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Plasticity of hot air-dried mannuronate- and guluronate-rich alginate films

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ABSTRACT

The plasticity of hot air-dried guluronate-rich (MG) and mannuronate-rich (MC) alginate films prepared from 2% and 4% (w/w) alginate solutions, which contained the same amount of polymer, through hot-air drying at 40–80 °C were investigated. These films were subjected to thermomechanical, differential scanning calorimetry, fourier-transform infrared, X-ray diffractometry, dimension, morphology, moisture content, viscosity and polymer molecular weight analysis. Film plasticity increased when dilute alginate solution and MC were employed in film preparation. This was due to decrease in polymer–polymer interaction at high-strength domains of matrix involving C–H, O–H, C–O and/or C=O moiety of alginate, attributing to plasticization effect of water and ease of molecular rearrangement of alginate. The plasticity of film decreased with an increase in drying temperature from 40 to 60 °C following heat-induced polymer–polymer interaction. A further increase in drying temperature to 80 °C nonetheless greatly promoted film plasticity through air bubble formation and reduced alginate molecular weight in film.

1. Introduction

Pharmaceutical films have long been employed as transdermal drug delivery system (Maeda, Kadota, Kajihara, Sano, & Fujioka, 2001; Murthy, Hiremath, & Paranjothy, 2004; Nicoli, Penna, Padula, Colombo, & Santi, 2006; Padula, Nicoli, Colombo, & Santi, 2007). The transdermal route is a preferred mode of drug delivery owing to it is a safe and painless administration pathway, and has gained a higher level of patient compliance when compared to intravenous and subcutaneous injection (Naik, Kalia, & Guy, 2000; Thomas & Finnin, 2004). Unlike oral administration, the use of transdermal route avoids hostile gastrointestinal environment as well as first pass metabolism which could bring about degradation of drugs (Bennett, 1998; Langer, 2004; Yuan, Ansari, Samaan, & Acosta, 2008). The typical dosing schedule can be reduced to once daily or even weekly, and the transdermal drug therapy can be interrupted through removal of drug delivery system at times when side effects of drugs are experienced by patients (Nitti et al., 2006; Zhan, Tang, Chen, & Mao, 2006).

Alginate is a polysaccharide derived mainly from brown seaweeds. It composes of D-mannuronate (*M*) and L-guluronate (*G*) linked by β(1–4) and α(1–4) glycosidic bonds in varying proportions. These components are arranged as mannuronate diads (*MM*), guluronate diads (*GG*) and heterodiads (*MG*). The relative fraction of each diad varies with species, part and age of seaweeds from which the alginate is isolated (Drury, Dennis, & Mooney, 2004; Kumar Naidu, Sairam, Raju, & Aminabhavi, 2005; Torres et al., 2007). D-mannuronate has $^4C_1$ conformation and its molecular chain is flexible (Avella et al., 2007; Grant, Morris, Rees, Smith, & Thom, 1973; Sartori, Finch, Ralph, & Gilding, 1997). L-guluronate has $^1C_4$ conformation and gives folded, rigid and stiff chain structure. Alginate is frequently employed as matrix polymer for encapsulation of drugs, proteins, cells and DNA (Gombotz & Wee, 1998; Heng, Chan, & Wong, 2003; Wong, Chan, Kho, & Heng, 2002, 2005). Owing to its excellent film forming, biocompatible, and non-toxic properties (Dong, Wang, & Du, 2006; Pongjanyakul, Priprem, & Puttipipatkhachorn, 2005; Yang, Chen, & Fang, 2009), alginate is deemed suitable for fabrication into film for use as a transdermal drug delivery system.

Pharmaceutically, films are commonly fabricated by means of solvent-evaporation technique (Maeda et al., 2001; Murthy et al., 2004; Nicoli et al., 2006; Nor Khaizan, Wong, Deepak, & Taib, 2007; Padula et al., 2007; Person, Puiggali, Baron, & Roques, 1998; Wong, 2008; Wong, Deepak, Taib, & Anuar, 2007). Hot air current, microwave, near infrared and freeze-drying are methods that can be used to remove the solvent from drying mass. The rate of solvent removal is governed by the propensity of surface liquid evaporation and internal liquid migration from core to exterior of drying mass which in turn is dependent partly on drying temperature and formulation of solution (Wong, 2008). The mechanical strength of film is greatly affected by drying condition (Denavi

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et al., 2009; Kaya & Kaya, 2000; Srinivasa, Ramesh, Kumar, & Tharanathan, 2004). Drying parameters, such as temperature, relative humidity, time, drying rate, type of method and matrix content, have been investigated with respect to their influences on film integrity (Denavi et al., 2009; Kaya & Kaya, 2000; Murthy et al., 2004; Srinivasa et al., 2004). However, there is no known study reporting the mechanical property of solid films which contain the same amount of polymer, but are prepared from solutions with varying polymer concentrations through drying. Mannuronate-rich alginate is conformationally more flexible than guluronate-rich alginate. It is hypothesized that mannuronate-rich alginate could respond differently from guluronate-rich alginate in their molecular rearrangement and interaction during film formation by drying towards variations in polymer solution concentration and drying temperature which are deemed to affect the mobility of polymer chains in liquid. This can affect the mechanical strength of film and its downstream transdermal application. As such, the present study aims to investigate the mechanical and molecular characteristics of solid mannuronate- and guluronate-rich alginate films of the same polymer content but prepared from solutions of varying polymer concentrations and at different drying temperatures.

2. Materials and methods

2.1. Materials

Two grades of sodium alginate were employed as the matrix polymer of films, namely guluronate-rich (MG, Manugel® DMB, ISP, USA) and mannuronate-rich (MC, Manucol® DMF, ISP, USA) alginates. These alginates had a nominal viscosity value of 300 mPa s and their mannuronate/guluronate ratios were 0.59 and 1.56 for MG and MC, respectively.

2.2. Methods

2.2.1. Preparation of films

The 2% and 4% (w/w) aqueous alginate solutions were prepared by dissolving the alginate in deionized water at a mixing speed of 300 rpm for 2 h. The formed solution was then left to stand for at least 2 h to remove the air bubble. The absence of air bubble in alginate solution was verified using a compound microscope. Keeping the content of solid polymer in all films at 0.4 g, an accurately weighed quantity of 2% or 4% (w/w) aqueous alginate solution was transferred into a glass petri dish (internal diameter = 9 cm). The bubble-free solution was subjected to hot-air drying in an oven (Memmert, Germany) at 40, 60 and 80 °C for 48 h to ensure all samples reached equilibrium moisture content. The formed films were peeled off and further conditioned in a desiccator at 25 ± 1 °C and at 25 ± 5 % relative humidity (digital thermohygrometer ETHG 880, RS Components Ltd, UK) for at least 5 days prior to physicochemical characterization. At least triplicates were carried out for each formulation.

