This is a repository copy of *The physico-mechanical and structural characteristics of blend film of poly(vinyl alcohol) with biodegradable polymers as affected by disorder-to-order conformational transition*.

White Rose Research Online URL for this paper:
http://eprints.whiterose.ac.uk/98115/

Version: Accepted Version

**Article:**

Shahbazi, M, Rajabzadeh, G, Rafe, A et al. (2 more authors) (2016) The physico-mechanical and structural characteristics of blend film of poly(vinyl alcohol) with biodegradable polymers as affected by disorder-to-order conformational transition. Food Hydrocolloids, 60. pp. 393-404. ISSN 0268-005X

https://doi.org/10.1016/j.foodhyd.2016.03.038

© 2016. This manuscript version is made available under the CC-BY-NC-ND 4.0 license
http://creativecommons.org/licenses/by-nc-nd/4.0/

**Reuse**
Unless indicated otherwise, fulltext items are protected by copyright with all rights reserved. The copyright exception in section 29 of the Copyright, Designs and Patents Act 1988 allows the making of a single copy solely for the purpose of non-commercial research or private study within the limits of fair dealing. The publisher or other rights-holder may allow further reproduction and re-use of this version - refer to the White Rose Research Online record for this item. Where records identify the publisher as the copyright holder, users can verify any specific terms of use on the publisher's website.

**Takedown**
If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.

eprints@whiterose.ac.uk
https://eprints.whiterose.ac.uk/

# The physico-mechanical and structural characteristics of blend film of poly (vinyl alcohol) with biodegradable polymers as affected by disorder-to-order conformational transition

Mahdiyar Shahbazi[a*], Ghadir Rajabzadeh[a], Ali Rafe[a*], Rammile Ettelaie[b], Seyed Javad Ahmadi[c]

[a]Research Institute of Food Science and Technology (RIFST), PO Box 91735-147, Mashhad, Iran.
[b]Procter Department of Food Science, University of Leeds, Leeds LS2 9JT, United Kingdom.
[c]Nuclear Science and Technology Research Institute, End of North Karegar Ave., P.O. Box 1439951113, Tehran, Iran.

## Abstract

The binary blend films of poly (vinyl alcohol) (PVA) were prepared with selected biodegradable polymers (Na-alginate, gelatin, chitosan, κ-carrageenan and carboxymethyl cellulose) at the point of their chain entanglement. The water resistance, water vapor permeability and mechanical assays were considered as a benchmark to select the superior blend film. The highest water resistant and water barrier property belonged to the blend that contains κ-carrageenan. Introducing the biodegradable polymers into PVA led to an increase in tensile strength, among which κ-carrageenan being further effective than the others. Accordingly, the influence of conformational change of κ-carrageenan chain from disorder-to-order mode on PVA matrix was monitored by hydrophobicity assay, FT-IR, FE-SEM and XRD. The conformational change of κ-carrageenan increased PVA hydrophobicity. The emergence of new characteristic bands regarding κ-carrageenan found in the fingerprint region of PVA at above κ-carrageenan coil-overlap concentration. FE-SEM exhibited that PVA surface became uniform along with the disappearance of cracks after κ-carrageenan inclusion. The pronounced κ-carrageenan peak appeared in diffraction pattern of PVA after the conformational transition of κ-carrageenan chain.

**Keywords**: Blend film, Coil-overlap concentration, Tensile strength, Surface hydrophobicity, X-ray diffraction, FE-SEM.

## 1. Introduction

There is a growing trend within the food industry toward the development of the innovative packaging based on the application of biodegradable polymers, rather than the use of the more traditional non-degradable ones (Mikkonen et al., 2007). A main reason for this tendency is reducing the environmental impacts of the non-degradable polymers (Hoagland & Parris, 1996). Poly (vinyl alcohol) (PVA) is a well-known biodegradable thermoplastic polymer with a wide range of applications in the food and pharmaceutical industries (Lei, Jie, Jun, & Ruiyun, 1994). PVA has a semi-crystalline structure with high hydrophilic character due to the ability of forming hydrogen bonding with water molecule (Skeist & Miron, 1990). PVA, such as other biodegradable polymers, is essentially unsuitable for most packaging applications and therefore, needs to be modified to increase its usefulness and value through using many different physical and chemical methods. Blending method is a desirable physical approach for synthesizing a polymeric film when polymers, in terms of the thermodynamic, are compatible. The performance of PVA film through blending can be modified in relation to resistance against water (Guohua et al., 2006), increasing the mechanical strength and improvement of water barrier property (Limpan, Prodpran, Benjakul, & Prasarpran, 2010).

The biodegradable polymers from the plant and animal sources, including Na-alginate, gelatin, chitosan, κ-carrageenan and carboxymethyl cellulose, are broadly used as the film matrix, which can also be introduced into the other polymers to make blend films. Na-alginate, chitosan and gelatin are commonly used for modification of the films based on konjac glucomannan (Xiao, Gao,

& Zhang, 2000), cellulose (Naidu, Sairam, Raju, & Aminabhavi, 2005) and soy protein isolate (Denavi et al., 2009). Carboxymethyl cellulose and κ-carrageenan are also incorporated into the various polymers with the aim of improving the physico-mechanical properties of the resulting blend films (Zhang, Zhang, Lu, & Liang, 2013; Paula et al., 2015).

The functional properties of a polymeric film, such as the physical, thermo-mechanical and structural properties are influenced by the conformation mode of the polymer chains, whether by if they have a disordered structure, then their chain interactions relate closely to the degree of space-occupancy by the chain coils. On the other hands, if they exist as ordered molecules, then they are capable of stable association into compact networks (Chronakis & Kasapis, 1995; Lazaridou, Biliaderis, & Kontogiorgos, 2003). Moreover, the role of the structural conformation of a polymer chain is of almost prominent in the kinetics of water solubility, their water vapor permeability and their tensile strength of films formed by such polymers (Kyotani & Kanetsuna, 1972; Lazaridou, Biliaderis, & Kontogiorgos, 2003).

The coil-overlap concentration (c*) represents the point where the individual polymer chains begin to come into contact with each other and can be considered as a border concentration between the dilute and the semi-dilute regime. During conformation change above c*, overlapping of the chains occurs and separate chains become entangled with one another. Due to the coil overlap and entanglement of the strands in this region, there are fairly strong interactions between polymer strands under the semi-dilute condition (c>c*). It leads to the formation of macrostructure assemblages and subsequently increasing the rigidity of the polymer. In contrast, below the coil overlap (c<c*), the biopolymers have a brittle structure with a weak tensile strength (Doi & Edwards, 1988).

