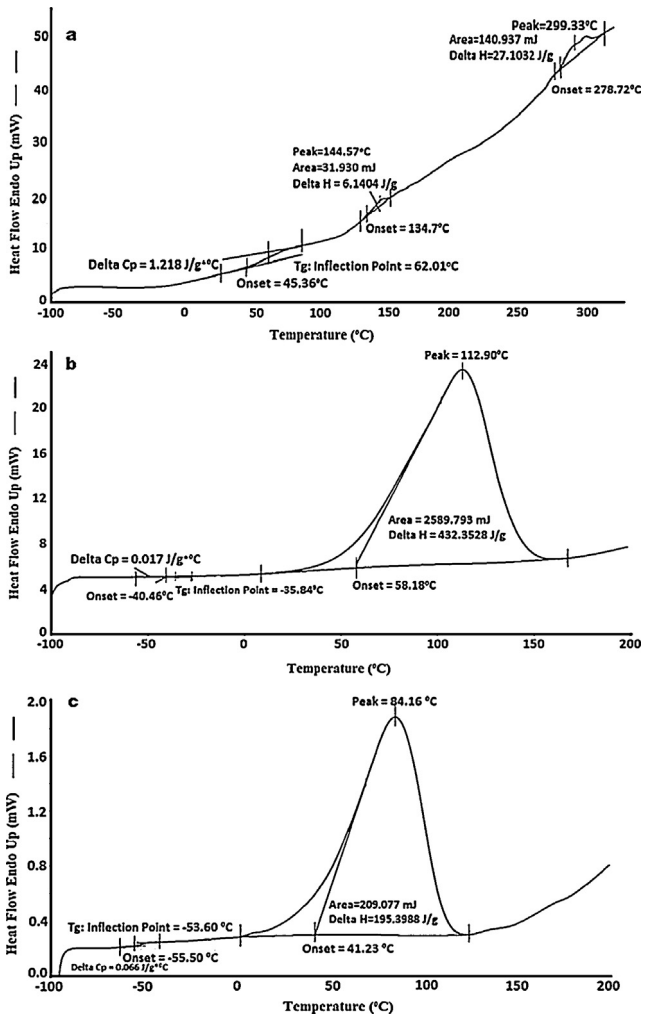

Fig. 3. DSC thermograms of (a) pure PAA, (b) pure MC (40,000) and (c) pure MC (83,000).

Aldrich (USA) and used without purification. The mixtures of MC and PAA were prepared by direct mixing of the initial aqueous polymer solutions of the same concentrations; thus, the total polymer concentration in the mixture was kept constant during each experiment at different pH (2.7, 4 and 7). The molar ratio (MC, 4×10^4 g/mol/PAA, M_1/PAA) and (MC, 8.3×104 g/mol/PAA, M_2/PAA) was close to 1:4 mol%. The experiments were performed at 25 °C.

2.2. Testing

The rheological properties were measured by using Bohlin rheometer model CS10, UK. The samples were measured using two measuring systems, namely, Cup Stainless (25 mm) and Cone Plate (CP4 40 mm) according to the state of the viscosity of the latex. The instrument was provided with PC software by which the conditions of measurement were first adjusted and the resultant data automatically obtained as a table, graph, and/or absolute value. In viscometry analysis, the conditions of measurement were adjusted as follows: start shear (0.08 s^{-1}), end shear (12.75 s^{-1}), range (linear), delay time (10 s), integration time (10 s), proportionality (constant), ramp dir (up), and the temperature mode (isothermal 25 °C). The measurement conditions adjusted for creep analysis were selected as follows: stress (1 Pa) creep time (100 s), recovery time (50 s), and the temperature mode (isothermal 25 °C).

Thermogravimetric analysis (TGA) was recorded on a TGA/SDTA851e, METTLER TOLEDO. Glass transition temperature of samples were measured using differential scanning calorimetry (DSC), on a NETZSCH DSC200 PC, using aluminum crimped pans under N_2 flow at 20 mL min^{-1}. The measurements were carried out between −50 °C and 200 °C at a heating rate of 10 °C min^{-1}. The tensile properties of the blend films were measured by using MTS 10/M tensile testing machine at a crosshead speed of 50 mm/min. An average of at least four measurements was taken, and the 1-kN load cell was used. The microstructure of the hydrophilic copolymers was investigated by scanning electron microscopy (SEM) recorded on a Carl-Ziess SMT, Oberkochen.