2.2.2. Characterization of films

The thickness (n = at least 9 points per film) and moisture content of films were examined using digimatic thickness gage (Mitutoyo, Japan) and skin hydration measurement device (Corneometer® CM825, Cologne, Germany), respectively as previously described by Nor Khaizan et al. (2007) and Wong et al. (2007). The mechanical strength and state of molecular interaction of films were analyzed using thermomechanical analyzer, differential scanning calorimeter, Fourier-transform infrared spectrometer and X-ray diffractometer, and the morphology of films was assessed using an image analyzer. The states of alginate molecular weight and viscosity of films were determined using gel permeation chromatography and U-tube viscometry techniques.

2.2.2.1. Mechanical strength analysis. The mechanical strength of films was examined using a thermomechanical analyzer (TMA/SS6100, SII Nano Technology Inc., Japan). Film of width 4.008 ± 0.002 mm, length 15.205 ± 0.006 mm and thickness 0.041 ± 0.001 mm was mounted onto tension clamp fixture, heated to 32 °C at a heating rate of 10 °C/min and oscillated at the amplitude of 40 mN and frequency of 0.01 Hz under constant purging of nitrogen at 100 ml/min without film tearing. The storage modulus (E'), loss modulus (E'') and loss tangent ($\tan\delta$) of film were computed. The elastic response of film is represented by E' and the viscous response of film is indicated by E''. The $\tan\delta$ is a dimensionless parameter, expressed as quotient of E'' to E'. It is equal to the ratio of energy loss to energy stored per cycle. At least triplicates were carried out for each batch of sample and the results averaged.

2.2.2.2. Differential scanning calorimetry (DSC) analysis. DSC thermograms were obtained using a differential scanning calorimeter (Pyris 6 DSC, Perkin Elmer, USA). Four milligrams of sample were crimped in a standard aluminum pan and heated from 30 to 380 °C at a heating rate of 10 °C/min under constant purging of nitrogen at 40 ml/min. The characteristic peak temperature and enthalpy values of endotherm and exotherm were recorded. At least triplicates were carried out for each batch of sample and the results averaged.

2.2.2.3. Fourier-transform infrared spectroscopy (FTIR) analysis. A total of 2.5% (w/w) of sample, with respect to potassium bromide (KBr) disc, was mixed with dry KBr (FTIR grade, Aldrich, Germany). The mixture was ground into a fine powder using an agate mortar before compressing into a disc. Each disc was scanned at a resolution of 4 cm^{-1} over a wavenumber region of 400–4000 cm^{-1} using a FTIR spectrometer (Spectrum RX1 FTIR system, Perkin Elmer, USA). The characteristic peaks of IR transmission spectra were recorded. At least triplicates were carried out for each batch of sample and the results averaged.

2.2.2.4. X-ray diffractometry analysis. The crystallinity state of sample was evaluated using X-ray diffractometer (MiniFlex II, Rigaku Corporation, Japan) with Cu-K_α radiation generated at 30 kV and 15 mA. The X-ray diffraction was operated at a scanning speed of 3°/min, ranging from 3° to 80° (2θ). At least triplicates were carried out for each batch of sample and the results averaged.

2.2.2.5. Morphology analysis. The morphology of film was assessed using an image analyzer (Video Test Size 5.0, Video Test, Russia) which consisted of a computer system connected to a digital camera (Nikon E8400, Nikon Corp., Japan) mounted on a compound microscope (Leica DMLP, Leica Microsystems Wetzlar GmbH, Germany). The image of each 2 cm × 2 cm film was captured at randomly selected locations using 10 × magnification following calibration of the size of projected image using an objective micrometer (OB-M 1/100, Olympus Optical, Japan). At each location, the size and number of air bubbles embedded in film were characterized, and the median size of air bubbles was calculated from the cumulative plot of air bubble number against its size. At least triplicates were carried out for each batch of sample and the results averaged.

2.2.2.6. Molecular weight analysis. The molecular weight of sample was determined using a gel permeation chromatography technique (1100 series, Agilent Technologies, Germany) by means of a refractive index detector. A PL aquagel-OH mixed column (7.5 × 300 mm; 8 μm; Agilent Technologies, United Kingdom) was used with mobile phase consisted of 0.1% (w/w) sodium azide (Ajax Finechem, Australia) dissolved in deionized water. The flow rate of mobile phase and column temperature was kept at 0.5 ml/min and 30 °C, respectively. Dextrans (Sigma Aldrich, Germany) with molecular weights of 50,000, 80,000, 150,000, 270,000, 410,000, 670,000 and 1,400,000 Da were used as standards. One mg/ml of standard or sample solution was filtered through a cellulose nitrate membrane (pore diameter = 0.45 μm, Sartorius, Germany) before analysis. At least triplicates were carried out for each batch of sample and the results averaged.

2.2.2.7. Viscosity analysis. The flow time of 3 mg/ml of sample solution was examined using a U-tube (Size B, Poulten Selfe & Lee Ltd., United Kingdom) at 30.0 ± 0.5 °C. The specific viscosity (*SV*) of solution was calculated using the following equation:

$$SV = F - F_O/F_O \tag{1}$$

where F = flow time of sample solution and F_O = flow time of deionized water which was used as solvent for the tested sample. At least triplicates were carried out for each batch of sample and the results averaged.

2.3. Statistical analysis

Student's *t*-test and Pearson correlation analysis of data were performed using Statistical Package for the Social Sciences (SPSS version 15, SPSS Inc., USA). The level of significance was set at $p < 0.05$.

3. Results and discussion

Drying of MG and MC solutions led to the formation of thin, flat and transparent films. The film thickness (MG film: 0.040 ± 0.005 mm; MC film: 0.042 ± 0.006 mm) and moisture content (MG film: 3.456 ± 0.381% (w/w); MC film: 2.938 ± 0.098% (w/w)) of both MG and MC films were unaffected by the polymer concentration of alginate solution and drying temperature used in the preparation of films.

3.1. Mechanical strength

Both MG and MC films had greater values of E' than E'' (Table 1; Student's *t*-test, $p < 0.05$). These films demonstrated predominantly elastic behavior. Films prepared using 2% (w/w) alginate solution had a higher degree of plasticity than those formed using 4% (w/w) alginate solution (Table 1; $p < 0.05$). The former exhibited higher tan δ values though films prepared using different solution concentrations of alginate carried the same amount of polymer. In comparison to MG films prepared under all drying and formulation conditions, the MC films had larger tan δ values and were more plastically deformable (Table 1; $p < 0.05$). Using 4% (w/w) alginate solution, drying of MG and MC solutions at 60 °C produced films with a lower degree of plasticity than those dried at 40 and 80 °C (Table 1; $p < 0.05$). Drying of MC solution at 80 °C led to the formation of films with a remarkable rise in their plasticity.

