Organic Polymer Material Research

Volume 1 | Issue 1 | 2019 June
ISSN 2661-3875 (Online)

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Volume 1 Issue 1 • June 2019 • ISSN 2661-3875 (Online)

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Volume 1 | Issue 1 | June 2019 | Page 1-26
Organic Polymer Material Research

Contents

Editorial

Article

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Organic Polymer Material Research
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EDITORIAL

A Foreword from the Editor-in-Chief

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ARTICLE INFO

Article history
Received: 25 October 2019
Accepted: 29 October 2019
Published Online: 31 October 2019

Accompanying the development of petrochemical industry, great progress has been achieved in the organic polymer materials. It is well known that the conventional polymer materials usually consist of organosilicon polymers, polycarbonates, polyethylene, polyamide, polyurethane, polysulfone, phenolic resin and so on. Although their synthesis and applications have been well developed, the further research on them still has great significance. Moreover, natural polymers such as polysaccharides, tannins, cellulose also occupy an important position in the family of the organic polymer materials.

However, the basic performance and functionality of the organic polymer materials have been greatly improved. Therefore, the novel development direction of polymer materials especially functional polymer materials has gradually extended to medicine, communication, electronics, optoelectronics and other aspects. Among the functional polymers, conductive polymers including polyaniline, polypyrrole, polythiophene and their derivatives are an up-and-coming type, as opens a new era of the research on the organic polymer materials.

Smart polymers refer to a new type of materials with the ability to perceive environmental changes and accomplish the instruction and execution through self-judgment and conclusions. Thanks to their feedback function and close relation to bionics and information, their advanced design ideas have been hailed as a major leap in the history of materials science and they have become one of the important development directions for the organic polymer materials.

Because the biotechnology to synthesize polymers is much safer, more environmentally friendly and less expensive than traditional methods, the biopolymers comprising spider silk, polylactic acid fiber, chitin fiber, collagen fiber and sea alginic acid fiber have attracted much interest of the researchers and many achievements have been made. Besides, more improvements on the green synthetic chemistry and environmentally friendly processing have been achieved to solve the problems such as environmental pollution and energy shortage caused by the rapid development of the industry. Therefore, the study on the green polymers and biodegradable polymers has become active. Furthermore, due to the order of the molecular arrangement of the liquid crystal state and the high orientation of the molecules during the processing of the liquid crystal state, the liquid crystal polymers with a lot of excellent performance are becoming the research

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DOI: https://doi.org/10.30564/opmr.v1i1.1337

hot spot. In addition, polymer composites combine the excellent properties of the components to modify the performance of the original polymer due to their synergetic effect so that they are getting increasing attention from the scientists all over the world.

For this new journal, the scope of the Organic Polymer Material Research includes but is not limited to organosilicon polymers; polycarbonates; natural polymers including polysaccharides, tannins, cellulose; conductive polymers such as polyaniline, polypyrrole, polythiophene, and their derivatives; smart polymers; biopolymers; green polymers; biodegradable polymers; liquid crystal polymers; polymer composites. The papers about the research on the organic polymer materials beyond this scope are also warmly welcomed. Hopefully, this journal may offer a new platform for all the scientists in the field of the organic polymer materials.

Yanmin Wang
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ARTICLE

Alkali Treatment to Maximize Adhesion of Polypyrrole Coatings for Electro-Conductive Textile Materials

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ARTICLE INFO

Article history
Received: 9 July 2019
Accepted: 3 September 2019
Published Online: 30 October 2019

Keywords:
Polypyrrole
Electromagnetic Shielding
Alkali Treatment
Polyester Fabric

ABSTRACT

In this paper polyester fabrics were pretreated with alkaline solution to improve the ability for the fabric surface to bond with polypyrrole (PPy) coating layer. In situ chemical oxidative polymerization of pyrrole monomer was performed on alkali treated polyester fabrics. Then the fabrics were characterized by FTIR and XRD analysis. The tensile properties of the yarns in both warp and weft directions were measured after alkali treatment and PPy coating processes. The abrasion resistance test was performed on PPy coated fabrics with and without alkali treatment. The surface electrical resistivity of PPy coated fabrics were searched. The electromagnetic shielding effectiveness (EMSE) properties of fabrics in terms of reflection, absorption and transmission behaviors were also investigated. A significant EMSE value increase (about 27%) was obtained with alkali treatment.