Although there are many articles in the literature concerning the fabrication, development and also more fundamentally revealing the properties of the biodegradable films, there are rather limited published studies that provide the effect of conformational transition of polymer chains on the physico-mechanical and structural properties of film.

The first aim of the current work is to designate the superior binary blend from PVA with several biodegradable polymers at the point of their coil-overlap concentration by using conventional physical and mechanical assays. The second is to test the behavior of the superior PVA blend film under the effect of conformational changes of biopolymer chains from dilute to semi-dilute regimes by some of the most structural experimental. Our initial hypothesis is based on the fact that the disorder-to-order transition of the biodegradable polymer chains can change the physico-mechanical and structural properties of the PVA-based film in a profound manner.

## 2. Materials and methods

### 2.1. Materials

The commercial Na-alginate (50–60 kDa), gelatin (43 kDa with bloom 93) and κ-carrageenan (25-30 kDa) were purchased from Sigma-Aldrich (St. Louis, MO, USA). The carboxymethyl cellulose (90 kDa with the degree of substitution ~0.51) and low molecular weight chitosan (45 kDa and >75% deacetylated) obtained from Merck Co (Merck, Germany). PVA with average molecular weight of 72000 g/mol (~1600 polymerization) and moisture content of 11.2% was kindly provided from Sigma-Aldrich (St. Louis, MO, USA).

### 2.2. Coil-overlap point, intrinsic viscosity and coil-overlap parameter

The point of coil-overlap concentration was considered for incorporation of the selected biodegradable polymers into the PVA matrix. Coil-overlap concentration (c*), intrinsic viscosity (η) and coil overlap parameters c[η] were measured by an Ostwald viscometer with nominal constant 0.011 mm.s$^{-2}$ (Witeg Co., Germany) that's equipped with a thermostatic water bath under precise temperature control. Various amounts of the biodegradable polymers (0.05-0.45 g/dL), excluding chitosan, were dissolved in deionized water to cover the span of concentrations from dilute to the semi-dilute regions. Chitosan although insoluble in water at pH=7, is nonetheless soluble in acetic acid solution. The chitosan was dissolved in 1% (v/v) of acetic aqueous solution and stirred at 60°C for 30 min to obtain a homogeneous solution. Starting with, exactly 2 ml of each solution, the system was manually diluted after generating at least three efflux time readings at each concentration. Then, the relative viscosity ($\eta_{rel}$), reduced viscosity ($\eta_{red}$) and the inherent viscosity ($\eta_{inh}$) were calculated by using Eqs. (1), (2) and (3), respectively as follows:

$$\eta_{rel} = \frac{\eta}{\eta_0} = \frac{t}{t_0} \cdot \frac{\rho}{\rho_0} \tag{1}$$

$$\eta_{red} = \frac{(\eta_{rel} - 1)}{C} \tag{2}$$

$$\eta_{inh} = \frac{\ln(\eta_{rel})}{C} \tag{3}$$

where, $t/t_o$ and $\rho/\rho_o$ are the ratio of efflux time of solution to solvent and the ratio of the density of the solution to the solvent, respectively. ($\eta_{rel}$-1) is specific viscosity ($\eta_{sp}$) and concentration of the biopolymers is represented as C.

The intrinsic viscosity is obtained from the extrapolation of Ln ($\eta_{rel}$)/c and $\eta_{sp}$/c to infinite dilution according to the Huggins's equation (4) and Kraemer's equation (5) as follows (Huggins, 1942; Kraemer, 1938):

$$\frac{\eta_{sp}}{C} = [\eta] + K_1[\eta]^2 C \tag{4}$$

$$\frac{\mathrm{Ln}(\eta_{rel})}{C} = [\eta] + K_2[\eta]^2 C \quad (5)$$

Here, $K_1$ and $K_2$ are the Huggins's and the Kraemer's constants, respectively (Morris, Cutler, Ross-Murphy, Rees, & Price, 1981).

### 2.3. Preparation of blend films

PVA as a film matrix was prepared by the casting method. The PVA powder was dissolved in deionized water (4 g/dL) at 75°C for 2 h. Separately, the specific concentration of each biodegradable polymers, in the accordance with its c*, dissolved in deionized water (in the case of chitosan, 1% (v/v) of acetic acid) and heated at 75°C under constant stirring. The each biodegradable polymer solutions were incorporated into the PVA solution to obtain binary blend solutions and keep stirring for 2 h at 75°C.

After the assessment, 20 ml of each solution was poured into the glass plate and transferred into the oven set at 48°C and a RH of 40%. The films were peeled off the glass plates after 18 h, and conditioned for 36 h at 45% RH in the ambient temperature for further experiments.

### 2.4. The blends comparison

The tensile strength and elongation at break from the mechanical assay, water vapor permeability and water resistance from the physical ones were performed for selecting the superior blend of PVA with biodegradable polymers. Then, the behavior of the eminent blend film was designated for further physical and structural experiments.

#### 2.4.1. Water solubility (WS)

The WS value of the film or total soluble matter was expressed as the weight percentage of the film solubilized after 24 h immersion in distilled water. The films were cut in 5×5 cm and dried at 105°C for 24 h. Then, they were placed in a Meyer flask (containing 250 ml distilled water) and vigorously shaken for 24 h. The film specimens were dried again at 105°C for 24 h. WS values were determined according to Eq. (6):

$$\mathrm{WS} = \frac{\mathrm{S}-\mathrm{S}_0}{\mathrm{S}_0} \qquad (6)$$

where, S is the insoluble dry matter and $S_0$ is the initial dry matter (initial sample weight × dry matter).

### 2.4.2. Water barrier properties

The water vapor transmission rate (WVTR) of the films was determined by using the E398-03 method with slight modifications (ASTM, 2003b). The dried specimens (5.5 cm) were attached to a poly (methyl methacrylate) permeation cell with an inner diameter of 50 mm containing dry silica gel and the permeation cell were placed in a special chamber. Relative humidity was controlled to be 32% using $MgCl_2$ at 40°C on one side of the film. The weight of each cup was regularly recorded every 2 h during on 18 h. The weight gain versus time was plotted and WVTR obtained from its slope by linear regression. The WVP (g/m.s.Pa) was calculated by the following equation:

$$\mathrm{WVP} = \frac{\mathrm{WVTR} \times \mathrm{L}}{\Delta \mathrm{P}} \qquad (7)$$

where, L is the film thickness (mm) and ΔP (Pa) is the partial pressure difference between two sides of the film.