3.2. DSC analysis

DSC analysis indicated that the thermograms of unprocessed MG and MC exhibited two melting endotherms and one exotherm (Fig. 1). The conversion of unprocessed alginates into films brought about thermograms which were characterized by a single melting endotherm and two exotherms (Figs. 1 and 2). The endotherms of both MG and MC films had lower peak temperatures and wider temperature distributions than unprocessed polymers. This was probably attributed to reduced strength of polymer–polymer interaction following plasticization of polymer chains by water during the process of film formation from alginate solution. The formation of endotherm at a low peak temperature with a wide temperature distribution, as well as, dual exotherms at high peak temperatures indicated that MG and MC films contained domains of varying strengths (Fig. 1). A loss in strength of polymer–polymer interaction at one domain was accompanied by a gain in strength of polymer–polymer interaction at the others during the forming of film.

The use of 2% and 4% (w/w) alginate solutions produced MG and MC films which carried the same amount of polymer, but were characterized by different thermal profiles. The exothermic enthalpy values of MG and MC films were smaller when 4% (w/w) alginate solution was employed in the preparation of matrix (Fig. 1). The extent of polymer–polymer interaction was higher at high-strength domains of films prepared from 4% (w/w) alginate solution. This conferred a higher degree of elasticity to these matrices. Using 2% (w/w) alginate solution, the MG and MC films were relatively plastic. The plasticity of these films was an attribute of reduced polymer–polymer interaction following matrix plasticization by water which was available in a greater quantity in 2% (w/w) alginate solution. This was in accordance to a report where water was indicated to be able to increase the intermolecular distance and main chain segmental mobility of polymer (Lazaridou, Biliaderis, & Kontogiorgos, 2003). The difference in tan δ values between MG films prepared from 2% and 4% (w/w) alginate solutions was greater than MC films (Table 1). The plasticity of MG films was greatly increased when a dilute alginate solution was used as film forming liquid. This was probably attributed to MG contained rigid guluronate-rich alginate chains. These alginate molecules experienced a greater extent of mobilization by water when compared to flexible mannuronate-rich MC molecules during the process of drying. Thus, there was a greater rise in exother-

Table 1
Storage moduli, loss moduli and loss tangent profiles of MG and MC films.

Drying temperature (°C)	Alginate solution concentration % (w/w)	E' (Pa)	E'' (Pa)	tan δ
40[d]	4 (MG)[c]	$1.898 \times 10^9 \pm 1.655$[a]	$1.053 \times 10^8 \pm 4.079$[a]	0.055
	4 (MC)[c]	$1.622 \times 10^9 \pm 1.254$[a]	$9.327 \times 10^7 \pm 6.711$[a]	0.058
60[d]	2 (MG)[c]	$2.222 \times 10^9 \pm 1.474$[a]	$1.214 \times 10^8 \pm 4.911$[a]	0.055[b]
	4 (MG)[c]	$1.974 \times 10^9 \pm 1.860$[a]	$9.054 \times 10^7 \pm 6.189$[a]	0.046[b]
	2 (MC)[c]	$2.097 \times 10^9 \pm 1.119$[a]	$1.217 \times 10^8 \pm 6.746$[a]	0.058[b]
	4 (MC)[c]	$1.659 \times 10^9 \pm 1.461$[a]	$9.223 \times 10^7 \pm 3.176$[a]	0.056[b]
80[d]	4 (MG)[c]	$2.802 \times 10^9 \pm 1.882$[a]	$1.744 \times 10^8 \pm 6.362$[a]	0.062
	4 (MC)[c]	$2.303 \times 10^9 \pm 1.204$[a]	$1.994 \times 10^8 \pm 5.939$[a]	0.087

[a] $E' > E''$ at corresponding drying temperature, alginate grade and solution concentration ($p < 0.05$).

[b] tan δ: 2% (w/w) sample >4% (w/w) sample at corresponding alginate grade and drying temperature ($p < 0.05$).

[c] tan δ: MC sample > MG sample at corresponding alginate solution concentration and drying temperature ($p < 0.05$).

[d] tan δ: 60 °C sample <40 and 80 °C samples at corresponding alginate grade and at 4% (w/w) alginate solution concentration ($p < 0.05$).

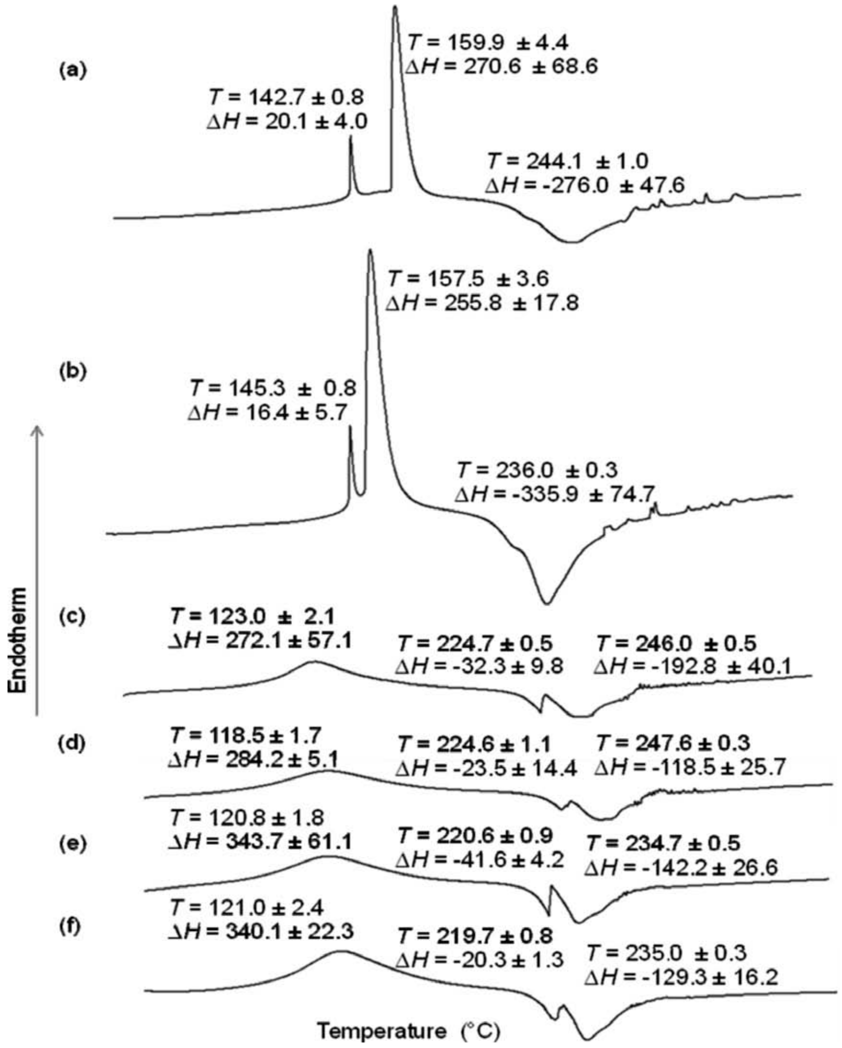

Fig. 1. DSC thermograms of (a) unprocessed MG, (b) unprocessed MC, MG films prepared from (c) 2% and (d) 4% (w/w) alginate solutions, and MC films prepared from (e) 2% and (f) 4% (w/w) alginate solutions at a drying temperature of 60 °C. *T*: endothermic/exothermic peak temperature (°C); Δ*H*: enthalpy (J/g).

