Cellulose (2013) 20:485–494
DOI 10.1007/s10570-012-9837-7

ORIGINAL PAPER

Hydrophobic modification of cellulose fibres by cationic-modified polyacrylate latex with core–shell structure

Yuanfeng Pan · Huining Xiao · Zhaoping Song

Received: 13 September 2012 / Accepted: 22 November 2012 / Published online: 4 December 2012

Abstract In cellulose fibre-based green packaging, the poor resistance or barrier against water or water vapour has remained as one of the key challenges. In this work, cationic polymer latex, butyl acrylate-co-styrene/2-ethylhexylacrylate-co-methyl methacrylate (BA-co-St/EHA-co-MMA), with core–shell structure was especially synthesized and used as a wet-end additive to render the fibre or paper hydrophobic. TEM observation confirmed that the latex particles obtained indeed possessed desired characteristic of core–shell structure. The experimental results showed that the cationic polymer was especially suitable for use in papermaking processes due to its high retention with cellulose fibres. The surface modification of the natural fibre by the adsorption of cationic latex on the fibre surfaces potentially created the thin films of polymers on fibre surfaces. The resulting paper is highly hydrophobic with improved barrier property, as demonstrated by the high contact angles and relatively low WVTR value. Moreover, the mechanical properties of paper were maintained or even improved in the presence of an appropriate level of the latex.

Keywords Cellulose fibre · Hydrophobic modification · Barrier properties · Nanosized latex · Core–shell

Introduction

Food packaging has become significantly more complex during recent years, mainly due to increased demands on product safety, shelf-life extension, cost efficiency, environmental issues and consumer convenience. In order to improve the performance of packaging to meet these varied demands, innovative-modified and controlled packaging materials have been developed and optimized for potential commercial use (Rhim and Ng 2007; Hult et al. 2010; Rodionova et al. 2011; Garcia-Ubasart et al. 2012). Currently these materials are largely produced from fossil-derived synthetic plastics, but with increasing environmental concerns, the materials derived from renewable resources are being extensively investigated as potential replacements.

It is advantageous to replace the synthetic and metal packaging with natural cellulose fibre due to its green features (e.g., sustainable, biodegradable and environmental friendly). However, the barrier properties of unmodified cellulose fibre network or paper products

---

Y. Pan · H. Xiao (✉) · Z. Song
Department of Chemical Engineering, University of New Brunswick, Fredericton, NB E3B 5A3, Canada
e-mail: hxiao@unb.ca

Y. Pan
Guangxi Key Laboratory of Petrochemical Resource Processing and Process Intensification Technology, School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, China

are far insufficient for high-barrier applications, moisture barrier in particular. Surface treatment of paperboard for the improvement of functionality has been dominated by lamination with low-cost, readily available plastic materials, e.g., polyethylene (PE), over the last decades (Hirvikorpi et al. 2010). Incorporation of tailored hydrophobic and barrier properties in cellulose fibre network is of great importance to the development of “green”-based packaging materials. To improve the hydrophobic properties and reduce the water vapour transfer rate (WVTR) of cellulose fibre-based packaging, a number of approaches via grafting or surface modification of cellulose have been attempted in the past. However, there are several unsolved issues or challenges remained, including the high efficiency of grafting or coupling for durability and tailored barrier properties. Whether hydrophobic medication leads to the lowering of WVTR also remains as an unsolved issue.

Polymer latexes prepared through emulsion polymerization have a great variety of applications (Moraes et al. 2012). It is to note that, to date, most of the studies on emulsion polymerization have been focused on systems with anionic surfactants and/or combination of anionic and non-ionic surfactants along with anionic or non-ionic free-radical initiators. The latex particles thus produced are negatively surface charged. However, positively surface charged latex particles are also required in many cases such as oil-field drilling, paper industries (Ridaoui et al. 2006; Li and Matyjaszewski 2011) and other recently emerged areas (Delair et al. 1994; Patrizi et al. 2009). However, relevant reports on cationic latexes are far fewer compared to those on anionic latexes. Cationic latexes using either styrene (Liu and Xiao, 2000; Liu et al., 2000), or methacrylate (Nagai and Ohishi 1987) or butyl acrylate (Luo and Schork 2001) with different vinyl containing quaternary ammonium monomer were reported. In other studies, cationic surfactants such as dodecyl trimethyl ammonium bromide (Ming et al. 1998) and cetyl trimethyl ammonium bromide (or chloride) (Landfester et al. 1999; Ramos et al. 2003) were used in the preparation of cationic latexes.