3. Results and discussion

3.1. Rheological behavior of MC/PAA blends

Rheology is the science of deformation and flow of materials (i.e., the relationships between force, deformation and time) (Wang & Xu, 1994; Steffe, 1992; Rao, 1999). It investigates the response of materials to an applied stress or strain (Mucha, 1997; Desbrieres, 2002; Ayoub, El-Awady, Nasr, & Negim, 2003). Rheological properties describe flow characteristics and textural behavior of substances. Molecular mass and pH play a significant role in determining the viscosity and shear dependent properties of a polymeric solution.

Plot of apparent shear stress versus shear rate (flow curve) of MC–PAA (1:4 mol %) with varied molecular weight of MC at different pH is shown in Fig. 1. It is evident that the results obtained

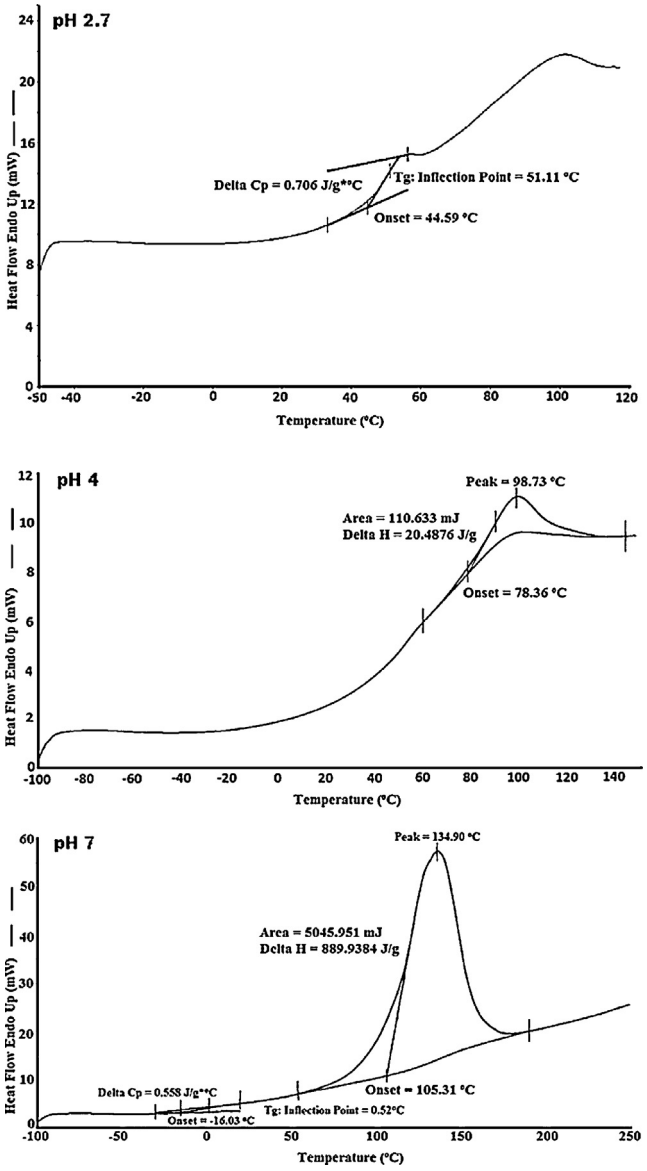

Fig. 4. DSC thermograms of MC (40,000)/PAA blend films at different pH.