mic enthalpy value of MG film than MC film when 2% (w/w) alginate solution was used as film forming liquid instead of 4% (w/w) alginate solution (Fig. 1).

The texture of MC films was more plastic than MG films (Table 1). DSC analysis indicated that the strength of polymer–polymer interaction at high-strength domains of matrix was lower in MC film than MG film. This was denoted by consistently lower peak temperatures of exotherms in MC films prepared from 2% and 4% (w/w) alginate solutions using drying temperatures of 40–80 °C than the corresponding MG films (Figs. 1 and 2). On the other hand, the extent of polymer–polymer interaction could be higher at the same domains or domain of low matrix strength in MC than MG films. This was indicated by higher endothermic enthalpy and lower exothermic enthalpy values of the former. A higher extent of polymer–polymer interaction was accompanied by a higher plasticity attribute of MC films when these matrices had reduced strengths at domains characterized by high peak temperatures.

Drying of MG solutions at 60 °C produced a more elastic film than at 40 and 80 °C (Table 1). This was ascribed to the higher extent of polymer–polymer interaction at high-strength domains of MG film dried at 60 °C, which was translated by its lower enthalpy values of exotherms at 224.6 ± 1.1 and 247.6 ± 0.3 °C (Fig. 2). However, the analysis of exotherm characteristics of MG films was not able to provide an explanation for the markedly higher degree of plasticity of film dried at 80 °C when compared to film produced at 40 °C (Table 1). The exothermic enthalpy values of MG film dried at 80 °C were smaller than MG film dried at 40 °C (Fig. 2). The endothermic peak temperature of MG film dried at 80 °C tended to be lower than the corresponding peak temperature of film dried at 40 °C (Fig. 2). The plasticity of MG film was probably induced through negating the propensity of polymer–polymer interaction at low-strength domain. Nonetheless, such changes in strength profile of MG matrix might not entirely account for the plasticity attribute of MG film as it was more likely that the film plasticity was largely governed by changes at high-strength domains of matrix. This was clearly transcribed from the relationship of thermal characteristics and plasticity between MG and MC films, as well as, films prepared using 2% and 4% (w/w) alginate solutions. Similar observation was noted in the case of MC films prepared through drying the alginate solutions at 40–80 °C and the plasticity attribute of MC film produced at 80 °C could not be aptly explained by the its thermal profiles against those dried at lower temperatures (Fig. 2).

3.3. FTIR analysis

FTIR analysis indicated that the transmission intensity of FTIR peaks ascribing MG at wavenumbers of 624.7 ± 1.9, 1095.4 ± 0.5

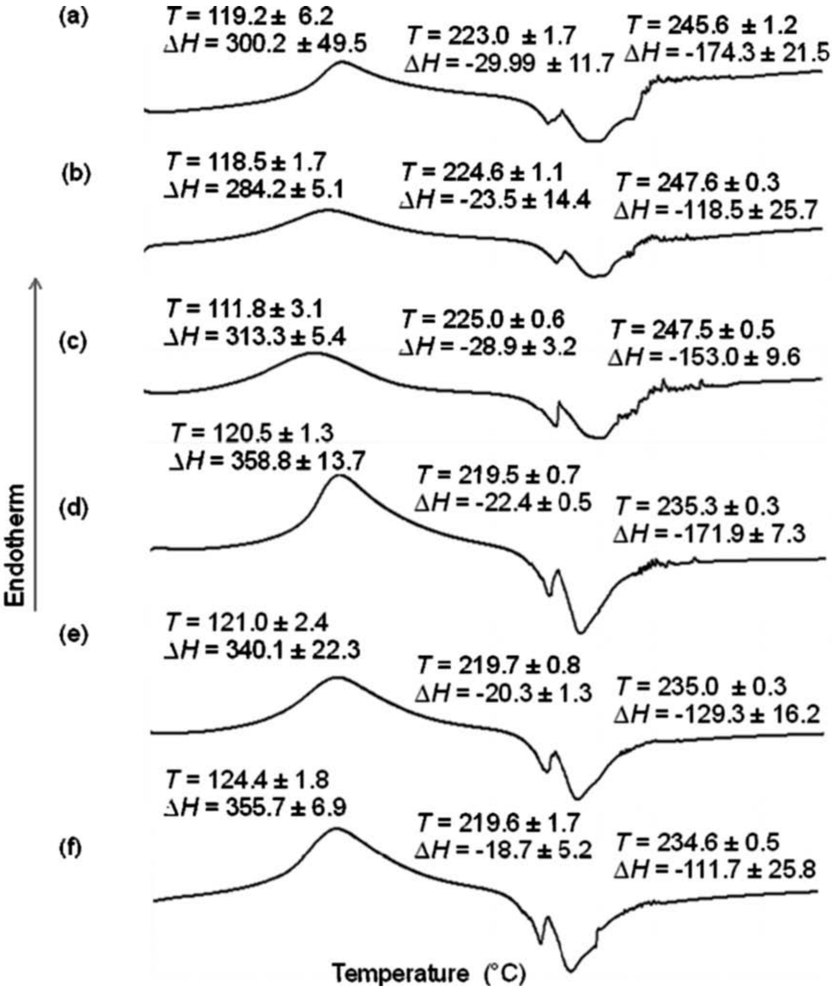

Fig. 2. DSC thermograms of MG films prepared from 4% (w/w) alginate solution using drying temperatures of (a) 40, (b) 60 and (c) 80 °C, and MC films prepared from 4% (w/w) alginate solution using drying temperatures of (d) 40, (e) 60 and (f) 80 °C. *T*: endothermic/exothermic peak temperature (°C); Δ*H*: enthalpy (J/g).