### 2.4.3. Mechanical properties

Tensile strength (TS) and elongation at break (EB) were obtained by using a texture analyzer (TA, TA-XT plus, UK) according to the ASTM D882-02 (ASTM, 2002). The rectangular strips of the films (8×1 cm) were preconditioned at 25°C with a RH of 50% for 24 h. Then, they were subjected to the tensile shearing in the grip of the TA. The Initial distance of grip separation was set at 6 cm and the speed was set at 20 mm/min. TS value was determined from the maximum force recorded prior to breakage divided by the cross section of the rectangular specimens. Elongation at break value was obtained from change in the initial length of 6 cm. All the data were analyzed by Exponent Lite Software (version 6.1.4).

## 2.5. Structural properties

### 2.5.1. Infrared spectroscopy

Infrared spectroscopy (Thermo Nicolet Avatar, 370 FT-IR instrument) was used to study the surface structure of the film. The samples placed in the KBr pellets for scanning spectral region at wave number ranges of 400 and 4000 $cm^{-1}$, and 50 scans were recorded with 1 $cm^{-1}$ resolution of the sample.

### 2.5.2. Surface hydrophobicity

Contact angle (CA) at a point of the three phase contact line between a solid phase (S), a liquid (L) and its vapor (V) is related to the three interfacial energies between these phases are described by Young-Dupre equation:

$$\gamma_{LV} \times cos\theta = \gamma_{SV} - \gamma_{SL} \quad (8)$$

where $\gamma_{LV}$, $\gamma_{SV}$ and $\gamma_{SL}$ are the interfacial tensions of the liquid–vapor, solid–vapor and solid–liquid, respectively (Young, 1805; Dupre, 1869).

The film was transferred into a flat surface and 5 μl drops of the tested liquids (Milli-Q water, glycerol, methlethylene iodide and toluene) and film forming solution with a Hamilton syringe (100 μl, Hamilton, Switzerland) placed on the film surface. The contact angle was measured with a contact anglemeter (OCA 20, Dataphysics, Germany) at natural light after 30s. The images were analyzed by Dino Lite Pro software.

### 2.5.3. Surface tension and critical surface tension determination

The surface tension of the blend film solutions ($\gamma_L$) was obtained through the sessile drop method and Laplace–Young estimation (Song & Springer, 1996). The estimation of the critical surface tension ($\gamma_C$) of the PVA film and PVA blends was determined through extrapolation from the Zisman plot (Zisman, 1964). Zisman plots were obtained by plotting the cosine of the contact angles (cos θ) of a series of the four different liquids (two of which are polar) include Milli-Q water, glycerol, methlethylene iodide and toluene, as well as the film forming solution on the film surface against the surface tension of the same liquids. The extents of $\gamma_C$ of the films are the mean of the extrapolation of cos θ at the intercept for the liquids that forms a straight line. Extrapolation of this line to the point where cos (θ) = 1, yields the $\gamma_C$ value, which is almost equal to the liquid surface tension ($\gamma_L$) at this point.

### 2.5.4. Surface free energy and wettability

The Owens–Wendt method (Owens & Wendt, 1969) was employed for obtaining the surface free energy and wettability based on the linear relationship between the contact angle and the surface tension of the film whose polar ($\gamma_S^P$) and dispersive ($\gamma_S^D$) interfacial energy components according to Eqs. (9) and (10):

$$\gamma_S = \gamma_S^D + \gamma_S^P \tag{9}$$

$$\gamma_L (1 + \cos \theta) = 2 \times [(\gamma_S^D \, \gamma_L^D)^{0.5} + [(\gamma_S^P \, \gamma_L^P)^{0.5}] \tag{10}$$

where, $\gamma_L^D$ and $\gamma_L^P$ are dispersive and polar surface tension of the specific liquid components. There is a two unknowns in this equation i.e. $\gamma_S^D$ and $\gamma_S^P$, so determination of the surface free energy is inadequate to obtain these two components. It is however possible to attain the polar and dispersive component of the surface tension from the intercept and slope of the curve. Rearranging Eq. (10) yields:

$$\frac{(1+\cos\theta)}{2} \times \frac{\gamma_L}{\sqrt{\gamma_L^D}} = \sqrt{\gamma_S^P} \times \sqrt{\frac{\gamma_L^P}{\gamma_L^D}} + \sqrt{\gamma_S^D} \tag{11}$$

It has been proposed that the interfacial tension of liquid–vapor is the sum of contributions from different intermolecular forces, according to existing attractive forces at a specific interface (Dupre, 1869). In the case of a pure liquid, when polar and dispersive interactions are known, and when the contact angle between the pure liquid and a solid is determined, the interaction can then be defined using the adhesion coefficient ($W_A$), as given using Dupre equation (Dupre, 1869):

$$W_A = W_A^D + \gamma_A^P \Rightarrow 2 \times [(\gamma_S^D \, \gamma_L^D)^{0.5} + [(\gamma_S^P \, \gamma_L^P)^{0.5}] = \gamma_L (1 + \cos \theta) \tag{12}$$

and the cohesion coefficient ($W_C$), given by:

$$W_C = 2\gamma_{LV} \tag{13}$$

Then, the extent of spreading coefficient ($W_S$) for a liquid upon a solid is the sum of adhesion and cohesion coefficients obtained by:

$$W_S = W_A - W_C = \gamma_{SV} - \gamma_{LV} - \gamma_{LS} \tag{14}$$

This is the work required to separate the liquid and solid from being in contact at a liquid-solid interface. It is noteworthy that the equilibrium spreading coefficient can only be positive or zero for a fully wetting case, or can be negative or equal to zero for a partially wetting liquid.

### 2.5.5. Morphological behavior by FE-SEM

The surface and cross section morphologies of the blend films were evaluated using a field-emission scanning electron microscope (S-4700, Hitachi, Japan). In the case of surface morphology, the specimens were coated with a thin layer of gold as in preparing any non-conducting material and 20.00 kX magnification objectives used. In the case of cross sectional assay, the film samples were first immersed in liquid nitrogen to freeze and then rapidly broken. Next, the specimens were attached on aluminum stubs by a double-sided tape, and coated with a thin layer of gold at 20 mA for 2 min (JEOL JFC-1600, Auto Fine Coater, Tokyo, Japan) and 3.00 kX magnification objectives were used. All tests were performed with an accelerating voltage of 5 kV.

