

Effect of Degree of Substitution on the Adhesive Properties of Methyl Cellulose Derived from Waste Bitter Orange [*Citrus Aurantium* (Linn.)] Mesocarp

^{1*}Hamza Abba

²Abdulqadir Ibrahim

¹Sani Uba

³Isuwa Kari

¹Department of Chemistry, Ahmadu Bello University, P.M.B. 1045, Zaria, Nigeria

²Department of Chemistry, Nigeria Police Academy, P.M.B. 3474, Wudil, Kano, Nigeria

³Nigerian Institute of Leather Science and Technology, P.M.B. 1034, Zaria, Nigeria

Doi:10.5901/ajis.2013.v2n13p19

Abstract

Cellulose was extracted from waste bitter orange mesocarp and chemically modified by etherification in propan-2-ol as solvent with varying amount of methyl chloride and the degree of substitution (DS) of the methyl group for H of the native cellulose calculated by acid-base titration. Nine pastes (seven etherified cellulose (methyl cellulose) and the native cellulose (control) were prepared by dispersing them in distilled water (35% w/v) and heating the eight dispersions to 45°C with continuous agitation for 15min. The solutions were then cooled to room temperature and allowed to gel. The effect of DS on the adhesive properties of the pastes (tack strength, rolling ball test, gelation time, drying time, optical clarity, relative viscosity, syneresis) was comparatively investigated. The results showed that the DS in the etherified cellulose ranged from 1.31 to 1.98 with the methyl cellulose giving higher values of viscosity and tack strength with increase in DS. However, lower values of syneresis, gelation time, optical clarity, drying time and rolling ball distance were recorded with increase in DS. Increase in desirable adhesive properties of the methyl cellulose is attributed to its relatively higher molecular weight compared to the native cellulose. Production and use of etherified cellulose, in place of petroleum-based synthetic adhesives, in remoistening applications such as envelope flaps, postage stamps, labels and other paper works in Nigeria and other developing economies is recommended from the viewpoints of economy, environment, health and safety.

Keywords: Adhesion, cellulose, degree of substitution, tack strength, viscosity

1. Introduction

Adhesion, attachment between an adhesive and a substrate, is the molecular attraction exerted between bodies in contact. An adhesive is any substance that, when applied to the surfaces of materials, binds the surfaces together and resists separation (Mittal and Pizzi, 2003; Notley and Norgren, 2006; Ebnesajjad, 2010). Use of adhesives offers many advantages over other binding techniques such as sewing, welding, bolting and screwing (Forsström *et al.*, 2005; Nolte *et al.*, 2009). These advantages include the ability to bind different materials together and distribute stress more efficiently across the joint, cost effectiveness as an easily mechanized process, improvement in aesthetic design, and increase in design flexibility (Maeda *et al.*, 2002; Chen *et al.*,

2005; Huang *et al.*, 2005; Eriksson *et al.*, 2007; Pettersson and Dedinaite, 2008). Carbohydrates, in the form of polymers such as cellulose, starch, and natural gums, are available in large quantities from various plant sources. Each of them has potentials for utilization as adhesive and in adhesive formulations (McMurry, 2012). Bioadhesives are preferred to petroleum-derived synthetic adhesives from the points of view of economy, environment, health and safety (Doraiswamy *et al.*, 2009; Blackman *et al.*, 2012). Cellulose is considered to be a natural condensation polymer of 2000 to 14000 β -1,4-glycosidically linked glucose residues, each carrying three reactive hydroxyl groups (Klemm *et al.*, 2005; Carraher, Jr, 2010; Karabulut and Wågberg, 2011):

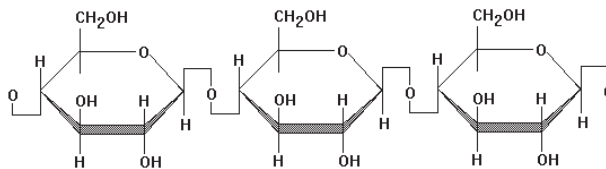


Fig. 1. Glucose Residues in Cellulose (adapted from Klemm *et al.*, 2005)