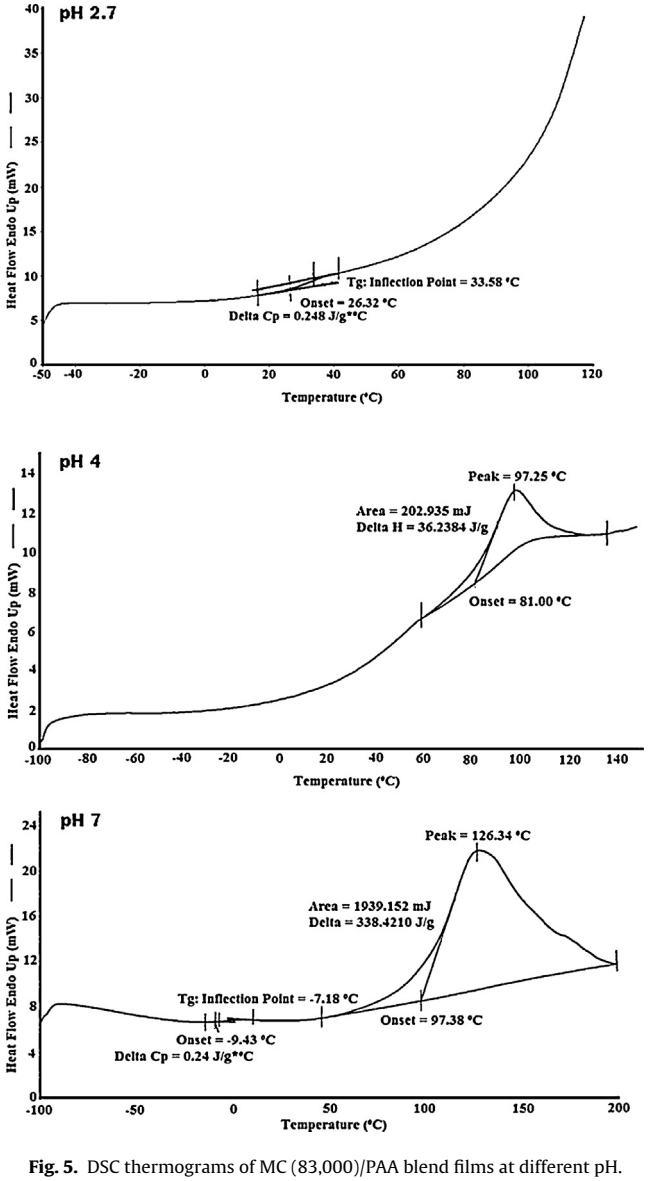

Fig. 5. DSC thermograms of MC (83,000)/PAA blend films at different pH.

depend on the molecular weight of the polymer and pH of the solution. It is seen that the shear stress increased with an increase of shear rate. Furthermore the shear rate increases with increasing pH of the solution from 2.7 to 7. In addition, these curves are convex to the shear stress axis and represent the state of increasing the shear rate. So it can be concluded that the polymer behaves as a non-Newtonian shear thinning (pseudoplastic) fluid, this finding is in good agreement with the report by Ayoub et al. (2003).

On the other hand, shear stress increases with increasing the molecular weight of MC from M_1 to M_2. The shear stress at higher shear rate for $M_2 = 8.3 \times 10^4$ g/mol is more than $M_1 = 4 \times 10^4$ g/mol, showing a higher pseudoplastic behavior for M_2, this is in good agreement with results reported elsewhere (George, Zhongwu, Nanda, & David, 2000). Finally, as pH is increased, fluid behavior is clearly pseudoplastic, the pseudoplastic character being more apparent as the molecular weight of MC is increased.

Viscosity of a polymer depends largely on the molecular mass of the polymer. The viscosity decreased by increasing the shear rate as seen from Fig. 2. The liquid shows shear thinning flow properties due to the following aspects: (1) orientation of non-spherical particles in the flow direction, (2) orientation of polymer chains in the flow direction and deformation of chains, (3) deformations of spherical particles to elliptical particles, and (4) breaking up of particle aggregates. In addition, increasing molecular weight of MC in the feed composition is accompanied by increasing viscosity with shear rate. This could be due to the formation of some gel aggregates with greater association of its particles in the polymer, which retards their mobility and increases their resistance, to flow. It can also be seen, that in the case of the polymer with higher pH = 7, there is a maximum in viscosity. Fernandes, Martins, Neto, and Pereira (2003) has reported the same sort of behavior for poly (acrylic acid) and it has been shown to be due to the polyelectrolyte effect, resulting in increased viscosity.

3.2. Differential scanning calorimetry (DSC)

Differential scanning calorimetry is a conventional technique to judge the miscibility of a polymer blend. A miscible blend exhibits one T_g, while an immiscible blend displays two T_g's, which correspond to the pure components. Generally, the observation of a single glass transition temperature (T_g) for a blend pair, between those of the homopolymers, is regarded as decisive evidence of a unique environment and of polymer miscibility, although different

Table 1
Thermal properties of MC/PAA blend films at different pH.

pH	T_g[a]		T_m[a]		IDT[b]		PDT_{max}[b]	
	MC/PAA (40,000)	MC/PAA (83,000)	MC/PAA (40,000)	MC/PAA (83,000)	MC/PAA (40,000)	MC/PAA (83,000)	MC/PAA (40,000)	MC/PAA (83,000)
2.7	51.11	33.58	100	0	280	280	400	420
4.0	84.4	85.9	98.73	97.25	310	310	390	390
7.0	0.52	−7.18	134.90	126.34	370	370	470	470