In this work, a range of core–shell polymer latexes with hydrophobic cores and shells was used for rendering cellulose fibre hydrophobic in an attempt to develop the green-based packaging materials with improved hydrophobic and barrier properties. Positive-charged polyacrylate latex (PBA-co-MMA/EHA-co-St) was prepared using a cationic surfactant cetyl trimethyl ammonium bromide (CTAB) and a cationic initiator -2, 2′-Azobis (2-methylpropion-amidine) dihydrochloride (AIBA). The monomers were selected based on the consideration of appropriate hydrophobicity and film formation after adsorption as well as the hardness or morphology of latex prior to adsorption. Among them, the hydrophobicity and filming were mainly contributed from butyl acrylate (BA), and 2-ethylhexylacrylate (EHA); whereas the hardness or morphology of latex was controlled by methyl methacrylate (MMA) and styrene (St). Upon adsorbing on fibres and over drying process, the latex particles tend to coalesce and form thin rubber-like films on fibre surfaces or within fibre networks (at drying temperature $T > T_g$ of CPBA-co-MMA/EHA-co-St). To optimize latex structure, the ratios between monomers were varied. The adsorption behavior of cationic latex on cellulose fibre was studied and thin film formation was proved by SEM observation. The characterization of hydrophobicity and barrier property were based on WVTR and contact angle measurements. Moreover, the mechanical properties for selected paper samples were also determined.

Experimental

Materials

Reagent-grade butyl acrylate (BA), styrene (St), and methyl methacrylate (MMA) were purchased from Sigma-Aldrich, washed with alkali solution and distilled under reduced pressure prior to use. 2-Ethylhexylacrylate (EHA), from Sigma-Aldrich, was washed with alkali solution prior to use. The initiator, 2, 2′-Azobis (2-methylpropion-amidine) dihydrochloride (AIBA), used in preparing cationic PBA-co-MMA/EHA-co-St (CPBA-co-MMA/EHA-co-St) latex via emulsion polymerization, and the emulsifier, CTAB, buffering solution, sodium bicarbonate ($NaHCO_3$) (reagent grade) and crosslinker, ethylene glycol dimethacrylate (EGDMA) (reagent grade) were also obtained from Sigma-Aldrich and used as received without further purification.

The bleached sulfite pulps were supplied by Fraser Papers in Edmundston, New Brunswick, Canada.

Preparation of cationic PBA-co-MMA/EHA-co-St Latex with core–shell structure and its adsorption on fibres

Synthesis of cationic PBA-co-MMA/EHA-co-St latex with core–shell structure

A two-step seeded semi-batch emulsion polymerization was employed for constructing core–shell latex. A typical emulsion copolymerization process is described as follows.

Firstly, 180 ml of distilled water, 30.0 g of BA/MMA mixed monomers at molar ratio of 1.5 (39/21 by mass), 0.15 g of initiator (0.50 % of the monomer weight), 0.3 g of EGDMA (1.0 % of the monomer weight) were used in core latex preparations. The amount of surfactant was varied from 0.3 to 3.0 % relative to the mass of the total monomers. The system was purged with nitrogen for 30 min and then heated to 60 °C with nitrogen purging for 20 min, followed by the addition of initiator. The emulsion polymerization then proceeded under constant stirring at 250 rpm for 2 h in order to achieve a high conversion of the core copolymer.

Secondly, 34.9 g of EHA/St mixed monomers at molar ratio of 0.66 (19/16 by mass), and 0.175 g of initiator (0.50 % of the monomer weight) were used in preparing the shell of the latex. The initiator was also dissolved in 20 ml of distilled water prior to being added. 18.9 g EHA, 16.0 g St and initiator solution were placed in funnels and dropped into the core copolymer emulsion over 2 h at 60 °C. The emulsion polymerization was carried out at 80 °C for another 2 h after the shell monomers and initiator were dropped completely. The synthesis route is presented in Scheme 1.

Adsorption of cationic latex on fibres for surface treatment

For the adsorption of the CPBA-co-MMA/EHA-co-St latex on the fibres, various amounts of latex were added to the pulp suspension with 1 % consistency under 80 rpm paddle stirring (paddle size 6 cm). To determine the adsorption isotherms, the supernatant of each suspension containing free latex, and the concentration of the latex in the supernatant was determined using an established calibration curve which represents the linear relationship between turbidity and concentration. The difference between the amounts of latex added and that found in the supernatant is attributed to the amount adsorbed on the fibres.

Preparation of hand-sheets from the modified fibres

The hand-sheets (grammage of 60 g/m^2) were made using the modified fibres above according to TAPPI Method T205. After pressed, the sheets were dried using a flat Labtech paper drier at 110 °C for 30 min; then put in a standard conditioning room for 48 h prior to the measurements of strength properties.

Characterization of latex and modified fibre

The zeta potential, mean particle size and size distribution of the latex particles were determined using Malvern Nano-ZS light scattering instrument in 0.1 mM KCl aqueous solution. Charge density of latex was determined using a Particle Charge Detector MÜtek PCD 03 (Herrsching, Germany) using the standard potassium polyvinyl sulfate (PVSK from Alchi-Sigma) solution (1.0 mM). Three repeats were conducted to get an average value for each sample.