and 1126.1 ± 1.1 cm^{-1} denoting C–H and C–O moieties (Leal, Matsuhiro, Rossi, & Caruso, 2008; Pavia, Lampman, & Kriz, 2001; Sartori et al., 1997) was lower than the corresponding peaks of MC (Fig. 3). In addition, the wavenumber of FTIR peak ascribing C–O moiety of MG at 1319.7 ± 0.6 cm^{-1} (Sartori et al., 1997) was higher than that of MC. The FTIR peak of MG ascribing O–H moiety at wavenumber of 3000–3600 cm^{-1} (Ho, Mi, Sung, & Kuo, 2009) exhibited a sharper band shape than MC. The results suggested that there was a lower propensity of polymer–polymer interaction via C–H and C–O moieties of MG than MC. The MC was characterized by O–H domains of varying strengths, probably owing to its extended chain structure which interacted flexibly with adjacent polymer chains. The transformation of MG and MC into films brought about a rise in the transmission intensity of FTIR peaks at wavenumber between 600 and 1400 cm^{-1} in the latter (Figs. 3 and 4). The films exhibited broader FTIR peaks at wavenumber ranged from 3000 to 3600 cm^{-1} when compared to MG and MC. The formation of films from MG and MC was accompanied by varying propensities of polymer–polymer interaction via C–H, C–O and O–H moieties thereby creating domains of varying strengths.

Using 2% (w/w) alginate solution, the MG film demonstrated a lower propensity of polymer–polymer interaction via C–H and at specific domain containing O-H moiety when compared with film prepared from 4% (w/w) alginate solution. The wavenumbers of FTIR peaks at 2929.2 ± 4.3 and 3076.1 ± 4.0 cm^{-1} ascribing C–H and O–H moieties of MG film prepared from 2% (w/w) alginate solution were higher than those of MG film prepared from 4% (w/w) alginate solution (Fig. 3). Similarly, the wavenumbers of FTIR peaks at 2931.1 ± 2.4 and 3148.7 ± 10.3 cm^{-1} of MC film prepared from 2% (w/w) alginate solution were higher than the corresponding peaks of MC film prepared using 4% (w/w) alginate solution. The MC film exhibited a lower propensity of polymer–polymer interaction via C–H and O–H moieties when a dilute alginate solution was used to prepare the matrix. A reduction in polymer–polymer interaction via C–H and O-H moieties of MG and MC films was responsible for the rise in plasticity of matrices. The difference in plasticity between MG films prepared from 2% and 4% (w/w) alginate solutions was greater than MC films (Table 1). The plasticity of MG films was greatly enhanced when a dilute alginate solution was used as film forming liquid. The increase in mobilization extent of rigid guluronate-rich MG chains in film could be attributed to a reduction in physical and/or chemical interaction propensity of polymers caused by the introduction of a greater fraction of water molecules during the film preparation process. In comparison to MC films, an excessively high exothermic enthalpy value was obtained with MG film prepared using 2% (w/w) instead of 4% (w/w) alginate solutions (Fig. 1). Nonetheless, FTIR analysis indicated that MC films experienced greater changes in chemical association propensity of polymer chains than MG films when solutions of different alginate concentrations were used (Fig. 3). Unlike FTIR, DSC study examined both physical and chemical profiles of matrix. It was envisaged that the preparation of MG film using 2% (w/w) alginate solution was accompanied by a remarkable reduction in physical interaction between polymer

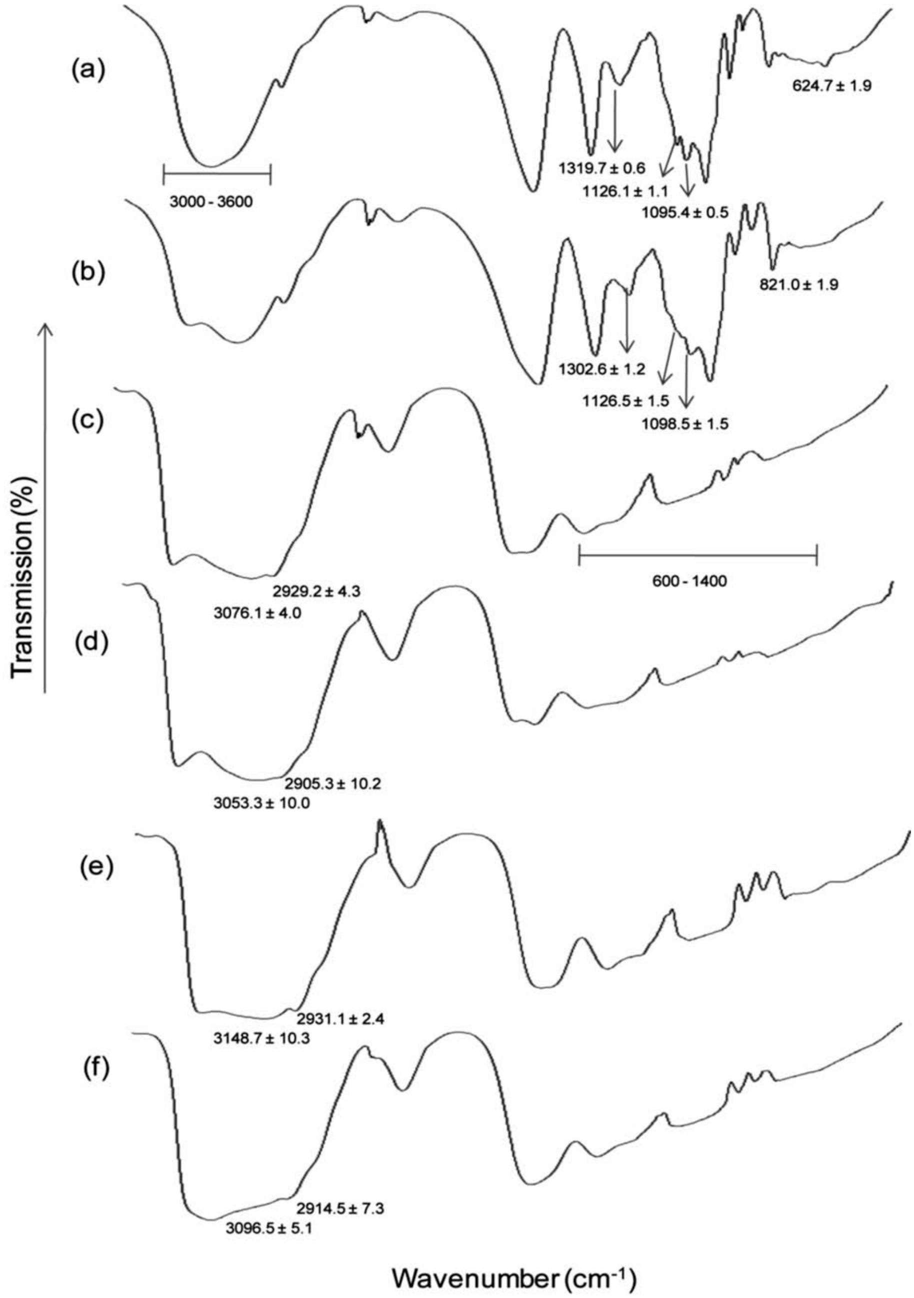

Fig. 3. FTIR spectra of (a) unprocessed MG, (b) unprocessed MC, MG films prepared from (c) 2% and (d) 4% (w/w) alginate solutions, and MC films prepared from (e) 2% and (f) 4% (w/w) alginate solutions at a drying temperature of 60 °C.

chains, in addition to chemical dissociation of matrix. This in turn brought about a marked increase in tan δ value of MG film when a dilute alginate solution was used to prepare the matrix.