[a] Determined from DSC curves.
[b] Determined from TGA curves.

methods of measuring T_g are sensitive to different scales of homogeneity (Overney, Buenviaje, Luginbühl, & Dineli, 2000). Differential scanning calorimetry (DSC) was used to assess the extent of blending between MC and PAA. Figs. 3 and 4 and Table 1 show DSC analysis of M_1/PAA and M_2/PAA at different pH (2.7, 4.0 and 7.0). The pure MC ($M_1 = 4 \times 10^4$ g/mol), MC ($M_2 = 8.3 \times 10^4$ g/mol) and PAA exhibit one T_g at −35.84 °C, −53.60 and 62.01 °C, respectively as shown in Fig. 3. Also, the melting temperatures T_m for all blend compositions were reasonably sharp and broadened. From Figs. 4 and 5, it is clear that, T_g of the blend increases with increasing pH from 2.7 to 4.0 and decreases with increasing pH to 7.0. The decrease in T_g is probably due to the loss of intermolecular hydrogen bonding in the polymer blend (Lei et al., 2006). Furthermore, glass transition of M_1/PAA is higher than that of M_2/PAA, meaning that the M_1/PAA is more homogeneous at the molecular scale than the M_2/PAA due to the inter-association between the hydroxyl

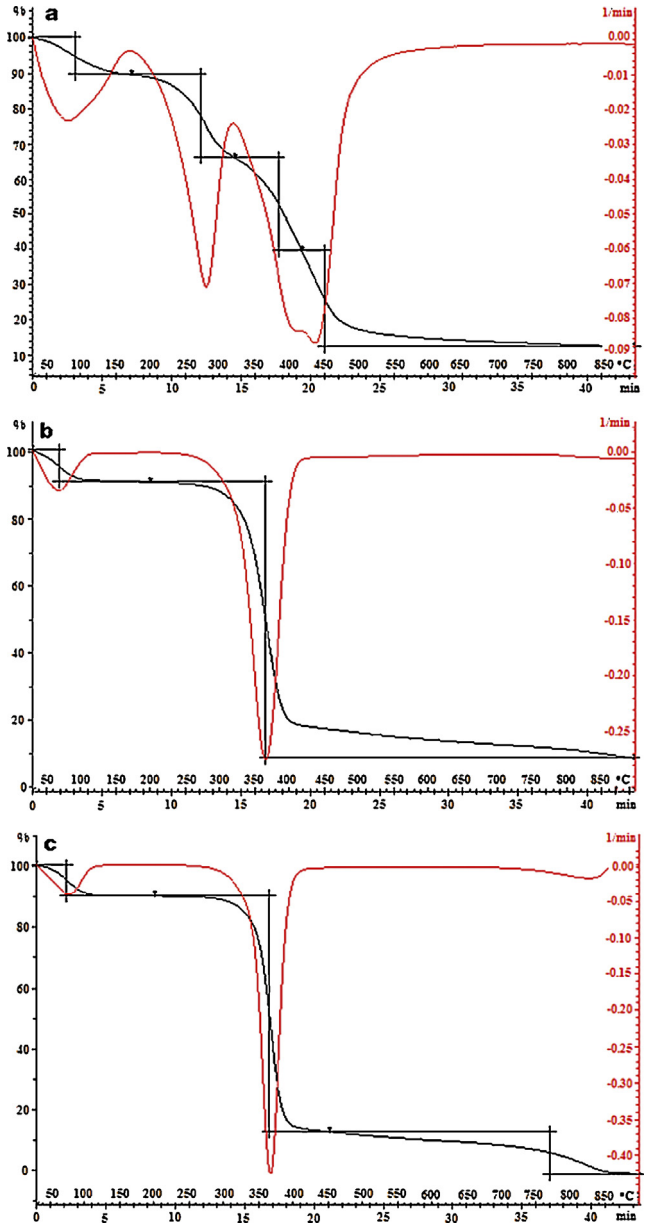

Fig. 6. TGA curves for (a) pure PAA, (b) pure MC (40,000) and (c) pure MC (83,000).