Replacing one or more of the cellulose's hydroxyls with other functional groups results in production of cellulose derivatives with desired functional properties (Ito *et al.*, 2007). Etherification, the process of making ether from alcohol, is an efficient method of modifying properties of polysaccharides, such as cellulose (Ahola *et al.*, 2008; Fox *et al.*, 2011). $[C_6H_7O_2(OH)_x(OCH_3)_y]_n$ is the condensed molecular formula of methyl cellulose, whose structural formula is (Carey, 2008; Henriksson *et al.*, 2008; Villetti *et al.*, 2011):

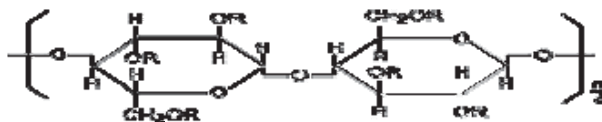


Fig. 2. Methyl Cellulose, R = CH₃ (adapted from Villetti *et al.*, 2011)

By varying both the length of the polymer backbone and the number of substitutive alkyl groups, derivatives of a wide range of modified cellulose grades can be manufactured to provide different levels of viscosity and tuning the several properties of the polymer for adhesive use. Thus, control of degree of substitution (DS) and uniform distribution of functional groups along the polymer's chain have been the major challenges confronting synthetic polymer chemists (Elomaa, 2004). Although the maximum DS for a glucose molecule would be 3, this is not practically possible to achieve because of other competing side reactions (Samios *et al.*, 1997). Amim and colleagues (2009) have reported average DS values between 1.3-2.6 for methyl cellulose with methoxy substitution between 27.5-31.5% (weight). Mario and associates (2005) have also reported 1.5-1.9 as the average number of substituent groups (DS) for sodium carboxymethyl cellulose. Bitter orange (*Citrus aurantium*) tree is a hybrid between *Citrus maxima* (pomelo) and *Citrus reticulata* (mandarin) that is spiny and evergreen (Rodrigues *et al.*, 2013). Many varieties of bitter orange are used for their essential oils in perfumery, as flavouring and as solvent, employed in herbal medicines as stimulant and appetite suppressant, due to its active ingredient, synephrine (Jordan *et al.*, 2004). However, Its supplements have, recently, been linked to a number of serious side effects and deaths to consumers of its fruit (Hess and Sullivan, 2005). The aim of this study was to extract cellulose from waste bitter orange mesocarp, chemically modify the native cellulose by adding varying amount of methyl chloride of varying degree of substitution and comparatively

investigate suitability of the products for remoistenable adhesive use in postage stamps, envelope flaps, labels and other paper works.

2. Methods and Procedures

Waste bitter orange (*Citrus aurantium*) mesocarp was obtained from local orange sellers at Samaru Market, Sabon Gari Local Government, Kaduna State. Analytical-grade reagents phenolphthalein, NaOH, HCl, propan-2-ol, ethanol, and methyl chloride were purchased from Sigma Aldrich (Munich, Germany) and used as supplied.

2.1 Extraction of Cellulose and its Derivatization to MC

Cellulose was extracted with 8% NaOH from the mesocarp of waste bitter orange according to the procedure reported by Pushpamalar *et al.*, 2006. The cellulose obtained was etherified to eight different MC products by adding 0.25, 0.30, 0.35, 0.40, 0.45, 0.50, 0.55 and 0.60g of methyl chloride to 2g of the native cellulose powder and heating the product to 27°C for 2h in 20mL of 15% in 20mL propan-2-ol. The product obtained was thoroughly washed with 75% ethanol and dried at 60°C in oven.