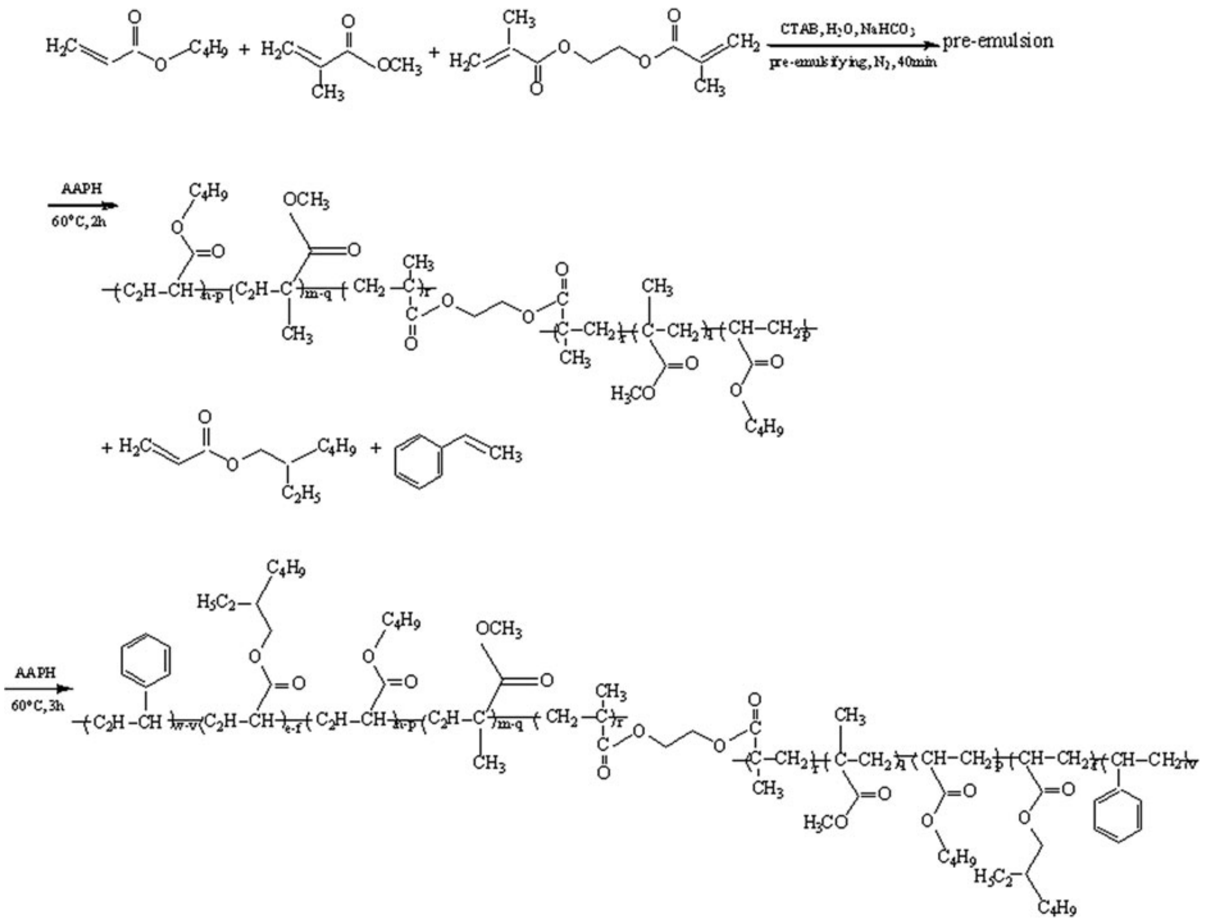
The fracture surfaces of the fibre specimens, coated with gold, were observed using a Scanning Electron Microscope (model Joel 6400 SEM). Thermogravimetric analyses (TGA) were collected with a Thermoanalyzer (TG 209, NETZCH Co.). Measurements were taken under nitrogen atmosphere and using a ramping temperature profile of 20 °C/min, within a temperature range of 25–700 °C.

Water absorption of films was measured by gravimetric variation before and after immersing the films into deionized water for 24 h.

WVTR of handsheets was determined with IGASorp (Hiden Isochema Limited, England); and the measurements were taken at 38 °C and inside R.H./outside R.H. = 76/2 %.

The hydrophobic property of modified paper sheets were characterized by the contact-angle measurement (OCA20, DataPhysics Instruments GmbH, Filderstadt).

The dry strength of paper, including tear and tensile strengths, was tested in accordance with TAPPI Standard T 494. Five repeats were conducted to get an average value for each sample.



Scheme 1 Synthesis route of CPBA-co-MMA/EHA-co-St latex

Results and discussion

Characteristics of latex

Influence of monomer ratios on various physical properties

Table 1 shows the influence of monomer ratios of latex on various physical properties, including Zeta potential, charge density, mean particle size, water absorption and T_g of latex films. As can be seen, the Zeta potential and charge density became higher as the shell monomer ratio increased since the emulsifier concentration increased accordingly (the amount of surfactant was maintained at 3.0 % (wt) relative to the total amount of monomers). The increase of CTAB dosage allowed more cationic surfactant to adsorb on latex particle surface, contributing to an increase in Zeta potential and charge density. Meanwhile, the mean particle size increased as the increasing of shell monomer ratio, confirming that the particles of latex possess core–shell structure, in which cores formed first and then coated with the shell layer. Polydispersity represents the particle size distribution of latex, which is also presented in Table 1. Obviously, the core and core–shell particles have narrow distribution or the latex tends to be mono-dispersed. The results in Table 1 also demonstrated that the type of monomers had significant effect on the hydrophobicity of latex once the films were formed. With the ratio of shell monomers EHA and St increasing, the water absorption decreased. Meanwhile, the addition of monomer MMA and St raised the T_g of latex films to about 29.2 °C, much higher than that of PBA-EHA (about −20 °C).