### 2.5.6. Crystallinity of the blend film

Crystalline property of the films was investigated by XRD (PHILIPS X-PERT PRO, Netherland) with 40 kV energy, 30 mA current and Co Kα irradiation ($\lambda$= 1.54056 Å). The samples were irradiated in the angle range of 2-90° and scanned at a speed of 0.018°/min at room temperature.

## 2.6. Statistical analysis

After conducting the measurements, an analysis of data on CRD was carried out using the analysis of variance (ANOVA), followed by Duncan's test procedure in SPSS software (Version 19, SPSS Inc., Chicago, IL). A value of $p<0.05$ was considered to be statistically significant. The results of all the experiments were analyzed in triplicate and the mean and standard deviation of the data were reported.

## 3. Results and discussion

### 3.1. Rheological characteristics

In order to reveal the appropriate concentration of each polymer aimed at incorporation into the PVA matrix, first we need to determine the chain entanglement of these polymers. The coil-overlap concentration was determined by plotting the zero shear specific viscosity $(\eta_{sp})_0$ as a function of biodegradable polymer concentration (Fig.1a). There is a master curve, which encompasses all the polymers used in this work, although the data fit is inferior for the lower concentrations. It can be found from Fig. 1a that there are two regions in the curve, which can be characterized by the two different slopes in each curve. The first slope behavior has a linear trend, where the individual chains are extant as the separated coils, related to the line with a slope of ~ 1.4. Another slope curve has been introduced as the overall hydrodynamic volume of the individual separate chains more than the volume of the solution. The slope of the curves changed sharply at a particular concentration, where a much more rapid increase found in the specific viscosity. This point was considered as the polymer coil-overlap concentration, and for Na-alginate, gelatin, κ-carrageenan (KC), chitosan and carboxymethyl cellulose (CMC) determined around 0.125, 0.175, 0.275, 0.325 and 0.375 g/dL, respectively.

It is indicated that the change of macromolecules conformation upon the coil overlap cause to the formation of the entanglements (Morris et al., 1981). Therefore, an aggregation in the chain causes by an entanglement involves reptation motion leads to a change in the chain conformational interaction (Doi & Edwards, 1988). At $c<c^*$, individual coils are separated and have little mutual interference, which flow behavior is Newtonian. Above $c^*$ ($c>c^*$), the chains become highly entangled that can move by reptating through the network and the macrostructure entanglement of those polymer formed due to the chain-chain interaction. When polymer concentration is the equal or higher than its coil-overlap concentration, the chains are forced to interpenetrate and form an entangled system, which expected rigidity and tightly increased. This is more prominent in the some features of a polymeric film such as mechanical properties, where rigidity can increase the tensile strength of the film.

The intrinsic viscosity is a relationship between volume associated with a given mass of the polymer and coil overlap. According to the Huggins and Kraemer's equations, the intrinsic viscosity is obtained from the mean value of the extrapolation of $(\eta_{rel}-1)/C$ and/or $\mathrm{Ln}\,(\eta_{rel})/C$ to zero concentration. As can be seen, the higher value of the intrinsic viscosity belongs to Na-alginate with a value of 30.59 dL/g, and the lower one pertains to the gelatin about 2.57 dL/g (Table 1). The intrinsic viscosity values for KC and gelatin were to some extent higher than that of other findings by some authors (Vreeman, Snoeren, & Payens, 1980; Brown, Foster, Norton, & Underdown, 1995).

The zero shear specific viscosity $(\eta_{sp})_0$ versus the concentration of a polymer varies depends on the molecular weight and its conformation due to the corresponding changes in the coil overlap (Doi & Edwards, 1988). The logarithmic curve of the coil-overlap parameter, as shown by $c[\eta]$, against $(\eta_{sp})_0$ exhibits two distinct districts (Fig. 1b). It indicates an extent of the overall volume occupied by all coils within a biopolymer (Kyotani & Kanetsuna, 1972). It can be found from Fig. 1b, the point of critical coil-overlap parameter $(c^*[\eta])$ of Na-alginate, KC and chitosan is obtained around ~4 (see Table 1), which is similar to the onset of coil-overlap parameter for the random coil polysaccharides that reported in previous studied (Morris et al., 1981). Moreover, the attained zero specific viscosity for the chitosan and KC at $c^*[\eta]$ was somewhat lower than the report of Morris and co-workers (1981). These authors reported that $(\eta_{sp})_0$ of the random-coil polysaccharides have a value of ~10 at the intersection point. In the some cases, the rigid biopolymers can be more efficiently packed (Smidsrød & Haug, 1971). Hence, the lower shear specific viscosity value regarding chitosan and KC at point of c*[η] may be attributable to the more rigid conformation of the biopolymers structure.

## 3.2. Physical properties of the blend films

### 3.2.1. Water solubility (WS)

The resistance against water or water solubility can be determined by measuring the total soluble fraction of the film (Rhim, 2012). As PVA is highly soluble in water, any improvement in the withstanding against water is extremely essential. As it can be seen in Table 2, the water solubility of PVA decreased as a function of the incorporation treatment with a considerable decrease regarding PVA/KC blend. Overall, the WS value of the PVA from 48.9% decreased to 44.0% after introducing of gelatin, and when Na-alginate and CMC are incorporated further decrease observed to around 40.5%. Comparison between the neat PVA and PVA/chitosan films exhibited that WS much more reduced to 29.4%. The development of hydrogen bonds by chitosan introducing may be inaccessible the hydrophilic groups of PVA from water. Although, some authors believe that increasing the number of the amino groups on the blend film leads to a decrease in WS (Wu, Zhong, Li, Shoemaker, & Xia, 2013). There is a greater decrease in WS of the PVA/KC compared the other blends, which allows the WS value decreased to 25.1%. The entangled KC chains can be formed more hydrogen interactions with PVA strands, in which the polar groups of PVA less exposure to water molecules (Shahbazi, Rajabzadeh, Ettelaie, & Rafe, 2016).

