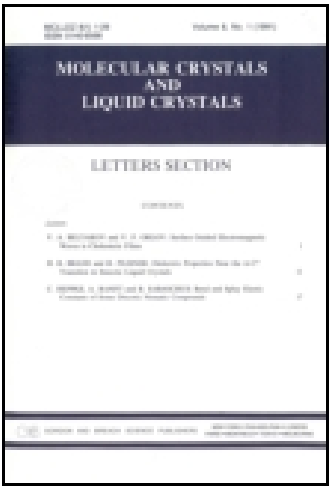
This article was downloaded by: [Xian Jiaotong University]
On: 11 December 2014, At: 13:22
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Characterization of Thin Chitosan/Polyacrylamide Blend Films

Katarzyna Lewandowska [a]

[a] Nicolaus Copernicus University, Faculty of Chemistry , 7 Gagarin Street, 87-100 , Torun , Poland

Published online: 28 Mar 2014.

To cite this article: Katarzyna Lewandowska (2014) Characterization of Thin Chitosan/Polyacrylamide Blend Films, Molecular Crystals and Liquid Crystals, 590:1, 186-192, DOI: 10.1080/15421406.2013.874233

To link to this article: http://dx.doi.org/10.1080/15421406.2013.874233

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Mol. Cryst. Liq. Cryst., Vol. 590: pp. 186–192, 2014
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2013.874233

Characterization of Thin Chitosan/Polyacrylamide Blend Films

KATARZYNA LEWANDOWSKA*

Nicolaus Copernicus University, Faculty of Chemistry, 7 Gagarin Street, 87-100 Torun, Poland

The structure and surface properties of blends containing chitosan (Ch) and partially hydrolyzed polyacrylamide (HPAM) were analyzed by contact angle measurements and atomic force microscopy (AFM). The results of contact angle and the surface free energy revealed that HPAM films are more polar than chitosan films. In the case of Ch/HPAM blends, the values of surface free energy and polar component are reduced significantly compared with pure polymers. This behavior indicates rather hydrophobic character of this surface. The roughness of the blends increases with the increase of Ch content. This may indicates a strong interaction between the polymeric components.

Keywords chitosan; polymer blend; thin film; partially hydrolyzed polyacrylamide; surface properties

1. Introduction

The physico –chemical properties of polymer blends are important from both scientific and practical points of view [1–3]. Chitosan - poly[β-(1→4)-2-amino-2-deoxy-D-glucopyranose] is copolymer of D-glucosamine and N-acetyl-D-glucosamine. This polysaccharide is a modified natural polymer, non-toxic, bioactive, biodegradable, derived by deacetylation of chitin [1–3]. This biopolymer is often combined with the synthetic, water-soluble polymers. It is, for example, mixed with PVP [4–6], starch [7–8], PVA [9–11] etc. The structure and properties of blends of chitosan with other polymers depend mainly on the molecular weight, and on the blend composition [3,6,11]. HPAM is also copolymer of acrylamide and sodium acrylate. It is a synthetic, an anionic polyelectrolyte and water-soluble polymer [12–14]. The blends composed of chitosan with polyacrylamide (PAM) or partially hydrolyzed polyacrylamide (HPAM) at various component ratios have been prepared as material designed for various applications such as food and cosmetic industries or biomedical. The aim of this study was to evaluate the physico –chemical properties of chitosan differing in molecular weight with partially hydrolyzed polyacrylamide on the basis of measurements of contact angles and atomic force microscopy.

---

*Corresponding author, Katarzyna Lewandowska. Tel.: +48 56 611 4551, Fax: +48 56 654 24 77. E-mail: reol@chem.uni.torun.pl

Table 1. Values of contact angles (deg), surface free energy (γ_s) and its polar ($\gamma_s{}^d$) and dispersive ($\gamma_s{}^p$) components for Ch I, HPAM and their blends (w_{Ch} –weight fraction of chitosan)

	Contact angle (○)				
w_{Ch}	G	D	γ_s (mJ/m^2)	$\gamma_s{}^d$ (mJ/m^2)	$\gamma_s{}^p$ (mJ/m^2)
0.0	49.9 ± 1.6	59.3 ± 2.2	42.9 ± 0.7	18.8 ± 1.5	24.1 ± 2.2
0.2	55.5 ± 2.7	60.4 ± 1.7	37.1 ± 1.2	17.8 ± 1.5	19.0 ± 2.0
0.5	63.9 ± 0.9	57.0 ± 0.3	36.3 ± 0.1	23.8 ± 1.1	12.4 ± 1.0
0.8	65.5 ± 1.2	56.8 ± 1.9	35.0 ± 1.1	23.2 ± 0.9	11.9 ± 0.4
1.0	61.3 ± 4.6	52.7 ± 0.4	38.2 ± 1.1	24.8 ± 0.7	10.4 ± 0.2

G – glycerol, D – diiodomethane.