Table 1 Zeta potential, charge density, mean particle size and polydispersity of latex particles and water absorption and T_g of latex films

BA: MMA(core):EHA: St (shell) (mol:mol)	Zeta potential (mV)	Charge density (ueq/g)	Mean particle size (nm)	Polydispersity	Water absorption (wt %)	T_g (°C)
3:2:0:0 (core only)	5.45	149	60.8	0.036	16.96	27.6
3:2:1:1	6.33	174	68.6	0.041	11.03	28.2
3:2:1:2	7.86	197	70.2	0.045	9.54	29.0
3:2:2:3	9.11	236	71.4	0.042	7.18	29.2

Morphology of core–shell latex revealed by TEM

The morphology of latex particles was observed using TEM; and phosphotungstic acid (PTA) was employed as a staining agent. Figure 1 shows a representative image of core shell latex particles with above recipe. The TEM image has demonstrated that most particles have clear core shell structure with visible (dark) shell. This result is consistent with the fact of core shell particle volume larger than core particle volume in above size measurement.

Meantime, the particle distribution appears to be uniform as shown in TEM image. However, the polydispersity of core–shell particles and core particles is not significantly different.

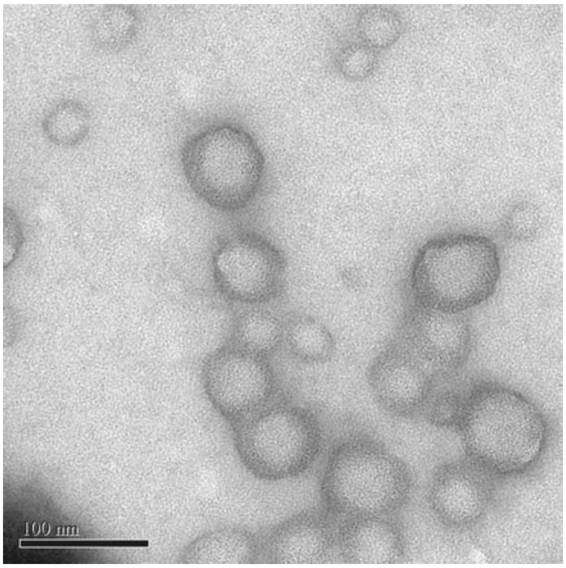


Fig. 1 TEM image corresponding to core–shell particles

Characterization of modified fibre

Surface-modification of wood fibres via cationic latex adsorption or deposition

Figure 2 presents the adsorption isotherms of latex on fibre surface. As can be seen, the latex adsorbed onto the fibre surfaces completely in the current range of latex addition (1.3–15.0 wt % on oven dried (o.d.) fibre, i.e., 0.13-1.50 g/L in fibre suspension), suggesting that the strong adhesion of cationic latex on fibres due to the electrostatic association between cationic latex and negative-charged cellulose fibres.

The thin films of cationic PBA-co-MMA/EHA-co-St on fibre surfaces could improve the fracture strength and the Zero-Span tensile of the wood fibre by the “elastic buffering” effect created by PBA-co-MMA/EHA-co-St layers. It should be noted that even those unadsorbed PBA-co-MMA/EHA-co-St latex, if entrapped into fibre networks mechanically, would also potentially enhance the mechanical properties and hydrophobicity of fibre networks. For the most samples prepared in this work,

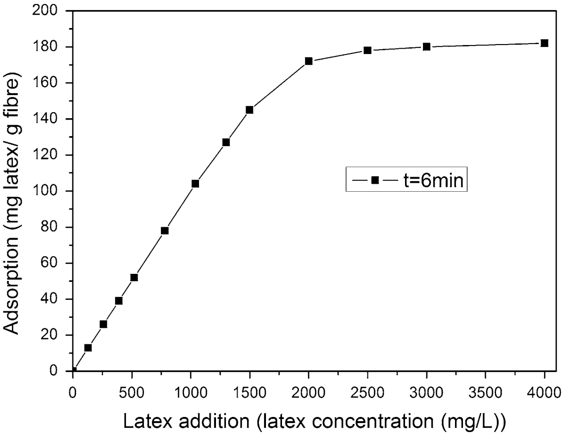


Fig. 2 Adsorption isotherm of latex CPBA-co-MMA/EHA-co-St on fibre surface. *Latex sample*: BA:MMA:EHA:St = 3:2:2:3 (mol/mol). [Fibre] = 10.0 g/L

the dosage of cationic PBA-co-MMA/EHA-co-St was controlled at 1.3–15.0 wt % on o.d. fibres.