### 3.2.2. Water barrier properties

Water vapor permeability (WVP) test is a common method to evaluate the potential of vapor penetration into the packaging, which is considered as an important parameter to design the packaging film (Binsi, Ravishankar, & Srinivasa Gopal, 2013). Table 2 shows the changes in WVP of the PVA film with respect to incorporation of the various biodegradable polymers. In our permeability study, a considerable increase in the barrier property was observed in the films that containing Na-alginate, KC and chitosan. Conversely, the incorporation of gelatin had a detrimental effect on the barrier property of PVA film, in contrast to that of the intact film. It is may be due to increasing the free-volume of the blend matrix results from the bulkier anionic side groups of the gelatin (Tong, Xiao, & Lim, 2008). It is worth noting that WVP value regarding PVA/CMC blend was almost similar to the neat PVA film. An improvement in the barrier property noticed after chitosan incorporation, where WVP from an initial value of $7.42\times10^{-7}$ g/m.s.Pa reduced to $1.03\times10^{-7}$ g/m.s.Pa. In the case of PVA/Na-alginate blend, the WVP value fell dramatically down to $0.11\times10^{-7}$ g/m.s.Pa. The Na-alginate chains at the entanglement point can have more strong interaction with PVA strands. This provides a denser structure in the film matrix, where $H_2O$ molecules hardly pass through the film matrix. Paula et al., (2015) reported that incorporation of Na-alginate into KC matrix leads to a notable decrease in WVP by 90%. The WVP results also represent a prominent resistance to the vapor transition in the PVA/KC film. The development of relatively tough structure is a result of linkage between hydrophilic groups of KC and PVA, which block the paths of water transport due to a reduction in the free volume of the film matrix (Xu, Kim, Hanna, & Nag, 2005).

### 3.2.3. Mechanical properties

The intermolecular and intramolecular interactions between biopolymer chains are the main factors affecting the film mechanical properties. These interactions relate to the arrangement and orientation of the chains in the biopolymer matrix, which often can be improved by the synthesis of blend films (Cuq, 2002).

The influence of the various biodegradable polymers on the tensile strength (TS) of PVA film is summarized in Table 2. As can be seen, the TS value of the PVA film was almost unchanged after incorporation of CMC (about 33 MPa). On the other hands, the extent of TS decreased when gelatin incorporated into the PVA matrix. The decline in the TS of a blend system can be ascribed to increased stress in the continuous phase (PVA) owing to the lack of the stress transfer across the blend matrix interface. Table 2 showed that the TS value of PVA film increased after introducing the Na-alginate, KC and chitosan, among them the lowest value belonged to PVA/chitosan film. Increase in the TS value is more pronounced, particularly concerning the PVA/KC film. The TS value of the neat PVA film was obtained 33.4 MPa, but increased to 71.2 MPa regarding PVA/KC film. The more improvement in stiffness of the blend film may be attributed to the formation of hydrogen bonds between biopolymer molecules. This makes the structure of the blend film to be much denser than the neat one (Cheftel, Cuq, & Lorient, 1985).

The biopolymers dependency of elongation at break (EB) for the blend film is also presented in Table 2. There is no significant difference in the EB after incorporation of CMC ($p<0.05$). The lowest EB belonged to the films containing Na-alginate and KC. It is observed that the EB value of the neat film from 28.4% decreased to 21.2 and 17.4% after blending with Na-alginate and KC, respectively. To explain this phenomenon the authors believe that the polar groups of biopolymers can form hydrogen bonds, which results in some degree of resistance against stretching (Xiao, Lim, & Tong, 2012).

### 3.3. Structural evaluation of PVA/KC blend

The obtained results already verified that the PVA/KC was as a superior blend in term of physico-mechanical properties. The following six sections are dedicated to describe in-depth some of the most structural properties of PVA film after incorporation with KC at the lower and upper the coil-overlap point of KC chains, in particular FT-IR spectroscopy, contact angle and wettability assays, surface free energy, microstructural evaluation by FE-SEM and X-ray diffraction.

### 3.3.1. FT-IR spectroscopy

FT-IR spectra of neat PVA, pure KC and their blends are given in Fig. 2. In the IR spectrum of KC, several noticeable characteristic peaks, ranging from 4000 to 400 cm$^{-1}$, are observed. The characteristic peak of KC shows a maximum at 1225 cm$^{-1}$. This can be attributed to the S–O asymmetric vibrational mode. Similarly, a band detected in 1040–1070 cm$^{-1}$ region is due to C–O and C–OH vibrations (Matsuhiro & Rivas, 1993). Furthermore, a well-defined band at 845–850 cm$^{-1}$ corresponds to α (1–3)-D-galactose C–O–S vibration.

The incorporation of KC up to 0.2 g/dL into PVA did not initiate any shifts of the peaks for the blends or caused the appearance of any new bands. In principle, then, this shows that there are no significant interactions between PVA and KC chains, at this level of KC. The intensity of the typical peak of PVA films containing 0.3 and 0.4 g/dL KC did decay in the first region (3700-2850 cm$^{-1}$). This is also somewhat true in the second area (1800-1500 cm$^{-1}$). For example, the intensity of C=O band at around 1740 cm$^{-1}$ observed to decrease after KC incorporation due to consumption of further free carbonyl groups. In the fingerprint region, the IR spectrum of PVA drastically changed with KC introducing at the level of the coil-overlap concentration. The appearance of several new characteristic bands regarding KC on the PVA spectrum observed at 1225 cm$^{-1}$ (assigns to S–O vibrational mode), 1070 cm$^{-1}$ and 850 cm$^{-1}$ (regards to C–O–S vibrational mode), which is a result of KC incorporating at the levels of 0.3 and 0.4 g/dL. This proves the presence of the higher degree of substitution of α (1–3)-D-galactose bond of KC in the blend structure.

### 3.3.2. Contact angle

The wetting property is determinative of the ability of a liquid to maintain contact with a surface of a solid, which corresponds to the intermolecular interactions between biopolymers in a film. Commonly, contact angle (CA) is used to evaluate the change in the surface hydrophobicity of blend film.