1. Introduction

Polyesters are one of the most important classes of synthetic polymers that are presented in fibers, elastomers, high-performance composites, engineering thermoplastics, and thermosetting resins [1]. It has found widespread applications in textile industry including medical and automotive textiles, protective clothing, sports and active wear because of its excellent resistance to chemicals, stretching, abrasion and wrinkling properties [2]. Although it exhibits good properties, it has also undesirable hydrophobic and inactive surface characteristics that cause problems in coating and finishing processes. In order to remedy these problems, polyester fiber surfaces have been treated by atmospheric plasma [3], acidic [4], enzymatic [5, 6], and alkaline [7-9] solutions. The alkali treatment of polyester fibers has been widely investigated for the enhancement of dyeability, handle, hydrophilicity, and moisture regain properties of the fibers. During the alkali treatment, hydroxyl anions cause the hydrolytic scission of ester bonds of the polyester polymeric chains, resulting in changes in the polymerization degree and overall crystallinity [6].

Recently, usage of electronic devices and wireless systems has increased in daily life, and more attention is paid to electromagnetic interference (EMI) notion. Electromagnetic waves emitting from the electronic devices may lead to malfunction of other electronic equipment and affect human health negatively. Thus the undesirable radiation

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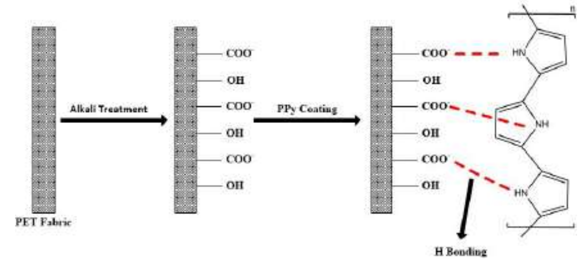
DOI: https://doi.org/10.30564/opmr.v1i1.1010

should be minimized by shields. Textile substrates are inherently insulator but they can be converted into conductive material by introducing metal fillers/coating [10,11] to the structure or by coating the surface with conductive polymers [12,13]. Metal coated materials exhibit very high electromagnetic shielding effectiveness (EMSE) about 40-100 dB but their shielding property is mainly based on reflection instead of absorption property because of their shallow skin depth. In contrast, conductive polymer coated textile surfaces show an absorption dominant shielding property towards electromagnetic waves [14].

Among the conductive polymers, polypyrrole (PPy) is the most promising one because of its high conductivity, good environmental stability, ease of synthesis, high temperature resistance, and less toxicological properties [14-16]. A number of studies have been conducted on PPy synthesis directly onto textile materials. In situ chemical oxidative polymerization of pyrrole monomer onto polyester fabrics has been performed using para-tolene-2-sulphonic acid monohydrate as dopant and ferric chloride hexahydrate as oxidant. The PPy coated polyester fabrics showed on average 8 dB EMSE value in 1-18 GHz frequency range [17]. Cotton fabrics have been coated by globular PPy and PPy nanotubes with in situ polymerization technique. The conductivity loss after washing and chemical cleaning processes has been investigated. Samples coated with PPy nanotubes exhibited higher fastness property against washing [18]. In order to enhance the adhesion of PPy layer on textile surfaces, various studies have been performed. For instance, polyamide 6.6 fabrics have been treated with ethanol, tetrachloroethylene, and formic acid at different times and temperatures. The most effective method on PPy deposition has been found as ethanol treatment [19]. In another researches, cold plasma discharge has been used to activate the polyester fabric surface prior to the PPy deposition [20,21]. Pyrrole monomer has been also functionalized by triethoxysilane to enhance the adhesion of PPy layer on polypropylene and viscose fabric surfaces [22]. For the catalytic activity enhancement of cotton and linen fabrics, nickel coating via electroless plating method has been employed before the in situ PPy deposition [23,24]. Cotton and polyester fabrics that are used in cell cultivation have been treated with NaOH in order to increase the adhesion of PPy layer [25].

Considering the all represented studies from literature, alkali treatment has never been used to improve the electromagnetic shielding activity of PPy coated fabrics. In this study, chemical oxidative polymerization of pyrrole monomer was carried out on polyester woven fabric surfaces. In order to increase the PPy amount and enhance the overall coating quality, samples were pre-treated by alkaline solution prior to the PPy coating. The experimental process can be seen in Scheme 1. By changing the alkali treatment duration, the surface electrical resistivity, EMSE, tensile properties, and abrasion resistance were all investigated.