Thermal analysis of modified fibres

The adsorption of cationic latex onto surfaces of fibre can also be confirmed by thermal analysis. The fibres were treated with 15 wt % latex and then washed with water for three times to remove the unadsorbed latex. As shown on Fig. 3a, there is only one decomposed temperature for untreated fibre (see Fig. 3b); whereas the treated one possesses two peaks (see Fig. 3c): one for fibre at 332 °C, and another for polymer film formed on the surfaces of fibres at 395 °C. More importantly, the adsorption amount is closed to the design value (i.e., 150 mg latex/g fibre). Similar behavior was observed for the samples containing relatively low content of latex.

Surface morphology of modified fibre

The morphology of fibres, revealed by SEM observation (see Fig. 4), indicates that the latex layer covers the fibre uniformly, thus smoothening the fibre surface. Even for the modified fibre without hot-press treatment, the surface of modified fibre appears to be as smooth as the one heat-treated; and no visible individual latex particles were observed on the surface yet. This could be attributed to the extremely small size of the latex and low glass transition temperature. The latex particles tend to form film immediately after the polymer particles adsorb onto the surface of fibre.

Impact of cationic latex on the water barrier property of the handsheets

Figure 5 shows the influence of different proportion of cationic latex added into pulp on the WVTR values of handsheets. Covering fibers with the thin films of hydrophobic polymer increased the hydrophobicity of fibre significantly (see Fig. 6). Meanwhile, the transfer of water vapor molecules through the handsheet was also retarded, especially with the sheet containing 10 % latex, which WVTR is reduced to 320 from 821 g/m^2 day, as shown in Fig. 5. The effective reduction of WVTR occurred at approximately 2.0 % of latex addition, though the overall the reduction on WVTR appears to be limited regardless of the latex dosages. Meanwhile, an increase in the ratio of shell monomers EHA and St appeared to lower the WVTR values, which is not surprising since shell monomers EHA and St are more hydrophobic than core monomers BA and MMA. Indeed, the coating of latex film on the surface of cellulose fibre decreased the WVTR of handsheet. This could be explained as following: The resultant cationic groups (i.e., quaternary ammonium salt) on the surface of latex promote their adsorption on the surfaces of cellulose fibres which are negative-charged. The repulsion between cationic particles prevents their homocoagulation and drives the particles to form monolayer of discrete particles on the natural fibre surface, which smoothed the paper surface and made it more homogeneous because the empty pores of cellulose structure, which contained nonpolar air, were filled with latex particles, thus, reducing transmission of water vapor.

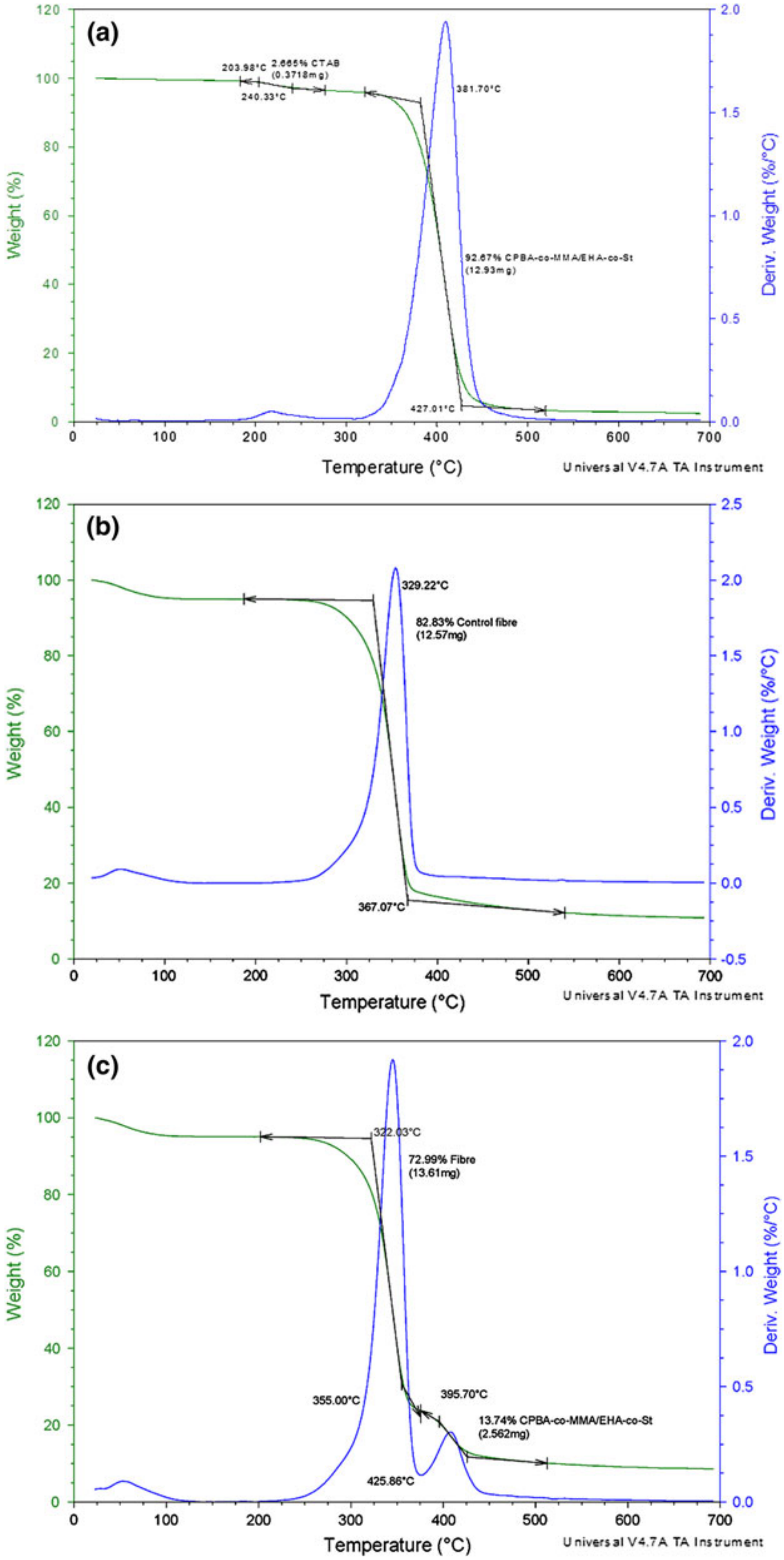
It is well known that the contact angle measurement is one of the most sensitive methods for providing information on the outer few angstroms of polymer surfaces and then was also performed at room temperature on handsheet surface to study the effect of latex thin films on fibre surface. The results, shown in Fig. 6, indicate that the contact angles of water on the surface of handsheet increased dramatically with the increasing of latex content; and reached the maximum (i.e., 106°) at 10 wt %, of latex (3:2:2:3). The high contact angle suggested that a stable hydrophobic surface of the handsheet or hydrophobic fibre network was created in the presence of the latex with core–shell structure. Moreover, the contact angle was increased substantially even at the latex dosage as low as 3.3 % (wt). Correspondingly, for the handsheet made from unmodified fibres, the water drop absorbed on paper surface instantly.