2. Experimental

Materials

Partially hydrolyzed polyacrylamide is a commercial polymer from Aldrich company with the degree of hydrolysis DH = 20% and a viscosity average molecular weight of 230 000. Chitosan samples have a degree of deacetylation of 86% with a viscosity average molecular weight of 470 000 for Ch I and of 880 000 for Ch II. Both chitosan samples were supplied by Aldrich. The viscosity average molecular weight of chitosan and HPAM was measured with the Ubbelohde viscometer and calculated from the viscosity of solutions according to the Mark–Houwink–Sakurada equation [15,16]:

$$[\eta] = K\bar{M}_v^a \tag{1}$$

using K and a values equal to 0.00181 and 0.93 for Ch [17] and 0.0063 and 0.82 for partially hydrolyzed polyacrylamide [18], respectively.

Ch/HPAM blends were prepared from mixed polymer solutions in aqueous 0.1 mol·dm^{-3} acetic acid. The composition of Ch/HPAM was 80/20, 50/50 and 20/80. Polymer films were obtained by casting solution onto glass plate at room temperature. The films were dried in the vacuum oven.

Glycerol (glycerin, propane-1,2,3-triol) and diiodomethane (POCh and Aldrich, respectively, analytical grade) were used as test liquids for contact angle measurements.

Measurements of Contact Angle

The measurements of contact angles (Θ) by the sessile drop method were performed at the room temperature using the DSA10 goniometer of Krüss GmbH (Germany), equipped with software for the drop shape analysis. The droplets of probe liquid (high purity, volume of 3 μl) were deposited on studied surface by a microsyringe. The drop image was recorded by video camera and digitalized. The drop shape was solved numerically and fitted by means of the mathematical functions using instrument software. Each value of contact angle is an average of 10 measurements.

Table 2. Values of contact angles (deg), surface free energy (γ_s) and its polar ($\gamma_s{}^d$) and dispersive ($\gamma_s{}^p$) components for Ch II, HPAM and their blends (w_{Ch} – weight fraction of chitosan)

	Contact Angle (○)				
w_{Ch}	G	D	γ_s (mJ/m^2)	$\gamma_s{}^d$ (mJ/m^2)	$\gamma_s{}^p$ (mJ/m^2)
0.0	49.9 ± 1.6	59.3 ± 2.2	42.9 ± 0.7	18.8 ± 1.5	24.1 ± 2.2
0.2	59.7 ± 0.7	58.7 ± 0.2	37.2 ± 0.4	20.8 ± 0.2	16.5 ± 0.5
0.5	61.4 ± 0.9	55.9 ± 1.3	37.2 ± 0.7	22.9 ± 0.6	14.3 ± 0.2
0.8	63.8 ± 1.2	56.4 ± 1.9	35.9 ± 1.1	23.0 ± 0.9	12.9 ± 0.3
1.0	59.9 ± 2.9	53.3 ± 1.4	38.7 ± 1.1	24.2 ± 0.7	14.5 ± 0.6

Atomic Force Microscopy (AFM)

Topographic imaging was performed using a multimode scanning probe microscope with a Nanoscope IIIa controller (Digital Instruments Santa Barbara, CA) operating in the tapping mode, in air, at room temperature. Surface images, using scan widths ranging from 1 μm to 5 μm, with a scan rate of 1.97 Hz were acquired at fixed resolution (512 × 512 data points). Commercial silicon tips with spring constant 2-10 N/m were used. The roughness parameter such as the root mean square (R_q) was calculated from scanned area (2 μm × 2 μm) using Nanoscope software. The AFM images and roughness calculations were obtained for different sample places and the most typical areas are presented.