DSC analysis indicated that unprocessed MG experienced a higher extent and strength of polymer–polymer interaction than unprocessed MC at high-strength domains of alginate particles. The MG had a higher endothermic enthalpy but a lower exothermic enthalpy, as well as, higher endothermic and exothermic peak temperatures at 159.9 ± 4.4 and 244.1 ± 1.0 °C, respectively, when compared to MC (Fig. 1). Inferring from FTIR study, the propensity of polymer–polymer interaction between MC chains via C–H, C–O and probably O–H moieties was higher than MG and the interaction between MG chains could therefore be largely ascribed to physical association of polymers (Figs. 1 and 3). Using FTIR, it was found that there was no clear trend indicated with respect to wavenumber and transmission intensity against tan δ values of MG and MC films. The difference in plasticity of films formed from MG and MC was likely a main function of physical interaction profiles of alginate chains. The strength of MG films was presumably higher owing to larger magnitude of physical forces linking the polymer chains as suggested by DSC study. This provided MG films with a lower degree of plasticity than MC films.

The elasticity of MG and MC films was higher when a drying temperature of 60 °C was used to prepare these films from 4% (w/w) alginate solution (Table 1). The FTIR peaks of MC film dried at 60 °C exhibited lower wavenumbers at 2914.5 ± 7.3, 3096.5 ± 5.1 and 3443.5 ± 4.4 cm^{-1} than films dried at 40 and 80 °C (Fig. 4). The propensity of polymer–polymer interaction via C–H moiety and O–H at specific domain of matrix was higher when MC film was prepared through drying at 60 °C. This in turn reduced

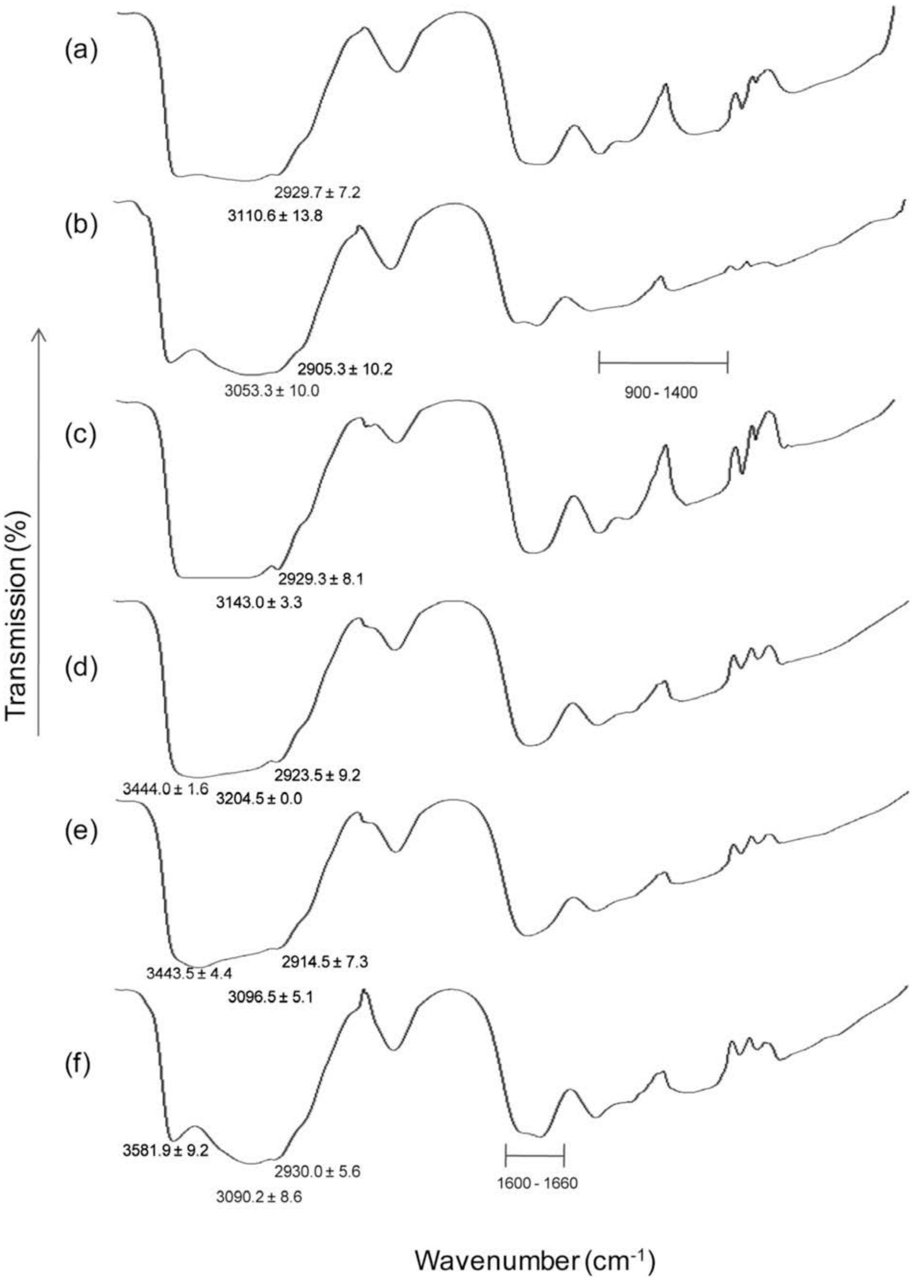

Fig. 4. FTIR spectra of MG films prepared from 4% (w/w) alginate solution using drying temperatures of (a) 40, (b) 60 and (c) 80 °C, and MC films prepared from 4% (w/w) alginate solution using drying temperatures of (d) 40, (e) 60 and (f) 80 °C.

its plasticity. In comparison to MC films dried at 40 and 60 °C, film dried at 80 °C was characterized by FTIR peaks with a greater level of band demarcation at wavenumber between 3000 and 3600 cm^{-1} and 1600 and 1660 cm^{-1} (Fig. 4). The formation of distinct bands at higher and lower wavenumbers of these FTIR peaks denoted the availability of domains with varying propensity of polymer–polymer interaction via O–H or C=O moiety. The formed domains of low polymer interaction propensity were deemed able to further promote the plasticity level of MC film. Similar to MC film, the MG film was relatively elastic and demonstrated a higher interaction propensity between polymer chains via C–H, C–O and O–H at specific domain of matrix when it was obtained by drying at 60 °C. The wavenumbers of FTIR peaks at 2905.3 ± 10.2 and 3053.3 ± 10.0 cm^{-1} ascribing C–H and O–H moieties of MG film dried at 60 °C were lower than films prepared using drying temperatures of 40 and 80 °C (Fig. 4). The transmission intensity of FTIR peaks at wavenumber ranged from 900 to 1400 cm^{-1} ascribing C–H and C–O moieties of MG film dried at 60 °C was higher than the corresponding peaks of films dried at 40 and 80 °C (Fig. 4).