In conclusion, the adsorption of cationic latex on fibre surface indeed increases the contact angle of the handsheet significantly. However, significant improvement in hydrophobility does not necessarily lead to the considerable lowering of WVTR. Further fundamental research is required to reveal the mechanism of inhibiting water vapour transmission in paper products.

Impact of cationic latex on the strength of the handsheets

Figure 7 displays the influence of different proportion of cationic latex added into pulp on the tear and tensile strengths of the handsheets. The relative standard

Fig. 3 Thermal analysis of (**a**) CPBA-co-MMA/EHA-co-St (3:2:2:3, mol/mol), (**b**) untreated fibre and (**c**) CPBA-co-MMA/EHA-co-St (3:2:2:3, mol/mol) modified fibre (latex addition was 15 wt % on o.d. fibres)



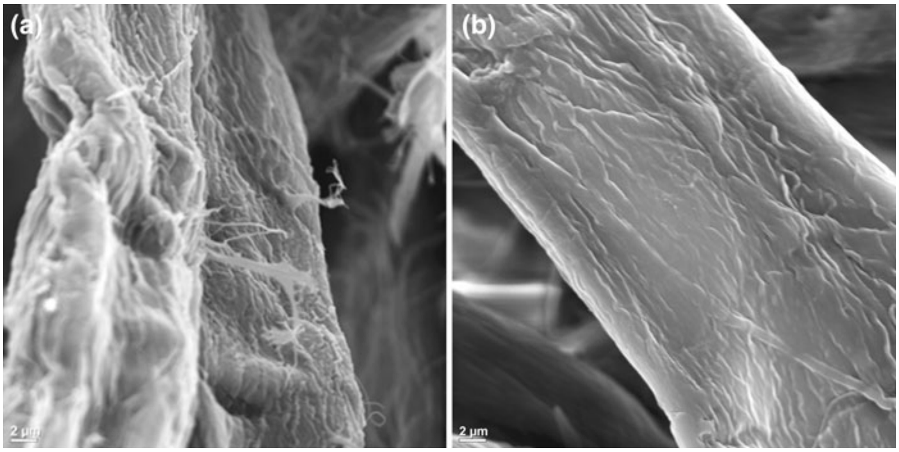


Fig. 4 SEM images of surface of (**a**) untreated fibre and (**b**) CPBA-co-MMA/EHA-co-St (3:2:2:3, mol/mol) modified fibre

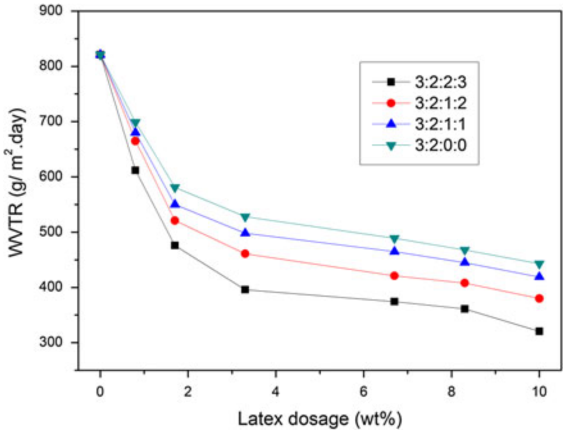


Fig. 5 WVTR of handsheet modified with CPBA-co-MMA/EHA-co-St latex as wet-end in different amount (Inside RH/outside RH = 76/2 %)