Table 3 shows the CA values of the four solvents (water, glycerol, methlethylene iodide and toluene), as well as the film forming solution drops on the PVA film surface, which the highest value belongs to water (θ=56.8°). Water has a much stronger interaction with PVA film than with the others, confirming that the PVA-based film has mostly a hydrophilic nature. The opposite is observed with toluene, which is a very apolar solvent, thus has the lowest value of CA (θ=18.2°). The influence of various KC contents on the water contact angle of the PVA film can be seen in Table 4. The CA value of the PVA films consist 0.1 and 0.2 g/dL of KC is similar to the neat PVA film (θ≃56-58°). An increase in the water contact angle of the PVA film by a value of 11.3° observed, when KC at the point of its entanglement incorporated into the film matrix. Among the PVA films that have undergone the incorporation treatment, the film contains 0.4 g/dL KC was accompanied by the highest CA value (θ=76.5°). This improvement essentially results from the formation of hydrogen bonds in the blend, leading to further rigidity of the film matrix.

The effect of KC on the CA of the biodegradable film has rarely been addressed by researchers. In one study conducted by Rhim (2012), the blend film based on agar/KC with various ratios prepared and the results showed that the ratio of 75/25 agar to KC had a greater value of CA. This author also found that increase in KC amount did not affect the surface hydrophobicity of the blend.

### 3.3.3. Surface tension and critical surface tension

This experiment was intended to evaluate the compatibility of PVA/KC film forming solutions when KC in a range close to c* incorporated into the PVA matrix. Most importantly, to confirm the sufficient bonding, spreading and wetting, the film forming blend solution should have a liquid surface tension ($\gamma_L$) higher than the critical surface tension ($\gamma_C$) of the PVA-based film forming solution.

Fig. 3 shows a Zisman plot with cos θ plotted against surface tension for the tested liquids, as well as the film forming solutions of PVA and PVA/KC blends. The high hydrophilicity of water and glycerol can lead to a strong interaction between these two liquids with PVA polymer. After incorporating KC at the levels of 0.3 and 0.4 g/dL, the value of $\gamma_C$ decreased notably (that indicated by $\gamma_{C2}$). The formation of entangled chains in KC molecule demonstrates this difference. The interaction of KC with PVA consumes more hydroxyl groups of PVA, leading to a decrease of the surface tension. By comparing the critical surface tension between the blends containing KC at the levels of 0.3 and 0.4 g/dL, it is found that PVA containing 0.4 g/dL KC had a lower $\gamma_C$ value than 0.3 g/dL sample. In general, the result of Fig. 3 revealed that the all film forming solutions had a $\gamma_C$ value in the range of 26.1–29.19 mN/m, which is very comparable to those for the common polymers (Han, Zhang, & Buffo, 2005). According to the Zisman plot, liquids with $\gamma_L \leq \gamma_C$ will fully spread on the film surface, thus wetting the surface. Therefore, it can be inferred that the liquids with $\gamma_L \leq 26.1$ mN/m can wet the film effectively. Since the incorporation of KC at the point of c* decreased the film surface tension, the wettability of the PVA-based film decreases. It must be borne in the mind that $\gamma_C$ is the critical surface energy of wetting and not equal to the actual surface energy of the films, which actually is higher than $\gamma_C$, particularly when considering the polar character of PVA.

Optimization of the wettability coefficient ($W_S$) requires optimization of adhesion work ($W_A$) and cohesion work ($W_C$). Cohesion force causes the shrinkage and adhesion ones drive the spreading of the liquid. The wettability results are presented in Table 3. The higher $W_C$ found in the case of the film forming solution droplet of the neat PVA and the lower one relates to PVA containing 0.4 g/dL KC. Higher cohesive value of a film forming solution results in the contraction of the droplet and hence preventing its spreading. So, it is expected that the PVA film forming solution consists 0.4 g/dL KC, with the lowest $W_C$, more wet the film surface than the other film forming solutions. But since this sample clearly had a lowest adhesion work, so $W_A$ value acted as a dominant factor for preventing from spreading. The $W_S$ value of neat PVA film forming solution decreased notably with the inclusion of KC at the levels of 0.3 and 0.4 g/dL from -2.5 down to -2.8 and -3.2, respectively.

### 3.3.4. Surface free energy

The values of the surface free energy and dispersive and polar components of the neat and blend PVA films are shown in Fig. 4 and data summarized in Table 4. For the pure PVA film, the surface free energy and the polar component were found to be higher in comparison to the blend films. This demonstrates the ability of PVA to take part in polar interactions with polar liquids. The existence of more hydrophilic functional groups in the PVA film led to an increase of the interfacial free energy with water, raising the polar phase. The KC at a level of 0.1 and 0.2 g/dL had no prominent effect on the surface free energy relative to that of the neat PVA. In contrast, the films containing 0.3 and 0.4 g/dL KC showed a lower interfacial free energy and reduced polar component compared to the neat PVA. These results confirm that the incorporation of KC at the entangled point, contribute to the increase in the film hydrophobicity. Conversely, KC chains which are presented as the disordered form, below its entanglement concentration, did not noticeably change the interfacial energy of the pure PVA film.

### 3.3.5. Microstructural evaluation

FE-SEM photographs of the neat PVA film and PVA/KC blends are shown in Fig. 5. The neat PVA film has a non-uniform and rough structure with many apparent micro-cracks and gaps on its surface (Fig. 5a). This can be further supported with a result of the lack of a suitable plasticizer in the neat PVA film. The plasticizers with decrease the intramolecular force between chains leads to the further mobility of the chain strands. This leads to an increase in the flexibility and elasticity of the film matrix.

The micrographs clearly displays that the surface morphology of PVA film become uniform with an even morphology after blending with KC (Figs. 5c-d). Although, the PVA film containing 0.1 g/dL KC retains uneven with some cracks on its surface (Fig.5b). The micrograph in Fig.5c shows the blend containing 0.2 g/dL of KC. This blend has a fairly smooth and flat morphology without any fracture in the film matrix. It is clear that the cracks have all but disappeared and the surface has become more uniform with the addition of 0.3 g/dL KC to the PVA matrix (Fig. 5d). The most prominent effect of KC introducing at the level of 0.4 g/dL into the PVA was the loss of film integrity and turns it into a rough structure (Fig. 5e). This can be explained by the development of some aggregates of KC chains with further addition of KC, up to 0.4 g/dL when incorporated into the PVA matrix.

Fig. 6 illustrates the cross-sectional micrographs of the PVA film and its blends with KC. Uneven fracture cross sections are apparent in the neat PVA film and PVA containing 0.1 g/dL KC (Figs. 6a and 6b). On the other hand, the cross-sectional microstructure of PVA containing 0.2 g/dL KC showed that some degree of roughness, but have a fairly uniform homogeneous texture (Fig 6c). In the cross section micrograph of PVA containing 0.3 g/dL KC, the blend showed a more homogeneous texture without any prominent phase separation, suggesting a good level of miscibility between PVA and KC (Fig. 6d). When KC was incorporated at the level of 0.4 g/dL, a rough structure in the blend film observed (Fig. 6e).