3. Results and Discussion

Tables 1 and 2 give the values of contact angles, surface free energy and its polar and dispersive components for polyacrylamide and two different samples of chitosan and their blends. As it can be observed, the surfaces of chitosan and Ch I/HPAM blends with $w_{Ch} \geq 0.5$ (weight fraction of chitosan) were rather hydrophobic as the values of glycerol contact angles were higher than the values of diiodomethane contact angles. Glycerol interacts with the surface by polar forces but diiodomethane interacts with the surface by dispersion forces [19]. The lowest value of glycerol contact angle is found for HPAM film, which suggests that the surface is the most hydrophilic. The blend with $w_{Ch} = 0.2$ is the most hydrophilic surface for the Ch I/HPAM blends. Owens – Wendt method was used to calculate the surface free energy [19,20]. The surface free energy as well as its polar and dispersive components indicates that the HPAM film has the highest polarity among the investigated systems because it has the highest polar component of surface free energy. The lowest polarity is characteristic for Ch/PAM blend films with $w_{Ch} \geq 0.5$. This behaviour indicates some interactions between polymer components in the blend. Thus, the functional groups of polymers are be hidden below the surface of the film. Similar direction of changes is observed for the Ch II/HPAM blends shown in Table 2. In the case of Ch II/PAM blends, the values of surface free energy and polar component are reduced significantly compared with pure polymers, especially for the blends with $w_{Ch} \geq 0.5$.

The morphology of investigated films is presented in Figs. 1 and 2. The AFM images show difference in surface properties films for the homopolymers and their blends. The