2.2 Determination of Degree of Substitution:

Each sample (0.5g) was placed in a 250-ml conical flask. Distilled water (50 ml) was added and the pH adjusted to 7.0 with 0.02M HCl. 0.5 M NaOH (25ml) was introduced and the mixture heated on hot plate until a transparent solution was obtained. The excess NaOH was titrated with HCl (using phenolphthalein as indicator) back to pH 7.0. Triplicate preparations were performed on each sample to obtain a mean DS value using: $DS = \frac{52.5 \times M_{NaOH} \times V_{NaOH} - M_{HCl} \times V_{HCl}}{1000 \times W - 42 \times (M_{NaOH} \times V_{NaOH} - M_{HCl} \times V_{HCl})}$ where M_{NaOH} = molarity of NaOH V_{NaOH} = volume of NaOH M_{HCl} = molarity of HCl used to back titrate NaOH V_{HCl} = volume of HCl used to back titrate NaOH W = sample weight (g)

2.3 Preparation of the Adhesive Pastes

Nine different dispersions of both native cellulose and MC were prepared by adding distilled water (5, 10, 15, 20, 25, 30, 35, 40 and 45% w/v) and heating the dispersions to 45°C with continuous agitation for 15min. The slurries were then cooled to room temperature (31°C) and allowed to form pastes.

2.4 Determination of Tack Strength

10mL of each paste was placed between two cardboard laminates measuring 15 x 3cm with bond area of 6 x 2cm. One end of the laminates was clamped, the other end turned 180° downwards and a pan attached with increasing standard masses added to the pan. The minimum load needed for the peel to begin was recorded.

2.5 Rolling Ball Test

Standard ASTM D 3121-94 method using 11.1mm diameter steel ball was employed to determine the rolling ball distances of the pastes (Anon, 1997).

2.6 Determination of Gelation Time

20g of each of the nine pastes was heated at 105°C, cooled to room temperature (31°C) and the time taken for it to form a firm gel was noted.

2.7 Determination of Drying Time

A uniform 150µm-thick film of each paste was cast on two glass slides with their edges tapped off with a layer of masking tape. The drying time for each paste was determined by touching the film lightly with index finger at an interval of 2min. The first time the film was felt to be tacky enough, but do not transfer a wet film to the finger was recorded.

2.8 Evaluation of Optical Clarity

Light transmittance (%T) of each of the nine pastes was determined at 650nm against water blank using Jasco V530 spectrophotometer (Jasco Corporation, Tokyo, Japan) following standard method (Sharma, 2011).

2.9 Determination of Relative Viscosity

The efflux time (t) it takes 20cm³ of each of the nine solutions to flow through an Ostwald viscometer was noted and related to the corresponding efflux time (t_o) for 20cm³ of water at room temperature (33°C). The relative viscosity (η_{rel}) of each solution was then obtained from the expression: $\eta_{rel} = \dot{\eta} / \dot{\eta}_o = t / t_o$ where $\dot{\eta}$ is the intrinsic viscosity of the test solution and $\dot{\eta}_o$ is the intrinsic viscosity of water, respectively. 10 minutes were allowed for the viscometer and test solution to attain thermal equilibrium.

2.10 Assessment of Syneresis

5g of each paste was transferred to a tube and refrigerated at -20°C for 24h, and then thawed at room temperature for 6h. The tube was taken out time and centrifuged at 3000 revolutions per minute (rpm) for 20min in L-550 centrifuge (Xiang-Yi Centrifuge Instrument Co. Ltd, Changsha, China). The water layer formed was decanted, the residual paste weighed and the percentage of water separated calculated using the formula:

$$\text{Syneresis} = \frac{m_2 - m_3}{m_2 - m_1} \times 100\%$$

Where m₁ is the weight of centrifuge tube (g), m₂ is the weight of centrifuge tube and the starch paste (g), m₃ is the weight of centrifuge tube and the starch paste after centrifuging (g).