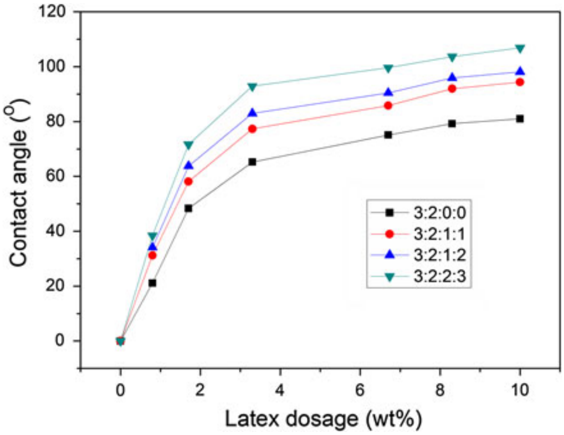


Fig. 6 Contact angle of handsheet modified with CPBA-co-MMA/EHA-co-St latex as a wet-end additive in different amounts

deviations for tensile and tear strengths ranged between 3 and 3.5 %. As can be seen from Figure, contrast to the control sample, the tensile strength and stretch of the handsheet prepared from modified fibers were improved at a low addition amount of latex and then decreased evidently as the latex addition was higher than 3.3 %. At a lower latex addition, latex deposits on the surface of fibres uniformly, forming a monolayer, which is more effective in developing contacts between the fibres. However, when latex addition was further increased, the film is no more uniform, the excess latex particles aggregate on the surface of fibre, which is less effective in developing contacts between the fibres or even weakens fibre bonding. Therefore, for the tensile strength and stretch enhancement, the amount of latex added should not beyond 3.3 %. It is of interest to note that tear strength had the same trend, implying that the latex might penetrate into fibre pores or lumen, thus increasing the fibre itself strength. These results seem to be different from those reported elsewhere (Fatehi et al. 2010; Fatehi and Xiao 2010). This might be attributed to the penetration of nano latex particles into porous structures of fibres, thus enhancing the strength of fibres themselves.

It is worth mentioning that the dosage of the latex addition at 3.3 % (wt) appeared to be critical or optimal for the current systems. At this dosage, both the increasing of hydrophobicity and the lowering of WVTR of the handsheets were significant; meanwhile, the strength of the handsheets was enhanced. Beyond this

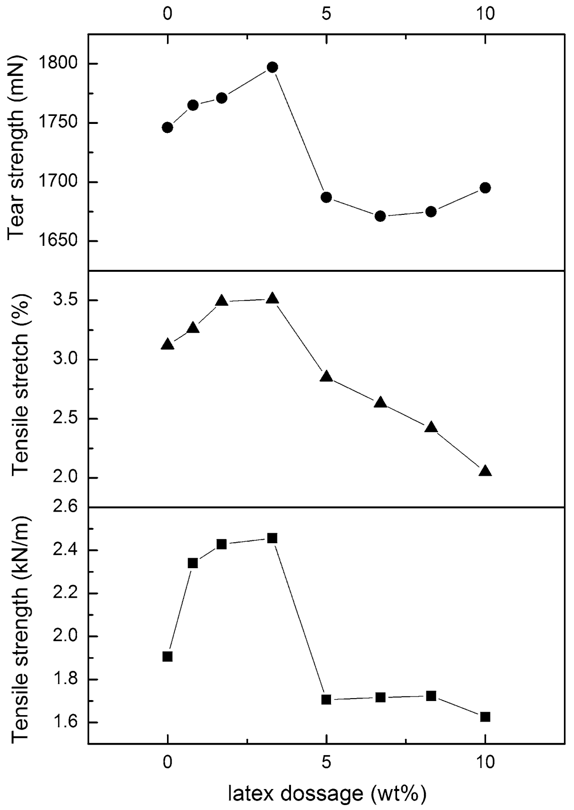


Fig. 7 Effect of cationic latex PBA-co-MMA/EHA-co-St (3:2:2:3, mol/mol) on the tensile and tear strength of handsheets

dosage, such effects became less significant; whereas the strength of the handsheets was even weakened. This might be associated with the appropriateness of the hydrophobic film structure created on cellulose fibre surfaces or within fibre networks. With such improved and balanced performance, the latex-modified paper would be promising as green-based packaging materials. Moreover, the high retention of the cationic nanosized latex with cellulose fibres also facilitates its application as a functional wet-end additive for value-added paper products. The as-synthesized latex developed in this work could also be used for surface treatment of cellulose fibre-based paper via a size press or coating process. The synergy between wet-end addition and coating is expected to further improve the barrier property.