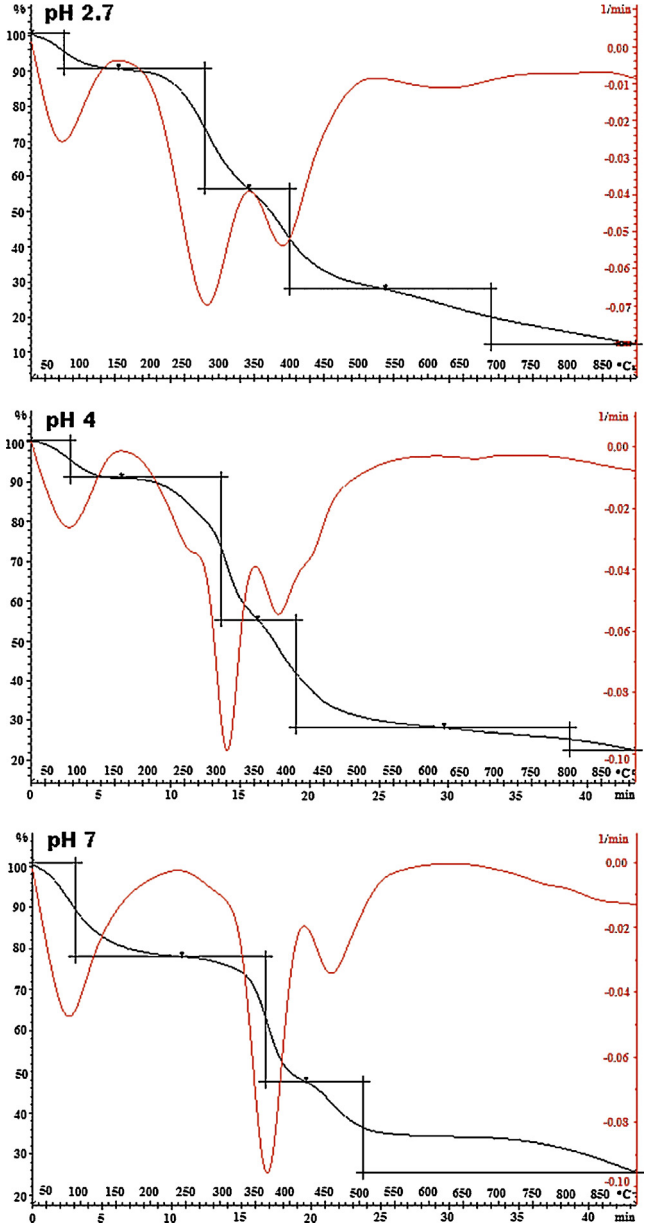

Fig. 7. TGA curves for MC (40,000)/PAA blend films at different pH.