3. Results

3.1 Tack Strength and Rolling-Ball Distance

The effect of degree of substitution of the eight etherified cellulose (1.31, 1.43, 1.54, 1.65, 1.75, 1.84, 1.92 and 98) and the control sample (0) on tack strength) and rolling-ball distance of the prepared adhesive pastes are shown in Figure 1. The minimum weight a bonded joint can support at a particular temperature before peeling (tack strength) of the nine samples ranged from 4.13g (for the native cellulose) to 21.27g (for the MC with highest DS value). This implies that for every 0.09 increase in DS, there is 2.14g increase in tack strength. As tack strength is the most important

parameter for choosing an adhesive for any use, the tack strength of the modified cellulose falls within the range recommended by standards bodies, such Adhesives and Sealants Council of the United States of America that recommends tack strength of a remoistenable adhesive to be within the range of 5 to 25g as reported by Nolte *et al* (2009). The superior tack strength of the methyl cellulose in comparison to the native cellulose and the direct linear relationship between DS and tack strength can be attributed to increase in molecular weight. With respect to the rolling-ball distance (distance the 11.1mm diameter steel ball moves before its movement is arrested) of the nine samples, it can be seen that their values decrease with increase in DS and ranged from 23.47cm (native cellulose) to 5.79cm (methyl chloride-containing cellulose with the highest DS value). These values roughly translate to a decrease of approximately 2.09cm for every 0.09 increase in DS. The difference in the trends of tack strength and rolling-ball distance values is expected because an adhesive with greater tack strength is expected to have shorter rolling-ball distance (shorter distance the steel ball moves before its movement is arrested by the adhesive), is attributed to higher molecular weight of MC compared to that of the native cellulose. Methyl cellulose being 49.5 atomic mass units greater than the native cellulose, it is not surprising that methyl cellulose to have shorter rolling-ball distance value than the native cellulose.

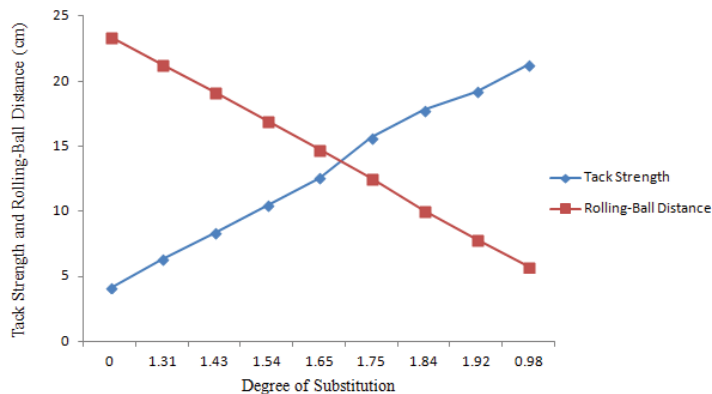


Fig. 3. Effect of Degree of Substitution on Tack Strength and Rolling-Ball Distance of the Native Cellulose and Methyl-Containing Cellulose Adhesive Pastes

3.2 Drying and Gelation Times

The effect of degree of substitution of the chemically modified cellulose (MC) and the native cellulose pastes on their drying and gelation times are shown in Figure 2. Drying time of the nine pastes ranged from 3.45min for native cellulose to 45.83min for the MC and increase with increase DS value. Thus, for each 0.09 increase in DS, there is a corresponding 5.21min increase in drying time. The gelation time of the samples ranged from 23.75min (control) to 11.22min (the most etherified). Thus, for each 0.09 increase in DS, there is a corresponding 1.57min decrease in gelation time. As gel firmness is a marked physical feature of an ageing gel, gelation time is a convenient means of monitoring efficiency of an adhesive product. This is so because gel firmness is an undesirable sign of decreases in adhesive quality of cellulose-based products, especially adhesives. It can also be seen from Figure 2 that although the relation between DS and time of gel formation is linear, it is an inverse one. That is, as DS increase, gelation time decrease in similar proportion, in agreement with earlier findings (Maeda *et al.*, 2002). If drying and gelation times of the chemically modified and native cellulose are compared, it can be observed that the drying time of MC is longer than that of native cellulose and increase with increase in DS value. Similarly,

gelation time of the MC is less than that of native cellulose and decrease with increase in DS value. The inverse relation between gelation and drying times with increase in DS is expected because of increase in molecular size; molecular weight of MC is greater than that of native cellulose by about 50 atomic mass units. The inverse relation between gelation and drying times with increase in paste concentration is expected because thicker gels tend to take relatively longer time to dry, as found by Mario *et al* (2005) who studied the synthesis and characterization of sodium carboxymethyl cellulose from Cavendish Banana.