3.4. Surface morphology analysis

Using a drying temperature of 80 °C, the plasticity of MG and MC films was promoted by reduced propensity of polymer–polymer interaction via C–H, C–O, O–H and C=O moieties. The negation of matrix interaction was caused by loss of chemical association between polymer chains during the forming of films. In addition, it could have brought about by the introduction of air bubbles in matrix of which was not indicated by both DSC and FTIR studies (Fig. 5). The air bubbles were formed following the expansion of air in alginate solution caused by the rise in temperature during drying. The degree of air bubble formation was particularly high

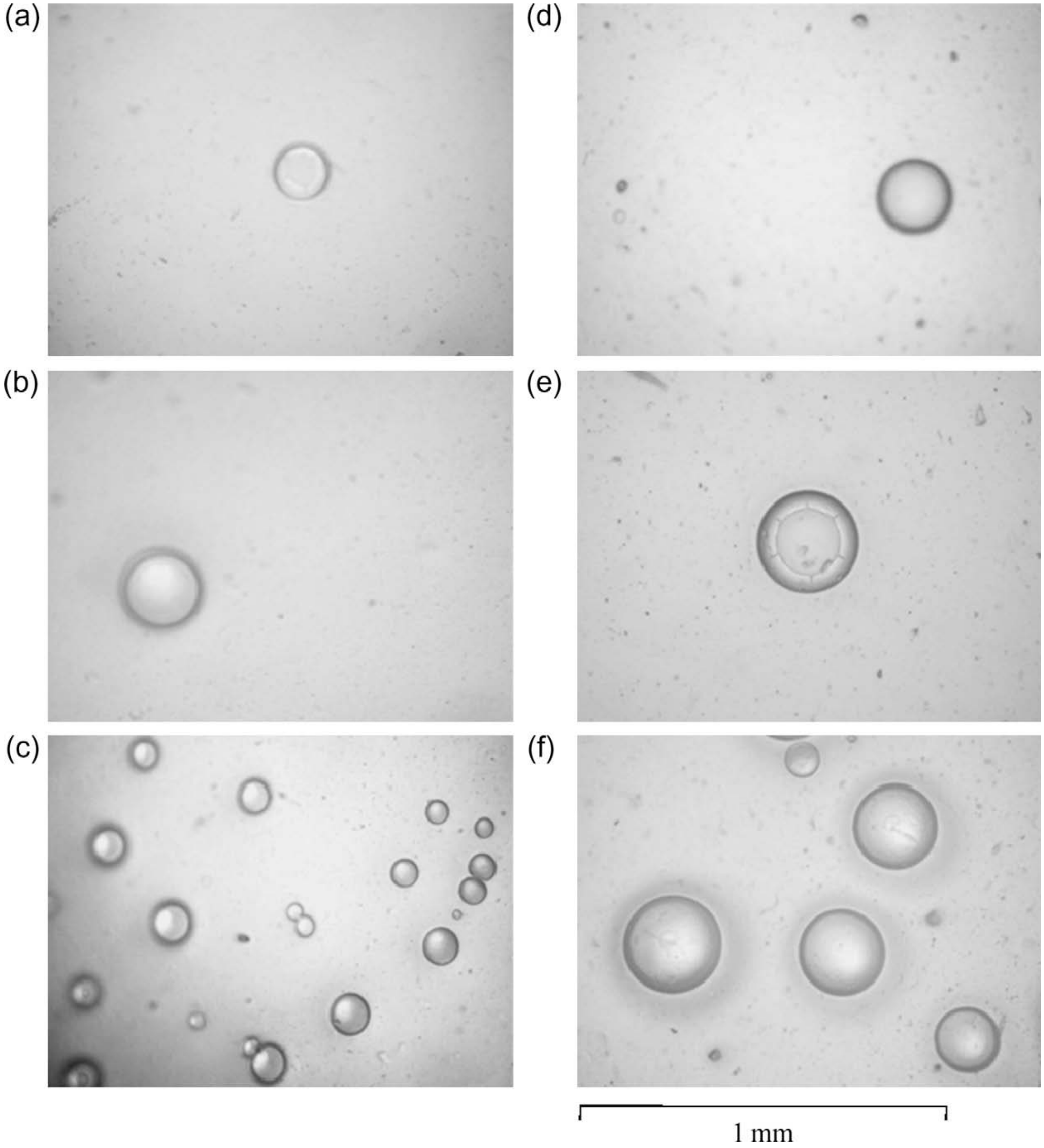

Fig. 5. Surface morphology of MG films prepared from 4% (w/w) alginate solution using drying temperatures of (a) 40, (b) 60 and (c) 80 °C, and MC films prepared from 4% (w/w) alginate solution using drying temperatures of (d) 40, (e) 60 and (f) 80 °C. Magnification factor = 10×; viewing area = 1.2 mm^2.

in MG and MC films prepared using a drying temperature of 80 °C (Fig. 5). These MG and MC films were thus becoming more plastic when compared to films obtained at lower drying temperatures (Table 1).

Hardin and Beckermann (2007) reported that the elastic modulus of a material decreased nonlinearly with its porosity. The stiffness of a material was not merely dependent on porosity, but also affected by other characteristics such as pore size and shape. With reference to MG and MC films prepared from 4% (w/w) alginate solution through drying at 40–80 °C, Pearson correlation analysis indicated that the alginate film plasticity was higher with an increase in the median size of air bubbles embedded in matrix. (Table 2; $r = 0.935$, $p < 0.05$). At corresponding drying temperatures, the median size of air bubbles embedded in MC film was found to be larger than MG film (Table 2). This partly resulted in the MC film being more plastic than MG film obtained at the respective drying temperatures.