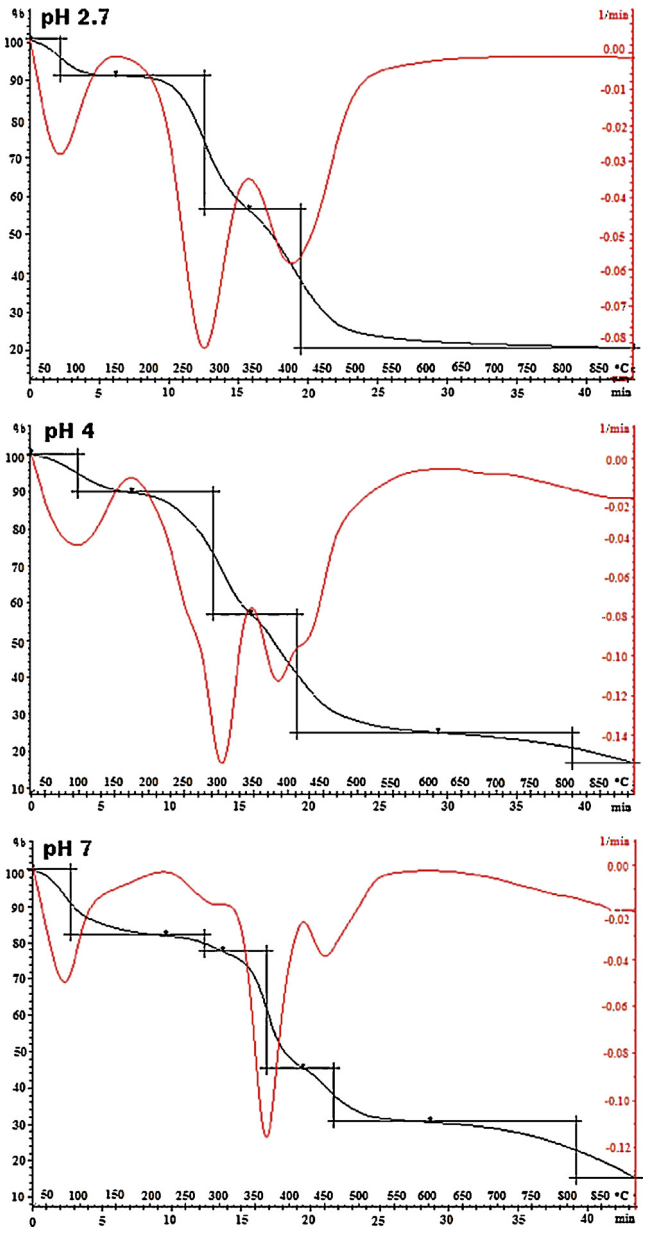

Fig. 8. TGA curves for MC (83,000)/PAA blend films at different pH.

group of MC (M_1) and carboxyl group of PAA which is stronger than between MC (M_2) and PAA. The DSC curve of each polymer blend showed a sharp endothermic peak, which appeared above 200 °C. This exothermic peak could be attributed to the melting temperature T_m. The pure M_1 and M_2 exhibit one T_m at 112.9 °C and 84.16, respectively but pure PAA has two T_m at 144.57 and 289.33 °C. Also the increasing pH shifts T_m to higher temperatures. The order of T_m for all the formulations which mainly depends on the pH are in the range: pH 7 > pH 4 > pH 2.7 > 0. In addition, for M_1/PAA samples, the higher melting temperature T_m than that of M_2/PAA is due to the level and nature of crystallinity (Roovers & Toporowski, 1992), ion content and perhaps molecular orientation.

3.3. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was employed to investigate the thermal stabilities, and the influence of the amount of ionic content on the loss of weight in the MC/PAA blend with pH 1.2, 4.0 and 7.0. Figs. 6–8 summarize the TGA results of the pure M_1, M_2,

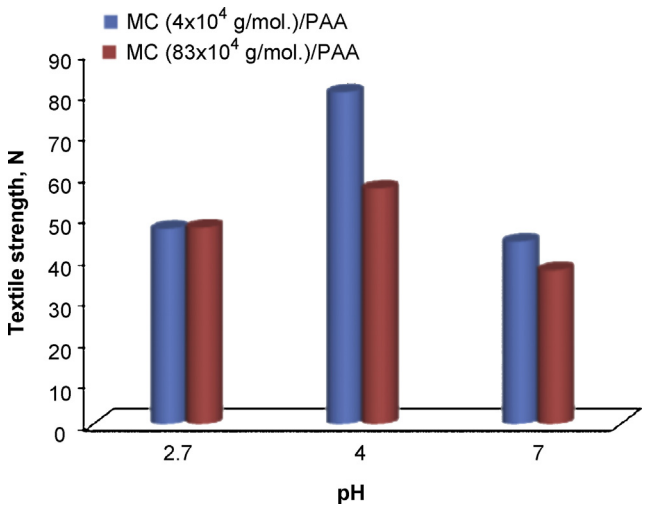

Fig. 9. The effect of pH on the tensile strength of MC/PAA blend films.

PAA and the MC/PAA blends composition ratio was kept constant at (1:4) and molecular weight of MC varied. These TGA's were performed from 20 °C to 850 °C at 20 °C/min in air. TGA measurements of all pure and blend polymers indicate that thermal degradation temperature is higher than 320 °C, which is above the highest rheological measurements employed in this study, as shown in Figs. 6–8. It is evident that the thermal degradation process for pure PAA sample proceeds in four steps as shown in Fig. 6 and Table 2. These results are somewhat different from those reported by Vitaliy et al. (2003). The first weight loss occurs between 29 and 170 °C, which corresponds to the removal of water. The second, third and fourth weight loss occurs between 170 and 894 °C correspond to anhydride decomposition with loss of CO_2. Pure M_1 and M_2 start to degrade at 362.5 and 325 °C, respectively. This behavior is in good agreement with the results obtained by other authors (Simanovich, Petropavlovskiy, Larina, Sazanov, & Stepanov 1991; Sashina, Vnuchkin, & Novoselov, 2006) for thermal degradation of MC, according to whom the mechanism of MC degradation includes the parallel processes of dehydration and demethoxylation (—OCH_3, —CH_2OCH_3).