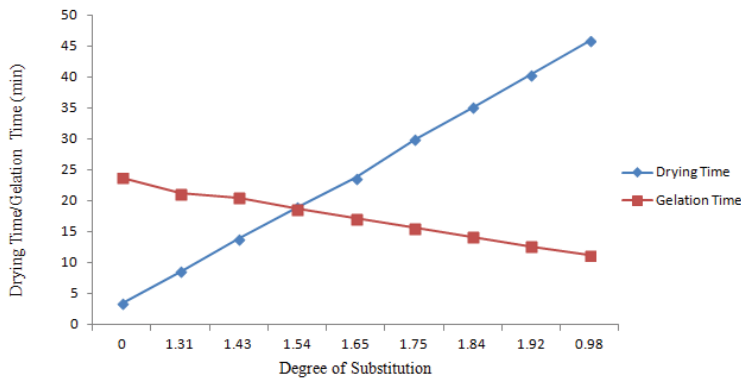


Fig. 4. Effect of Degree of Substitution on Drying and Gelation Times of the Native Cellulose and Methyl -Containing Cellulose Adhesive Pastes

3.3 Optical Clarity, Relative Viscosity and Syneresis

Optical clarity (expressed as percentage of light transmitted through a substance) that is, the quantity of light a paste allows to pass through it, relative viscosity (the relative ease with which a fluid sample flows in comparison with water as solvent) and syneresis (the amount of water seeped from or released by a substance) of the nine adhesive pastes (MC and native cellulose) are shown in Figure 3. From the figure, it can be seen that optical clarity decreases with increase in DS value of the methyl chloride-containing cellulose. The optical clarity of the samples ranged from 62.57 (native cellulose) to 22.34% (the MC with the highest value of DS), which translate to 5.03% decrease in transparency of the pastes for every 0.09 increase in DS value. The results implied that the pastes are not suitable for use as remoistenable adhesives where transparency is critical, in agreement with the findings of Amim *et al* (2009) who studied the solution behaviour of carboxymethylcellulose acetate butyrate. The relative viscosity of the samples, in contrast to optical clarity, increase with increase in DS value of the methyl chloride-containing cellulose and ranged from 18.73% (native cellulose) to 42.86% (the MC with the highest value of DS). This implies that there is 3.02% increase in relative viscosity of the methyl chloride-containing cellulose for every 0.09 increase in DS value. The inverse relationship between optical clarity and relative viscosity is expected because thicker adhesive (one with higher relative viscosity value) is expected to allow less light to pass through it than a thinner one (having lower relative viscosity value). The syneresis values of the samples, like that of optical clarity can be seen to decrease with increase in DS value of the methyl chloride-containing cellulose. The syneresis values of the samples ranged from 18.57g (native cellulose) to 2.06g (the MC with the highest value of DS), meaning 2.06% decrease in the amount of water released for every 0.09 increase in DS value of the methyl chloride-containing cellulose. The decrease in syneresis with increase in DS is attributed to the higher water-holding capacity of modified cellulose in comparison to the native cellulose. Another contributing factor may be the increase in molecular weight as the native cellulose is etherified.