Scheme 1. Schematic representation of the production of carboxyl groups on PET surface by hydrolysis, and formation of PPy layer on the fabric surface

2. Experimental

In the experimental process, a plain-weave polyethylene terephthalate (PET) fabric (95 g/m^2, 40 warp/cm, 32 weft/cm) was used. Sodium hydroxide (NaOH), hydrochloric acid (HCl), ethanol, and reagent grade pyrrole (Py) monomer were all purchased from Sigma-Aldrich and used as received. Ferric chloride hexahydrate ($FeCl_3.6H_2O$) was supplied from Merck.

Alkali treatment was applied to the fabrics prior to the PPy coating process. Fabric samples were cut into 10x10 cm dimensions and immersed in an aqueous solution of NaOH (4 mol/L) at 70 ^oC for various durations (0.5-2.5 h). They were then washed with ethanol and 1 M HCl solution respectively in order to neutralize the fabric surface, and dried in open air [7]. The weight loss after alkali treatment process was measured as about 6.5 %. The in-situ chemical oxidative polymerization process was performed as follows; fabric sample was laid out in a glass vessel containing 1 M Py solution in distilled water at room temperature. After 0.5 h mixing with magnetic stirrer, 0.5 M $FeCl_3$ solution in distilled water was added to the vessel dropwise in 30 minutes to initiate the reaction. The polymerization reaction was ended after 2 h when the characteristic black color of PPy was observed in the whole fabric surface. Several washing cycles were applied to the samples with ethanol, 1 M HCl solution, and distilled water, and then the samples were dried in open air [26].

The FTIR spectra (Perkin Elmer Spectrum 100 FTIR) were obtained from the fabric surfaces after alkali treatment and PPy coating processes with the help of an ATR sampling holder. X'Pert^3 X-ray diffractometer (PANalytical, USA) was used to analyze crystal structure of untreated, alkali treated and PPy coated fabrics in steps of 0.017. The formation of a PPy layer in both samples with and without alkali treatment, was investigated by a light microscopy (OLYMPUS CH-2) equipped with image capturing software (Kameram KSCMOS/1). Surface electrical resistivity of the PPy coated samples were measured using a Keithley 6517A Electrometer/High Resistance Meter instrument according to the ASTM D257-07 standard [27]. A Network Analyzer (ROHDE&SCHWARZ) was used for EMSE measurement with the coaxial transmission line method in 0-3 GHz according to ASTM D4935-10 standard [28,29]. Tensile testing from the yarns was performed using an Instron 4411 in both warp and weft directions on the alkali treated samples both before and after PPy coatings [30]. Each sample was measured 5 times and the average of these results were taken in order to increase the accuracy of the tensile testing. Abrasion resistance test was performed on PPy coated fabrics without alkali treatment and with 2 h alkali treatment according to ISO 5470-1 standard by using a Martindale pilling and abrasion instrument [31].

3. Results and Discussion

3.1 FTIR Spectroscopy

Figure 1 shows the FTIR spectra of the polyester fabrics both before and after alkali treatment as well as PPy coating processes. Considering the untreated and alkali treated fabric samples, there was no significant changes in FTIR spectra. Only slightly changes were observed in peak intensities after alkali treatment process. These intensity changes can be explained by the conformational changes of crystalline and amorphous regions of polyester's structure after the alkali treatment [32]. In the spectra of untreated polyester fabric, the strong carbonyl stretching band at 1719 cm^{-1} was slightly moved to a lower wavenumber (1717 cm^{-1}) due to the 2 h alkali treatment [7]. In the spectra of PPy coated polyester fabric, some newly formed peaks were observed, verifying the PPy formation. The peaks at 735 and 1094 cm^{-1} are the characteristic peaks of PPy, correspond to the N-H plane inner deformation peaks that occur in the deprotonation process. The peaks at 1037 and 1303 cm^{-1} come from the =C-H in plane bending vibration from the PPy ring. The peak at 911 cm^{-1} refers to =C-H out of the plane bending vibration while the peak at 1547 cm^{-1} belongs to C=C stretching, respectively [33, 34].