3.5. Molecular weight analysis

Preliminary viscosity test of solutions prepared from alginate film indicated that MG had a higher specific viscosity profile than MC in spite of these alginates were reported to have a nominal viscosity value of 300 mPa s (Table 2). In addition, drying of MG and MC in solution at the higher temperatures led to a greater reduction in the specific solution viscosity of the formed film. The rigid MG was found to have a larger molecular weight than the flexible MC (Table 2). Remarkably shorter MG and MC chains were formed

Table 2
Median size of air bubbles, and specific viscosity and molecular weight of alginate in MG and MC films prepared from 4% (w/w) alginate solution.

Alginate grade	Drying temperature (°C)	Air bubble median size (μm)[b, d]	Specific viscosity	Molecular weight (Da)[a, c, d]
MG	40	10.70	18.05 ± 0.41	$5.666 \times 10^6 \pm 2.753 \times 10^5$
	60	9.06	16.27 ± 0.13	$5.387 \times 10^6 \pm 1.095 \times 10^5$
	80	12.50	11.78 ± 0.11	$4.437 \times 10^6 \pm 2.655 \times 10^5$
MC	40	17.88	11.18 ± 0.05	$4.179 \times 10^6 \pm 1.202 \times 10^5$
	60	14.69	10.46 ± 0.01	$4.201 \times 10^6 \pm 2.018 \times 10^5$
	80	171.88	8.10 ± 0.03	$3.434 \times 10^6 \pm 1.634 \times 10^5$

[a] Molecular weight: MG = $5.703 \times 10^6 \pm 1.423 \times 10^5$ Da; MC = $4.260 \times 10^6 \pm 1.742 \times 10^5$ Da.

[b] Air bubble median size vs tan δ ($r = 0.935$, $p < 0.05$).

[c] True alginate molecular weight vs tan δ ($r = -0.785$, $p < 0.05$).

[d] Air bubble median size vs true alginate molecular weight ($r = -0.687$, $p = 0.07$).

in films dried at 80 °C following heat-induced scission. Pearson correlation analysis of the relationship between tan δ and true alginate molecular weight showed that the plasticity of alginate film was significantly induced by reducing the molecular weight of alginate chains in matrix, probably through lowering the interaction propensity of polymers (Table 2; $r = -0.785$, $p < 0.05$). The induction of film plasticity by reduced alginate molecular weight was indicated by higher levels of amorphousness of MC film than MG film, as well as films prepared at higher drying temperature (Fig. 6). It was further supported by previous research and molecular model findings where the plasticity of a polymer was found to increase with reduced polymer molecular weight (Drozdov, 2001; Lazaridou et al., 2003).

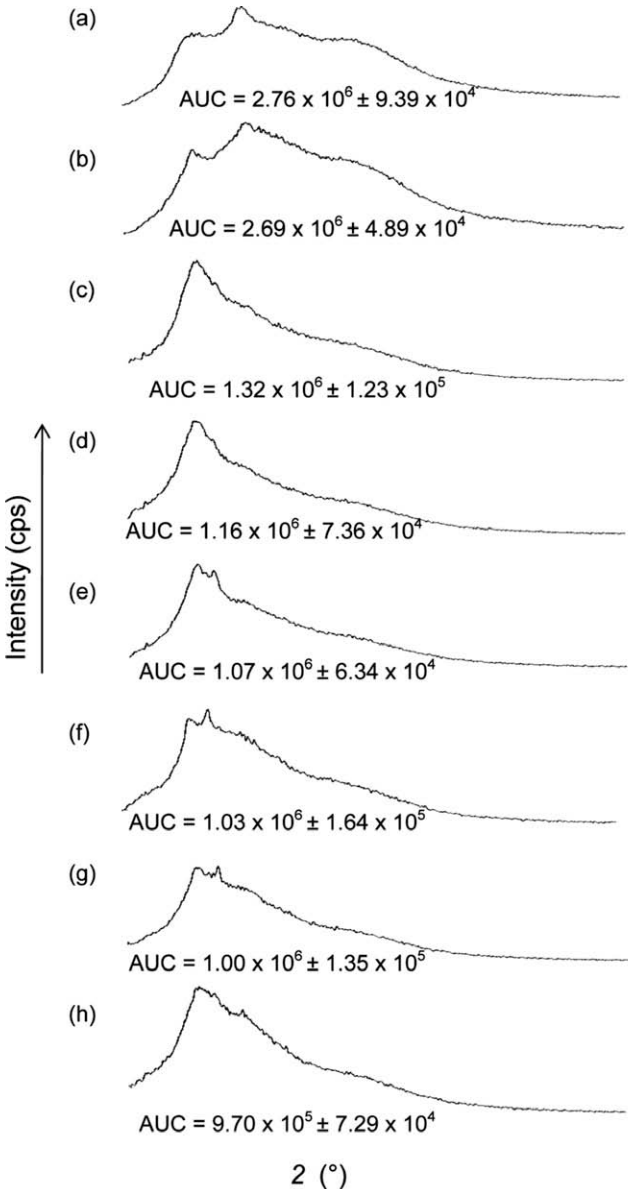

Fig. 6. X-ray diffractograms of (a) unprocessed MG, (b) unprocessed MC, MG films prepared from 4% (w/w) alginate solution using drying temperatures of (c) 40, (d) 60 and (e) 80 °C, and MC films prepared from 4% (w/w) alginate solution using drying temperatures of (f) 40, (g) 60 and (h) 80 °C.

The film plasticity was affected by air bubble encapsulation ($r = 0.935$) to a greater extent than reduced alginate molecular weight in matrix ($r = -0.785$). Using 40 and 60 °C as the drying temperatures, the molecular weights of MG and MC were not substantially negated. At a higher drying temperature of 60 °C, relatively elastic MG and MC films were formed instead due to heat-induced polymer–polymer interaction during drying.

The formation of plastic film was critically affected by the median size of air bubbles embedded in film. The formation of large air bubbles in MC film or films prepared using a high drying temperature was weakly related to the presence of alginate chains of lower molecular weights (Table 2; $r = -0.687$, $p = 0.07$). The formation of larger air bubbles in film was probably due to the ease of arranging air pockets in an environment with flexible mannuronate-rich alginate chains and/or air expansion by high drying temperature.

4. Conclusions

Both MG and MC films were predominantly elastic. The alginate film plasticity can be modulated via changing drying temperature, alginate solution concentration and choice of alginate conformer. The film plasticity was promoted through using lower alginate solution concentration, MC as film former and drying temperatures of 40 or 80 °C. This was attributed to reduced strength or extent of polymer–polymer interaction at high-strength domains of matrix involving C–H, O–H, C–O and/or C=O moiety of alginate. The plasticity of film increased with a decrease in drying temperature from 60 to 40 °C. Nonetheless, the film plasticity was greatly promoted using a drying temperature of 80 °C due to air bubble formation and reduced alginate molecular weight in film. Special precaution in selection of drying temperature shall be made when fabricating alginate film of specific plasticity.

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