Conclusion

In this work, cationic nanosized latex with core–shell structure, prepared via an emulsion copolymerization of BA-co-St/EHA-co-MMA using CTAB as surfactant was used for hydrophobic modification of cellulose fibre networks or handsheets. Due to the high retention of cationic latex within fibre networks after addition, the hydrophobicity of the modified handsheet was increased significantly. Meanwhile, the barrier performance in terms of WVTR as well as paper strength was also improved to some extent. The approach developed in this research gives a new way to enhance the hydrophobic properties of handsheet and has less negative impact on fibre bonding strength. The latex can be used as a functional wet-end additive, thus facilitating its application in papermaking process with the existing facilities. In the presence of 2–3.3 % of latex for fibre treatment, the overall performance of the resulting paper was optimized, which led to the paper with high hydrophobicity or contact angle, relatively low value of WVTR and enhanced mechanical properties.

Acknowledgments The research was financially supported by NSERC Strategic Network – Innovative Green Wood Fibre Product (Canada); the Dean Project of Guangxi Key Laboratory of Petrochemical Resource Processing and Process Intensification Technology and the Scientific Research Foundation of GuangXi University (Grant No. GXZ090126).

References

Delair T, Pichot C, Mandrand B (1994) Synthesis and characterization of cationic latex-particles bearing sulfhydryl-groups and their use in the immobilization of fab antibody fragmaents. Colloid Polym Sci 272(1):72–81

Fatehi P, Xiao H (2010) Effect of cationic PVA characteristics on fiber and paper properties at saturation level of polymer adsorption. Carbohyd Polym 79(2):423–428

Fatehi P, Liu X, Ni Y, Xiao H (2010) Interaction of cationic modified poly vinyl alcohol with high yield pulps. Cellulose 17:1021–1031

Garcia-Ubasart J, Colom JF, Vila C, Hernandez NG, Roncero MB, Vidal T (2012) A new procedure for the hydrophobization of cellulose fibre using laccase and a hydrophobic phenolic compound. Bioresource Technol 112:341–344

Hirvikorpi T, Vahaa-Nissi M, Vartiainen J, Penttila P, Nikkola J, Harlin A, Serimaa R (2010) Effect of corona pre-treatment on the performance of gas barrier layers applied by atomic layer deposition onto polymer-coated paperboard. Appl Surf Sci 257(3):736–740

Hult EL, Iotti M, Lenes M (2010) Efficient approach to high barrier packaging using microfibrillar cellulose and shellac. Cellulose 17(3):575–586

Landfester K, Bechthold N, Tiarks F, Antonietti M (1999) Miniemulsion polymerization with cationic and nonionic surfactants: a very efficient use of surfactants for heterophase polymerization. Macromolecules 32(8):2679–2683

Li WW, Matyjaszewski K (2011) Cationic surface-active monomers as reactive Surfactants for AGET emulsion

ATRP of n-butyl methacrylate. Macromolecules 44(14): 5578–5585

Liu Z, Xiao H (2000) Soap-free emulsion copolymerization of styrene with cationic monomer: effect of ethanol as a co-solvent. Polymer 41(19):7023–7031

Liu Z, Xiao H, Wiseman N (2000) Emulsifier-free emulsion copolymerization of styrene with quaternary ammonium cationic monomers. J Appl Polym Sci 76(7):1129–1140

Luo Y, Schork FJ (2001) Emulsion copolymerization monomer using interfacial of butyl acrylate with cationic redox initiator system. J Polym Sci Pol Chem 39(16):2696–2709

Ming W, Jones FN, Fu S (1998) Synthesis of nanosize poly (methyl methacrylate) microlatexes with high polymer content by a modified microemulsion polymerization. Polym Bull 40(6):749–756

Moraes RP, Zavecs I, Lauvernier P, Smeets NMB, Hutchinson RA, McKenna TFL (2012) The effect of cosurfactants and the initiator concentration on the polymer to surfactant concentration in nanolatexes. J Polym Sci Pol Chem 50(5):944–956

Nagai K, Ohishi Y (1987) Polymerization of surface-active monomers. 2. Polymerization of quarternary alkyl salts of dimethylaminoethyl methacrylate with a different alkyl chain-length. J Polym Sci Pol Chem 25(1):1–14

Patrizi ML, Diociaiuti M, Capitani D, Masci G (2009) Synthesis and association properties of thermoresponsive and permanently cationic charged block copolymers. Polymer 50(2):467–474

Ramos J, Martin-Molina A, Sanz-Izquierdo MP, Rus A, Borque L, Hidalgo-Alvarez R, Galisteo-Gonzalez F, Forcada J (2003) Amino-functionalized latex particles obtained by a multistep method: development of a new immunoreagent. J Polym Sci Pol Chem 41(15):2404–2411

Rhim JW, Ng PKW (2007) Natural biopolymer-based nanocomposite films for packaging applications. Crit Rev Food Sci 47(4):411–433

Ridaoui H, Jada A, Vidal L, Donnet JB (2006) Effect of cationic surfactant and block copolymer on carbon black particle surface charge and size. Colloid Surface A 278(1–3): 149–159

Rodionova G, Lenes M, Eriksen O, Gregersen O (2011) Surface chemical modification of microfibrillated cellulose: improvement of barrier properties for packaging applications. Cellulose 18(1):127–134