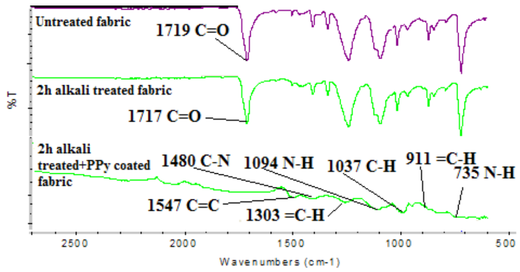


Figure 1. FTIR spectra of untreated, 2h alkali treated, and PPy coated polyester fabric samples

3.2 X-Ray Diffraction Analysis

The effect of alkali treatment and PPy coating on polyester fabric was analyzed using X-ray diffraction analysis with a scanning range in 2Θ from 10 to 40^{o} at a scan speed of 10^{o} per minute. Figure 2 (a) and (b) shows X-ray diffraction patterns of untreated, alkali treated and PPy coated polyester fabrics. Figure 2 (a) shows that there is no significant change in polyester after alkali treatment. Apparently, the characteristic peaks of polyester at 18^{o}, 23^{o} and 26^{o} are presented in all X-ray diffraction patterns [35]. According to the characteristic XRD patterns of PPy, a broad peak, indicating the amorphous structure of PPy, should be observed in around 23^{o} [16]. Figure 2 (b) does not show any distinct peak of PPy suggesting that the characteristic peak of PPy in diffraction pattern is merged with peaks of polyester in the range between $23\text{-}26^{0}$. Therefore, it can be said that alkali treatment does not affect the crystal structure of polyester and the peaks of PPy almost overlap with polyester peaks.

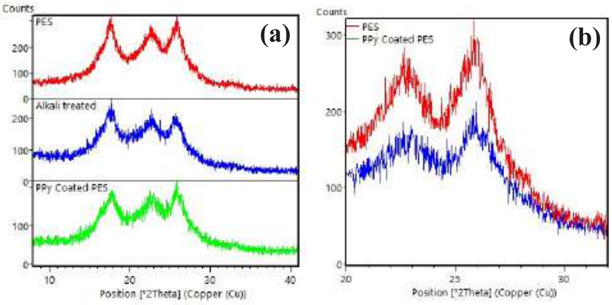


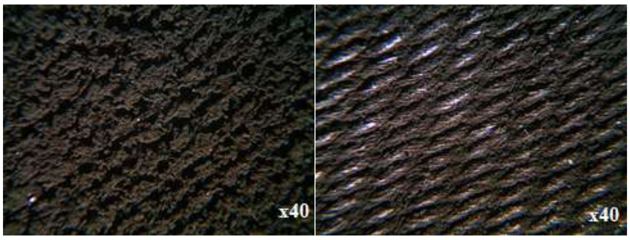
Figure 2. (a) X-ray diffraction patterns of untreated, alkali treated and PPy coated polyester fabrics. (b) Peak resolution diffraction patterns of untreated and PPy coated polyester fabrics

3.3 Light Microscopy Imaging

The light microscopy images of the PPy coated samples without alkali treatment (a) and with 2h alkali treatment (b) can be seen in Figure 3. When the sample is directly coated with PPy, the PPy formation occurs only on the surface layer of the fabric. PPy particles cannot penetrate among the warp/weft yarns, and agglomeration of PPy particles can be observed (Figure 3a). Whereas when the alkali treatment was applied prior to the PPy coating process, a more uniform PPy coating can be observed without any agglomeration (Figure 3b). Due to the hydrolysis of polyester surface

DOI: https://doi.org/10.30564/opmr.v1i1.1010

by sodium hydroxide solution, carboxyl groups are formed on polyester structure. The formation of strong hydrogen bonding (Scheme 1) between the newly formed COO^- groups of the alkali treated polyester and NH groups of the PPy, supplies a good penetration of PPy layer on polyester without any agglomeration (Figure 3b) [7].



(a) (b)

Figure 3. Light microscopy images of the PPy coated samples (a) without and (b) with alkali treatment

3.4 Surface Electrical Resistivity

Table 1 shows the weight uptake and surface electrical resistivity values of the samples after PPy coatings for various alkali treatment times. Accordingly, when a fabric without any alkali treatment was coated with PPy, a weight uptake of 15.8 % was observed. In alkali treated samples, the weight uptake value reached up to 59.7 %. Weight uptake values increased monotonically with increasing alkali treatment time. Considering the surface electrical resistivity values, the lowest resistivity in other words the highest conductivity was observed when the fabric was treated for 2h in alkaline solution prior to the PPy coating process. The sample with 2 h alkali treatment showed more than ten times higher conductivity in comparison to the sample without alkali treatment. Although the sample with 2.5 h alkali treatment showed a great level of PPy uptake, it also showed a lower electrical conductivity. This is due to the excessive PPy agglomeration and non-uniform coating on the fabric surface.