Fig. 7 and Table 3 show the lost wt.% of M_1/PAA with increasing pH from 2.7 to 7.0. Four stages decomposition were observed for M_1/PAA in pH 2.7 and 4.0 and a three-stage decomposition is seen in pH 7.0. The decomposition steps are as follows: the first step is between 29 and 244.12 °C, which is due to moisture vaporization. In the second, third and fourth steps, in the range of 342–893 °C and weight loss (15–34.1%) are attributed to the decomposition of MC. The maximum polymer degradation temperature (PDT_{max}) corresponds to the temperature at which the maximum rate of weight loss occurred and appeared in the range 390–470 °C for the M_1/PAA blend and at 440 °C for pure PAA. The PDT_{max} increases as pH of the polymer increases. It can be seen that the apparent thermal stability of the polymers with regards to level of ionic content increases with the increase of the level of pH due to the presence of ionic interactions which originate either from a proton transfer or coulombic interactions between the carboxylic group and hydroxyl group.

Fig. 8 and Table 3 show the results of thermogravimetric analysis of M_2/PAA blend at different pH. M_2/PAA showed initial degradation temperature (IDT) and PDT_{max} in the range (280–370 °C) and (390–470 °C), respectively. It is similar to M_1/PAA and pure PAA as shown in Table 1; however the thermal degradation step of M_2/PAA increases from 3 to 5 steps with increasing pH from 2.7 to 7.0. It is suggested that the intermolecular hydrogen bonds between the two components do not affect the process of anhydride formation

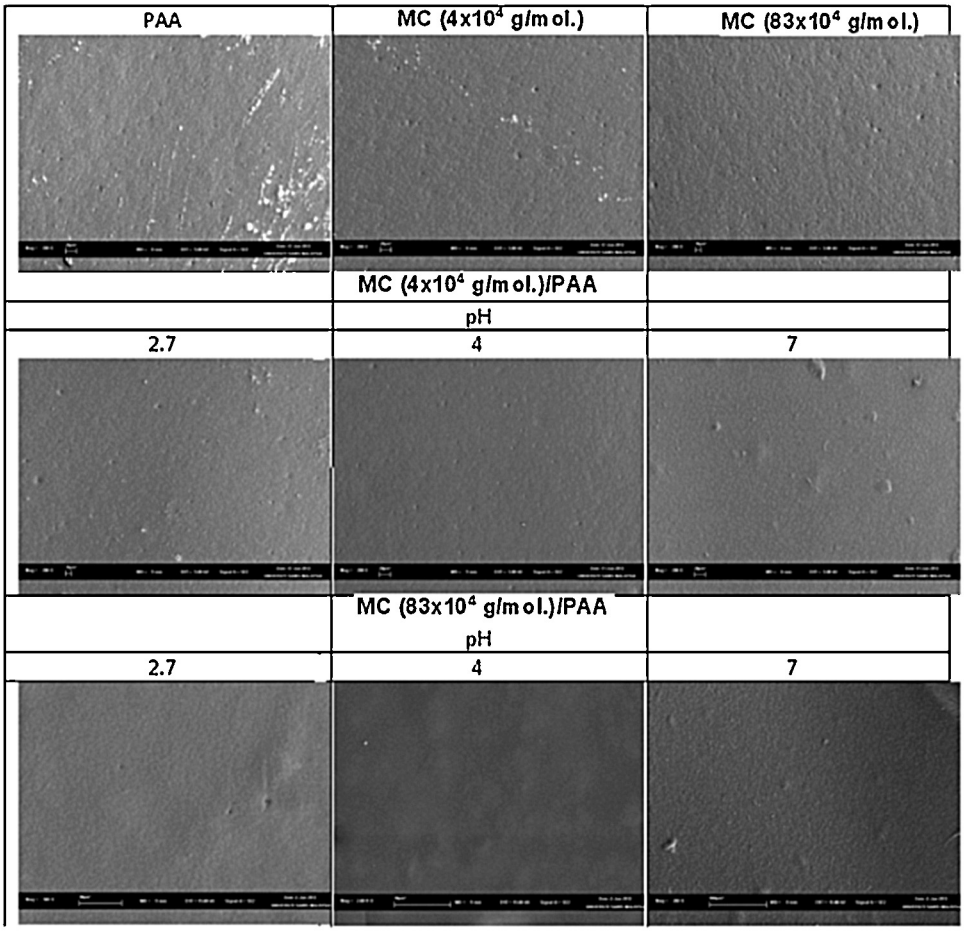

Fig. 10. Scanning electron micrographs of the Pure PAA, MC and MC/PAA blend films.