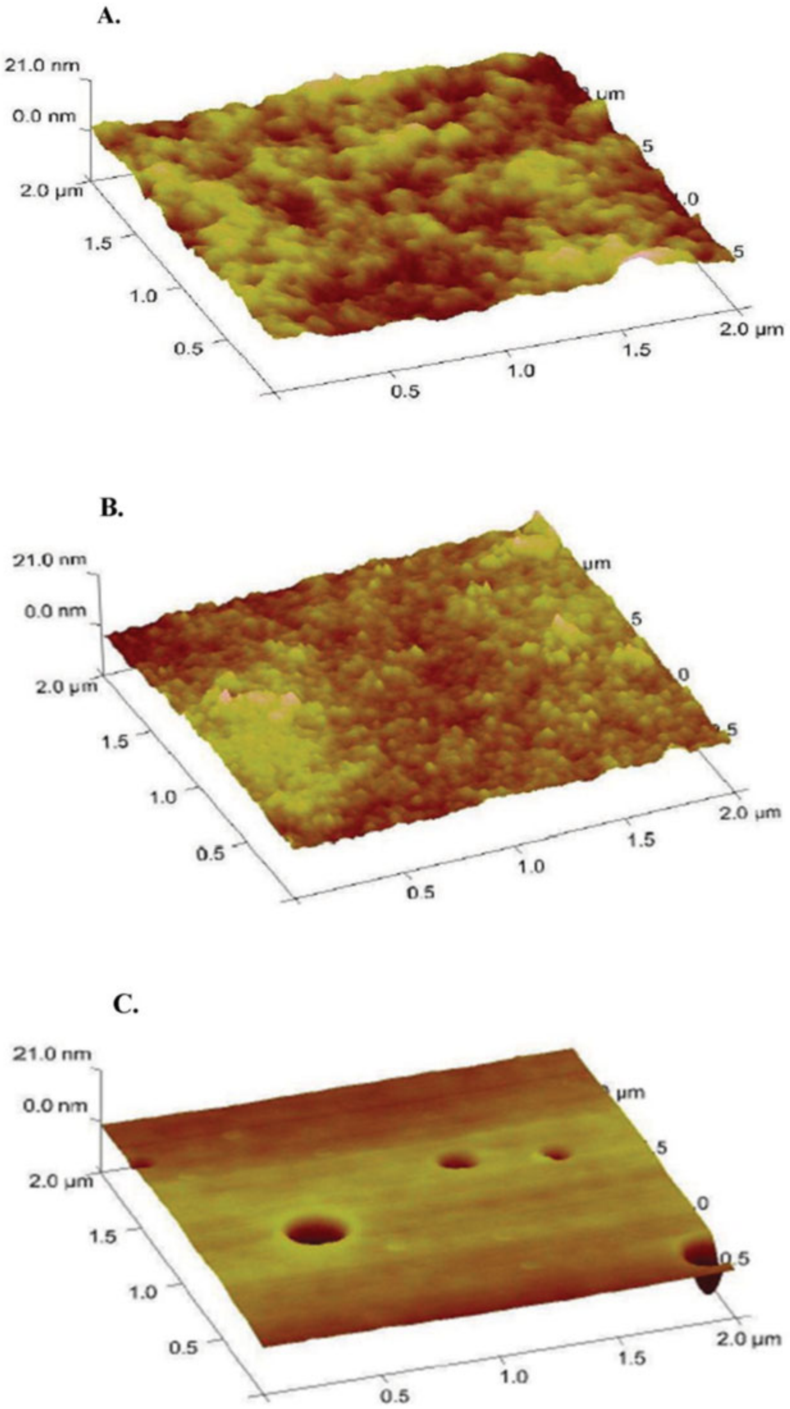


Figure 1. AFM images: A. chitosan I, B. chitosan II C. HPAM.

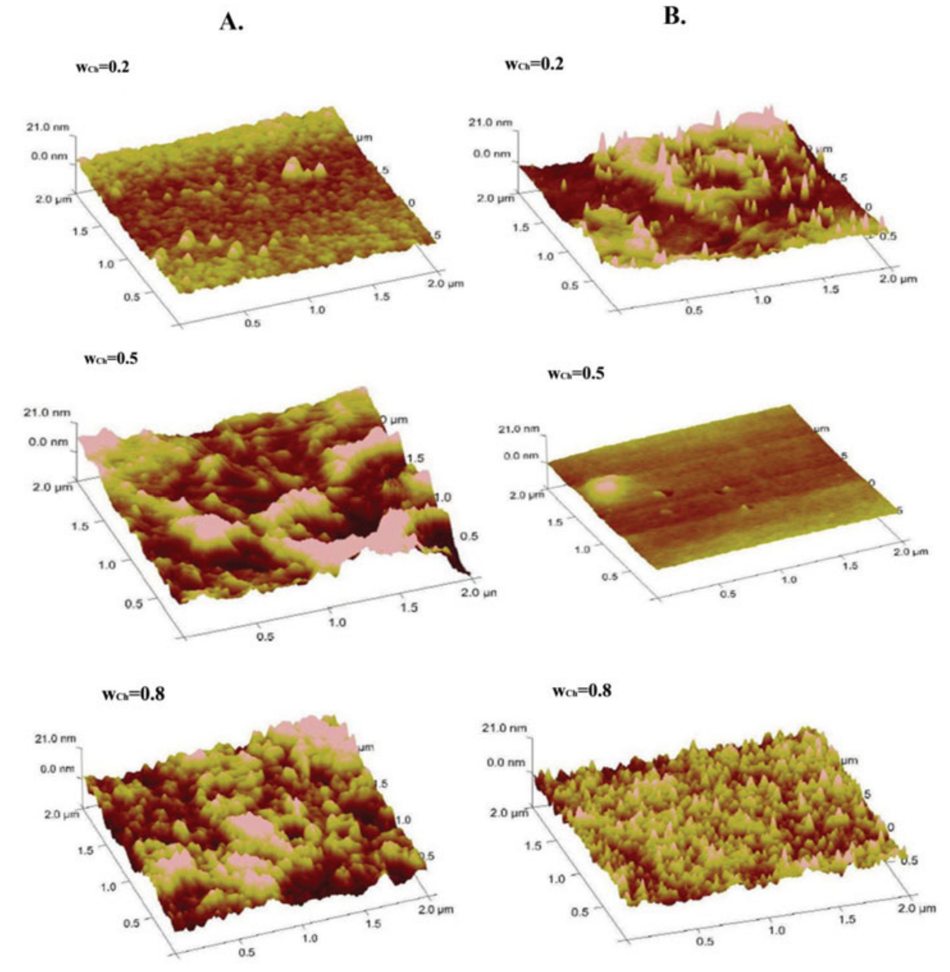


Figure 2. AFM images of Ch /HPAM blends: A. Ch I/HPAM blends, B. Ch II/HPAM blends.

surface morphology of pure Ch films is considerably rough, which can result from the crystalline of the sample. A previous study [21] showed the similar morphology of chitosan sample. In the case of HPAM sample, the film has a relatively flat and smooth surface, which is the consequence of its amorphous state. Figure 2 shows the topography of blend films. As it can be observed the surface morphology of blend depends on its composition. The surface of blends is slightly more folded than the surface of chitosan film. The observed changes in morphology are related to the interactions between polymeric compounds. Table 3 gives the values of the roughness parameters for the investigated samples. As it can be observed the roughness of the blends increases with the increase of Ch content. The value of the roughness of the Ch II/HPAM blend with $w_{Ch} = 0.5$ is the lowest (Table 3). This may indicate an increase in the homogeneity of this blend in comparison to other compositions.