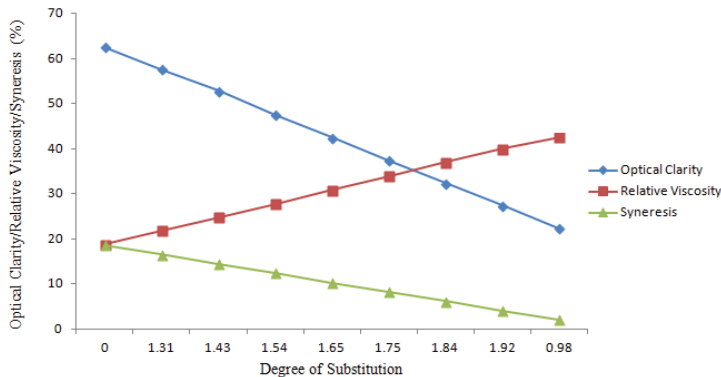


Fig. 5. Effect of Degree of Substitution on the Optical Clarity, Relative Viscosity and Syneresis of the Native Cellulose and Methyl-Containing Cellulose Adhesive Pastes

4. Conclusion

The results obtained from this work have shown that etherification of native cellulose has enhanced its adhesive properties and utilization in remoistenable applications, especially where transparency is not a critical parameter. Due to their relatively high bond strength, low syneresis biodegradability, renewability, environment friendliness and non-toxicity, production and use of MC from native cellulose in commercial scale is highly recommended. Nigeria stands a very good chance of improving her economy if cellulose can be sourced from non-edible plants and agricultural wastes and economically modified with safe and readily available reagents, such as methyl chloride.

References

- Ahola, S., Salmi, J., Johansson, L. S., Laine, J. and Österberg, M. (2008). Model Films from Native Cellulose Nanofibrils. Preparation, Swelling, and Surface Interactions. *Biomacromolecules* 9: 1273-1282.
- Amim, J., Petri, D. F. S., Maia, F. C. B. and Miranda, P. B. (2009). Solution behavior and surface properties of carboxymethylcellulose acetate butyrate. *Cellulose* 16: 773-782.
- Anonymous (1997). American Society for Testing and Materials. ASTM Special Technical Publication No. 360, 123-134. Review of Methods for the Measurement of Tack, PAJ1 Report No. 5.
- Blackman, A., Bottle, S. Schmid, S., Mocerino, M. and Wille, U. (2012). Chemistry, 2nd edn, John Wiley and Sons, Inc., New York, pp.977-1000.
- Carey, F.A. (2008). Organic Chemistry, 7th edn, McGraw-Hill Higher Education, New York, pp.1022-1061.
- Carraher, Jr, C.E. (2010). Introduction to Polymer Chemistry, 2nd edn, CRC Press Boca Raton, pp. 85-140.
- Chen, N., Maeda, N., Tirrell, M. and Israelachvili, J. (2005). Adhesion and Friction of Polymer Surfaces: The Effect of Chain Ends. *Macromolecules* 38: 3491-3503.
- Doraiswamy, A., Dunaway, T. M., Wilker, J. J. and Narayan, R. J. (2009). Inkjet Printing of Bioadhesives. *Journal of Biomedical Materials Research* 89: 28-35.
- Ebnesajjad, S. (2010). History of Adhesives. Handbook of Adhesives and Surface Preparation: Technology, Applications and Manufacturing. Elsevier, Amsterdam, p.137-154.
- Elomaa, M. (2004). Determination of the degree of substitution of acetylated starch by hydrolysis, ¹H NMR and TGA/IR. *Carbohydrate Polymers* 57: 261-267.
- Eriksson, M., Notley, S. M. and Wågberg, L. (2007). Cellulose Thin Films: Degree of Cellulose Ordering