Table 2
Thermal properties of pure MC and PAA.

Polymer	Temperature range (°C)	Weight lost (wt.%)	Residue (wt.%)	IDT (°C)	PDT_{max} (°C)
PAA	29.62–170.74	10.3	89.7	282.5	440
	170.24–320.71	23.7	65.9		
	320.71–416.21	26.6	39.4		
	416.21–894.09	27.3	12.1		
MC (40,000)	29.45–198.61	9.5	90.9	320	362.5
	198.61–892.28	82.6	8.4		
MC (83,000)	29.41–200.24	9.9	90.6	325	340
	200.24–450.28	77.4	12.7		
	450.28–893.55	13.9	0.0		

Table 3
Thermal properties of MC/PAA blend films at different pH.

pH	Temperature range (°C)		Weight lost (wt.%)		Residue (wt.%)	
	MC/PAA (40,000)	MC/PAA (83,000)	MC/PAA (40,000)	MC/PAA (83,000)	MC/PAA (40,000)	MC/PAA (83,000)
2.7	30.2–155.6	30.1–158.2	9.9	9.2	90.6	91.2
	155.6–342.7	158.2–347.1	34.1	34.7	56.4	56.4
	342.7–539.1	347.1–897.7	28.6	35.9	27.8	20.5
	539.1–898.1		15.7		12.01	
4	29.7–158.2	29.8–172.8	9.2	10.4	90.8	89.8
	158.2–353.9	172.8–345.3	35.7	32.8	55.1	56.9
	353.9–618.5	345.3–610.2	27.1	31.9	28.1	24.9
	618.5–894.4	610.2–892.2	5.8	8.5	22.2	16.6
7	29.4–244.1	29.4–221.2	22.5	18.2	77.9	81.9
	244.1–422.0	221.2–303.6	30.5	4.4	47.5	77.4
	422.0–893.1	303.6–418.3	22.5	32.1	25.2	45.4
		418.3–597.3		14.8		30.5
		579.3–891.9		15.54		15.1

which corresponds to water loss and crosslinking, as the same result was obtained by authors (Vitaliy et al., 2003).

For temperatures higher than 342 °C, MC/PAA films show a lower weight loss than pure PAA film which could be attributed to a stabilizing effect of MC is in agreement with the experimental results of the authors (Vitaliy et al., 2003).

3.4. Tensile strength

The tensile strength of the MC/PAA films with respect to pH are shown in Fig. 9, the data indicate that the tensile strength of MC/PAA blends increase with increasing pH from 2.7 to 4.0 and decreases with increasing pH to 7.0. M_1/PAA showed the largest tensile compared with M_2/PAA. This is presumably due to the increased chemical crosslinks and hydrogen bonding density between MC and PAA. This improvement of tensile strength is related to an increase in the packing density of the polymer chains in blends through filling of the cavities in the structure of MC by flexible PAA, as well as to an attractive interaction between the polymer components. Results obtained are in agreement with the experimental results of Sashina, Vnuchkin, and Novoselov (2006). The tensile properties confirm with DSC that pH improves significantly the physico-mechanical properties of the blends over the entire range of compositions at pH = 4.

3.5. Scanning electron microscopy (SEM)

Fig. 10 shows the SEM pictomicrographs for pure MC, pure PAA and MC/PAA blends. In general, SEM morphology results are not taken as direct evidence for polymer miscibility owing to limit of scales of phase resolution. It can be seen from Fig. 10 the films of pure PAA, M_1, M_2 and MC/PAA blends have homogeneous morphology with no domains which confirms the miscibility of the polymers.

4. Conclusions

The physico-mechanical properties and miscibility behavior of MC/PAA have been studied by several techniques. Viscometry showed that all the MC/PAA blends are characterized by non-Newtonian pseudoplastic properties. Differential scanning calorimetry was the main experimental technique used to study the thermal behavior of the blends. Through the measurement of glass transition temperature and melting point of the blends. For blends with well-determined glass transition temperature T_g, DSC proved miscibility of the blends due to hydrogen bonding. All the blends exhibit one T_g and increased with increasing pH from 2.7 to 4. MC/PAA blend samples show good mechanical properties and thermal stability especially at pH = 4. The DSC results are in agreement with those obtained from the tensile strength and TGA study. The SEM's of CM/PAA showed that no phase separation occurs, when compared with the pure MC and PAA.

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