Table 3. The roughness parameters (R_q) for films of Ch/HPAM blends of different composition

Ch I/HPAM		Ch II/HPAM	
w_{Ch}	R_q (nm)	w_{Ch}	R_q (nm)
0.0	1.9	0.0	1.9
0.2	1.8	0.2	3.5
0.5	5.1	0.5	1.3
0.8	4.2	0.8	2.7
1.0	1.8	1.0	1.5

4. Conclusions

1. The surfaces of Ch and Ch/HPAM blends have similar values of surface free energy.
2. The highest polarity of surface is characteristic of partially hydrolyzed polyacrylamide film.
3. Ch/HPAM blends have significantly less polarity of surface. The exception is the Ch I/PAM mixture with $w_{Ch} = 0.2$.
4. In the case of Ch/HPAM blends, the surface free energy and its polar component decreases with the increase of Ch content which indicates that between functional groups of Ch and HPAM are the interactions particularly in the bulk of the blend.
5. The surface of HPAM is a relatively flat and smooth.
6. AFM images show differences in surface properties between HPAM films and films made of blend of chitosan and HPAM. The surface roughness of blends increases with the increase of Ch content.

References

[1] Roberts, G. A. F. (1992). *Chitin chemistry, first ed.*, Macmillan Press Ltd., London.
[2] Rinaudo, M. (2006). *Prog. Polym. Sci.*, *31*, 603.
[3] Sionkowska, A. (2011). *Prog. Polym. Sci.*, *36*, 1254.
[4] Fang, L., & Goh, S. H. (2000). *J. Appl. Polym. Sci.*, *76*, 1785.
[5] Yeh, J. T., Chen, Ch. L., Huang, K. S., Nien, Y. H., Chen, J. L., & Huang, P. Z. (2006). *J. Appl. Polym. Sci.*, *101*, 885.
[6] Lewandowska, K. (2011). *Thermochim. Acta*, *517*, 90.
[7] Zhai, M., Zhao, L., Yoshii, F., & Kume, T. (2004). *Carbohyd. Polym.*, *57*, 83.
[8] Nanaki, S., Koutsidis, I. A., Koutri, I., Karavas, E., & Bikiaris, D. (2012). *Carbohyd. Polym.*, *87*, 1286.
[9] Miya, M., Yoshikawa, S., & Iwamoto, R. (1984). *J. Appl. Polym. Sci.*, *22*, 1149.
[10] Srinivasa, P. C., Ramesh, M. N., Kumar, K. R., & Tharanathan, R. N. (2003). *Carbohyr. Polym.*, *53*, 431.
[11] Lewandowska, K. (2009). *Thermochim. Acta*, *493*, 42.
[12] Briscoe, B., Luckham, P., & Zhu, S. (1999). *Rheol. Acta*, *38*, 224.
[13] Lewandowska K. (2007). *J. Appl. Polym. Sci.*, *103*, 2235.
[14] Lewandowska K. (2012). Progress on Chemistry and Application of Chitin and Its Derivatves, Monograph, Vol. XVII, Polish Chitin Society, In: Jaworska M. (ed), Lodz, 53.

[15] Flory, P. J. (1953). *Principles of polymer chemistry. 1st ed.* Cornell University Press, Ithaca New York.

[16] Bohdancký, M., & Kovář, I. (1982). Viscosity of Polymer Solution. vol. 2, In A. D. Jenkins ed., Elsevier Science, Amsterdam.

[17] Roberts, G. A. F., & Domoszy, J. G. (1982). *Int. J. Biol. Macromol.*, *4*, 374.

[18] Klein, J., & Conrad, K. D. (1978). *Makromol. Chem.*, *179*, 1635.

[19] Rudawska, A., & Jacniawska, E. (2009). *International Journal of Adhesion & Adhesives*, *29*, 451.

[20] Owens, D. K., & Wendt, R. C. (1969). *J Appl Polym Sci*, *13*, 1741.

[21] Lewandowska, K. (2012). *Appl. Surf. Sci.*, *263*, 115.