### 3.3.6. XRD assay

The XRD pattern of the PVA film and its blends are shown in Fig. 7. Pure PVA showed a sharp characteristic diffraction peak at an angle of 2θ=19.6°, which is also observed for the other blends. As can be seen in Fig. 7, the diffraction pattern of KC has a pronounced peak at 2θ=6.2°, along with another broad hump in the range of 2θ=9.4-27.7º, which indicated an amorphous or somewhat semi-crystalline form of KC structure. The crystallinity of KC mostly depends on the oriented packing of the chain helices in this biopolymer (Anderson, Campbell, Harding, Rees, & Samuel, 1969). The PVA pronounced peak after blending with 0.1 and 0.2 g/dL KC, was found not to change or emergence new peak. This is attributed to the facts that at these concentrations, KC chains have a coil-like conformation and has not as yet overlapped with each other. As already mentioned, in the dilute region, KC chains exist as a spatially separate individual coil and the molecular conformation has an amorphous state. The phase transition from amorphous to semi-crystalline state occurs at a concentration above the level of critical coil-overlap point. So, KC at the levels of 0.1 and 0.2 g/dL still retains its amorphous nature and, therefore, has no effect on the peaks arising from PVA in the spectra.

The deeper change was happened in the XRD pattern of PVA, when KC incorporated at the point of c*. With the addition of KC at the levels of 0.3 and 0.4 g/dL, a significant peak appeared at $2\theta=6.2°$ on PVA peak, corresponding to the characteristic peak of KC. The interaction and binding between biopolymer strands, i.e. PVA and KC, gives rise to a certain degree of crystallinity in the blend structure, as characterized by the distinctive peak at two theta of 6.2°.

In the case of d-spacing of PVA layers ($d_{001}$), the KC at the lower point of its coil-overlap could not be changed d-spacing of the PVA layers, but at the levels of 0.3 and 0.4 g/dL, the extent of $d_{001}$ value was decreased notably. The peak that is located at $2\theta=19.6°$ regarding the neat PVA film and those containing 0.1 and 0.2 g/dL KC, have comparable $d_{001}$ spacing value (5.1Å). This result indicates that the crystalline structure of the PVA blend films was not significantly affected by KC at the disorder state. In contrast the $d_{001}$ value of the sample contains 0.3 g/dL KC from an initial value of 5.1Å fell down to 4.6Å. A further decrease in $d_{001}$ observed in the sample contains 0.4 g/dL KC, which in this, d-spacing considerably decreased to 4.3 Å at the angle of $2\theta=19.6°$. This is an indication that the intermolecular interaction between PVA and KC happens in the crystalline region of PVA.

## 4. Conclusion

Binary blend films of poly (vinyl alcohol) were developed using selected biodegradable polymers based on Na-alginate, gelatin, chitosan, κ-carrageenan and carboxymethyl cellulose. Preliminary results showed that the binary blend films exhibited relatively good water barrier property and resistance against water, as well as somewhat good mechanical properties, except poly (vinyl alcohol)/gelatin film. Among the biodegradable polymers that were introduced into poly (vinyl alcohol) matrix, κ-carrageenan was highly suitable to form a binary blend film due to low water solubility and water vapor permeability values, as well as high tensile strength parameter. Therefore, the effects of disorder-to-order transition chains of κ-carrageenan on poly (vinyl alcohol) matrix were performed by structural studies. Hydrophobicity of poly (vinyl alcohol) film increased with κ-carrageenan incorporating, especially at the point of its chain coil-overlap or higher. It can be concluded that the characteristic peak regarding κ-carrageenan was appeared in the fingerprint region of poly (vinyl alcohol) at the above point of chain entanglement of κ-carrageenan. The coil-overlap effect of κ-carrageenan was reflected in the surface morphology of poly (vinyl alcohol), where micro-cracks were eliminated. At the point of κ-carrageenan entangled chains or higher, the new pronounced peak appeared on poly (vinyl alcohol) pattern as shown by X-ray diffraction.

## References

Anderson, N., Campbell, J., Harding, M., Rees, D., & Samuel, J. (1969). X-ray diffraction studies of polysaccharide sulphates: double helix models for κ-and ι-carrageenans. Journal of molecular biology, 45(1), 85-97.

ASTM. (2002). Standard test method for tensile properties of thin plastic sheeting (D882-02). In Annual book of ASTM standards. Philadelphia: American Society for Testing and Materials.

ASTM. (2003b). Standard test method for water vapor transmission rate of sheet materials using dynamic relative humidity measurement (E398-03). In Annual book of ASTM standards. Philadelphia: American Society for Testing and Materials.

Binsi, P., Ravishankar, C., & Srinivasa Gopal, T. (2013). Development and characterization of an edible composite film based on chitosan and virgin coconut oil with improved moisture sorption properties. Journal of Food Science, 78(4), E526-E534.

Brown, C., Foster, T., Norton, I., & Underdown, J. (1995). Influence of shear on the microstructure of mixed biopolymer systems. Biopolymer mixtures, 65-83.

Busscher, H. J., Bialkowska-Hobrzanska, H., Reid, G., van der Kuijl-Booij, M., & van der Mei, H. C. (1994). Physicochemical characteristics of two pairs of coagulase-negative staphylococcal isolates with different plasmid profiles. Colloids and Surfaces B: Biointerfaces, 2(1), 73-82.

Cheftel, J., Cuq, J., & Lorient, D. (1985). Amino acids, peptides, and proteins. Food Chemistry, 2, 245-369.

Chronakis, I. S., & Kasapis, S. (1995). Food applications of biopolymer—theory and practice. Developments in Food Science, 37, 75-109.

Cuq, B. (2002). Formation and properties of fish myofibrillar protein films and coatings. Protein-based films and coatings, 213-232.

Denavi, G. A., Pérez-Mateos, M., Añón, M. C., Montero, P., Mauri, A. N., & Gómez-Guillén, M. C. (2009). Structural and functional properties of soy protein isolate and cod gelatin blend films. Food hydrocolloids, 23(8), 2094-2101.

Doi, M., & Edwards, S. F. (1988). The theory of polymer dynamics (Vol. 73): oxford university press.