- and Its Influence on Adhesion. *Biomacromolecules* 8: 912-919
- Forsström, J., Eriksson, M. and Wågberg, L. (2005). A new technique for evaluating ink cellulose interactions: initial studies of the influence of surface energy and surface roughness. *Journal of Adhesion Science and Technology* 19: 783-798.
- Fox, S.C., Li, B., Xu, D. and Edgar, K.J. (2011). Regioselective esterification and etherification of cellulose: a review 12(6): 1956-1972.
- Henriksson, M., Berglund, L. A., Isaksson, P., Lindström, T. and Nishino, T. (2008). Cellulose nanopaper structures of high toughness. *Biomacromolecules* 9: 1579-1585.
- Hess, A.M. and Sullivan, D.L. (2005). Potential for toxicity with use of bitter orange extract and guarana for weight loss. *The Annals of pharmacotherapy* 39(3): 574-585.
- Huang, Y. Y., Zhou, W., Hsia, K. J., Menard, E., Park, J-U., Rogers, J. A. and Alleyne, A. G. (2005). Stamp Collapse in Soft Lithography. *Langmuir* 21(17): 8058-8068.
- Ito, T., Yeo, Y., Highley, C.B., Bellas, E., Benitez, C.A. and Kohane, D.S. (2007). The prevention of peritoneal adhesions by in situ cross-linking hydrogels of hyaluronic acid and cellulose derivatives. *Biomaterials* 28: 975-983.
- Jordan, S., Murty, M. and Pilon, K. (2004). Products containing bitter orange or synephrine: suspected cardiovascular adverse reactions. *Canadian Medical Association Journal* 171(8): 356-367.
- Karabulut, E. and Wågberg, L. (2011). Design and characterization of cellulose nanofibrilbased freestanding films prepared by layer-by-layer deposition technique. *Soft Matter* 7: 3467-3474.
- Klemm, D., Heublein, B., Fink, H. P. and Bohn, A. (2005) Cellulose: Fascinating biopolymer and sustainable raw material. *Angew. Chemistry-International Edition* 44: 3358-3393.
- Maeda, N., Chen, N., Tirrell, M. and Israelachvili, J.N. (2002). Adhesion and Friction Mechanisms of Polymer-on-Polymer Surfaces. *Science* 297 (5580): 379-382.
- Mario, P., Adinugraha, D.W. and Haryadi, M. (2005). Synthesis and characterization of sodium carboxymethyl cellulose from Cavendish Banana Pseudostem (*Musa cavendishii* Lambert), *Carbohydrate Polymers* 62: 164-169.
- McMurry, J. E. (2012). Organic Chemistry, Brooks/Cole Cengage Learning, Belmont, pp.1001-1034.
- Mittal, K.L. and Pizzi, A. (2003). Historical Development of Adhesives and Adhesive Bonding. *Handbook of Adhesive Technology* (2nd ed., revised and expanded), Marcel Dekker, Inc., New York, p.11-32.
- Nolte, A. J., Chung, J. Y., Walker, M. L. and Stafford, C. M. (2009). In situ Adhesion Measurements Utilizing Layer-by-Layer Functionalized Surfaces. *ACS Appl. Mater. Interfaces* 1: 373-380.
- Notley, S. M. and Norgren, M. (2006). Measurement of interaction forces between lignin and cellulose as a function of aqueous electrolyte solution conditions. *Langmuir* 22: 11199-11204.
- Pettersson, T. and Dedinaite, A. (2008). Normal and friction forces between mucin and mucin-chitosan layers in absence and presence of SDS. *Journal of Colloid Interface Science* 324: 246-256.
- Pushpamalar, V., Langford, S. J., Ahmad, M. and Lim, Y. Y. (2006). Optimization of reaction conditions for preparing carboxymethyl cellulose from sago waste. *Carbohydrate Polymers* 64: 312 -318.
- Rodrigues, M., Alves, G. and Falcão, A. (2013). Investigating herb-drug interactions: the effect of *Citrus aurantium* fruit extract on the pharmacokinetics of amiodarone in rats. *Food Chemistry and Toxicology* 60: 153-159.
- Samios, E., Dart, R. K. and Dawkins, J. V. (1997) Preparation, characterization and biodegradation studies on cellulose acetates with varying degrees of substitution. *Polymer* 38: 3045-3054.
- Sharma, B.K. (2011). Industrial Chemistry, Krishna Prakashan Media (P) Ltd, Meerut, pp. pp.1371-1380
- Villetti, M.A., Bica, C.I., Garcia, I.T., Pereira, F.V., Ziembowicz, F.I., Kloster, C.L. and Giacomelli, C. (2011). Physicochemical properties of methylcellulose and dodecyltrimethylammonium bromide in aqueous medium. *Journal of Physical Chemistry Part B* 115(19): 5868-5876.