Dupre, A. (1869). The’ore Mechanique de la Chaleur. Gauthier-Villars, Paris, 369.

Guohua, Z., Ya, L., Cuilan, F., Min, Z., Caiqiong, Z., & Zongdao, C. (2006). Water resistance, mechanical properties and biodegradability of methylated-cornstarch/poly (vinyl alcohol) blend film. Polymer Degradation and Stability, 91(4), 703-711.

Han, J., Zhang, Y., & Buffo, R. (2005). Surface chemistry of food, packaging and biopolymer materials. Innovations in Food Packaging., San Diego, California, Elsevier Ltd, 45-59.

Hoagland, P. D., & Parris, N. (1996). Chitosan/pectin laminated films. Journal of agricultural and food chemistry, 44(7), 1915-1919.

Huggins, M. L. (1942). The viscosity of dilute solutions of long-chain molecules. IV. Dependence on concentration. Journal of the American Chemical Society, 64(11), 2716-2718.

Jańczuk, B., & Białlopiotrowicz, T. (1989). Surface free-energy components of liquids and low energy solids and contact angles. Journal of colloid and interface science, 127(1), 189-204.

Kraemer, E. O. (1938). Molecular weights of celluloses and cellulose derivates. Industrial & Engineering Chemistry, 30(10), 1200-1203.

Kyotani, H., & Kanetsuna, H. (1972). Effect of molecular weight on conformation of poly (β-benzyl L-aspartate) in films. Journal of Polymer Science: Polymer Physics Edition, 10(10), 1931-1939.

Lazaridou, A., Biliaderis, C. G., & Kontogiorgos, V. (2003). Molecular weight effects on solution rheology of pullulan and mechanical properties of its films. Carbohydrate Polymers, 52(2), 151-166.

Lei, R., Jie, X., Jun, X., & Ruiyun, Z. (1994). Structure and properties of polyvinyl alcohol amidoxime chelate fiber. Journal of Applied Polymer Science, 53(3), 325-329.

Limpan, N., Prodpran, T., Benjakul, S., & Prasarpran, S. (2010). Properties of biodegradable blend films based on fish myofibrillar protein and polyvinyl alcohol as influenced by blend composition and pH level. Journal of Food Engineering, 100(1), 85-92.

Matsuhiro, B., & Rivas, P. (1993). Second-derivative Fourier transform infrared spectra of seaweed galactans. Journal of applied phycology, 5(1), 45-51.

Mikkonen, K. S., Rita, H., Helén, H., Talja, R. A., Hyvönen, L., & Tenkanen, M. (2007). Effect of polysaccharide structure on mechanical and thermal properties of galactomannan-based films. Biomacromolecules, 8(10), 3198-3205.

Morris, E. R., Cutler, A., Ross-Murphy, S., Rees, D., & Price, J. (1981). Concentration and shear rate dependence of viscosity in random coil polysaccharide solutions. Carbohydrate Polymers, 1(1), 5-21.

Naidu, B. V. K., Sairam, M., Raju, K. V., & Aminabhavi, T. M. (2005). Thermal, viscoelastic, solution and membrane properties of sodium alginate/hydroxyethylcellulose blends. Carbohydrate Polymers, 61(1), 52-60.

Owens, D. K., & Wendt, R. (1969). Estimation of the surface free energy of polymers. Journal of Applied Polymer Science, 13(8), 1741-1747.

Paula, G. A., Benevides, N. M., Cunha, A. P., de Oliveira, A. V., Pinto, A. M., Morais, J. P. S., & Azeredo, H. M. (2015). Development and characterization of edible films from mixtures of κ-carrageenan, ι-carrageenan, and alginate. Food hydrocolloids, 47, 140-145.

Rhim, J. W. (2012). Physical-Mechanical Properties of Agar/κ-Carrageenan Blend Film and Derived Clay Nanocomposite Film. Journal of Food Science, 77(12), N66-N73.

Shahbazi, M., Rajabzadeh, G., Ettelaie, R., & Rafe, A. (2016). Kinetic study of κ-carrageenan degradation and its impact on mechanical and structural properties of chitosan/κ-carrageenan film. Carbohydrate Polymers, 142, 167-176.

Skeist, I., & Miron, J. (1990). Introduction to adhesives Handbook of Adhesives (pp. 3-20): Springer.

Smidsrød, O., & Haug, A. (1971). Estimation of the relative stiffness of the molecular chain in polyelectrolytes from measurements of viscosity at different ionic strengths. Biopolymers, 10(7), 1213-1227.

Song, B., & Springer, J. (1996). Determination of interfacial tension from the profile of a pendant drop using computer-aided image processing: 1. Theoretical. Journal of colloid and interface science, 184(1), 64-76.

Tong, Q., Xiao, Q., & Lim, L.-T. (2008). Preparation and properties of pullulan–alginate–carboxymethylcellulose blend films. Food Research International, 41(10), 1007-1014.

Vreeman, H., Snoeren, T., & Payens, T. (1980). Physicochemical investigation of k-carrageenan in the random state. Biopolymers, 19(7), 1357-1374.

Wu, J., Zhong, F., Li, Y., Shoemaker, C., & Xia, W. (2013). Preparation and characterization of pullulan–chitosan and pullulan–carboxymethyl chitosan blended films. Food hydrocolloids, 30(1), 82-91.

Xiao, C., Gao, S., & Zhang, L. (2000). Blend films from konjac glucomannan and sodium alginate solutions and their preservative effect. Journal of Applied Polymer Science, 77(3), 617-626.

Xiao, Q., Lim, L.-T., & Tong, Q. (2012). Properties of pullulan-based blend films as affected by alginate content and relative humidity. Carbohydrate Polymers, 87(1), 227-234.

Xu, Y., Kim, K. M., Hanna, M. A., & Nag, D. (2005). Chitosan–starch composite film: preparation and characterization. Industrial crops and products, 21(2), 185-192.

Young, T. (1805). An essay on the cohesion of fluids. Philosophical Transactions of the Royal Society of London, 65-87.

Zhang, L., Zhang, G., Lu, J., & Liang, H. (2013). Preparation and characterization of carboxymethyl cellulose/polyvinyl alcohol blend film as a potential coating material. Polymer-Plastics Technology and Engineering, 52(2), 163-167.

Zisman, W. A. (1964). Relation of the equilibrium contact angle to liquid and solid constitution.