Table 1. Weight increment and surface electrical resistivity values of the samples after PPy coating

Alkali Treatment Time (h)	Weight Uptake After PPy Coating (%)	Surface Electrical Resistivity (ohm/sq)
No treatment	15.8	2.9 x 10^3
0.5	22.3	1.9 x 10^3
1	26.4	1.4 x 10^3
1.5	32.1	5.2 x 10^2
2	37.3	4.8 x 10^2
2.5	59.7	5.6 x 10^2

3.5 EMSE Measurement

The EMSE values of the PPy coated fabric samples with various alkali treatment times can be seen in Figure 4. Accordingly, all the samples showed a better EMSE results in the 2000-2500 MHz frequency range. The highest EMSE value of 12.06 dB was observed at 2115 MHz in the 2 h alkali treated sample, whilst the sample without alkali treatment showed the lowest EMSE value of 9.5 dB at this frequency. Alkali treatment leads an up to 27 % increase in EMSE results, due to the deeply penetration and good bonding of PPy layer on polyester structure.

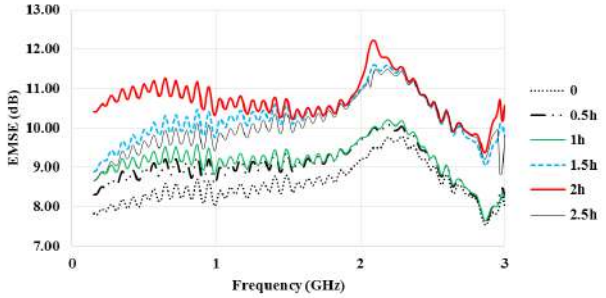


Figure 4. EMSE values of PPy coated fabrics with various alkali treatment durations

Table 2 shows the shielding effectiveness (SE), absorption (A), reflection (R) and transmission (T) values of PPy coated fabrics with various alkali treatment times. Results were given specifically at the frequencies of 1005, 1500, 1800, and 2505 MHz because they are the mostly exposed

Table 2. Shielding effectiveness (SE), absorption (A), reflection (R) and transmission (T) values of the PPy coated fabrics for various alkali treatment durations

Alkali Treatment Time (h)	Frequency (MHz)															
	1005				1500				1800				2505			
	SE (dB)	A	R	T	SE (dB)	A	R	T	SE (dB)	A	R	T	SE (dB)	A	R	T
0	**8.18**	0.73	0.12	0.15	**8.72**	0.70	0.16	0.14	**8.73**	0.78	0.08	0.14	**9.02**	0.85	0.03	0.12
0.5	**8.73**	0.72	0.14	0.14	**9.28**	0.69	0.19	0.12	**9.25**	0.78	0.10	0.12	**9.26**	0.85	0.03	0.12
1	**9.00**	0.74	0.13	0.13	**9.35**	0.70	0.18	0.12	**9.28**	0.79	0.09	0.12	**9.30**	0.85	0.03	0.12
1.5	**9.94**	0.65	0.24	0.11	**10.49**	0.60	0.31	0.09	**10.49**	0.74	0.17	0.09	**10.61**	0.83	0.09	0.08
2	**10.50**	0.73	0.18	0.09	**10.61**	0.68	0.23	0.09	**10.48**	0.79	0.12	0.09	**10.68**	0.86	0.05	0.09
2.5	**9.62**	0.72	0.17	0.11	**10.27**	0.68	0.23	0.09	**10.36**	0.79	0.12	0.09	**10.64**	0.85	0.07	0.08

DOI: https://doi.org/10.30564/opmr.v1i1.1010

frequencies emitting from electronic devices in daily life. As mentioned, conductive polymer coated materials are intended to absorb the electromagnetic waves instead of reflect or transmit them [14]. The highest electromagnetic wave absorption value of 0.86 was obtained in the 2 h alkali treated sample. Increasing the alkali treatment duration caused a small decline in shielding efficiency and absorption values, due to the agglomeration of PPy layer on fabric surface.

3.6 Abrasion and Tensile Testing

Abrasion test was employed in order to observe the effect of alkali treatment on PPy deposition. The abrasion test was performed based on the mass loss percentage after 100 cycle abrasion on a standard wool fabric [31]. Accordingly, PPy coated fabrics without alkali treatment and with 2 h alkali treatment showed 13.2 % and 4.5 % weight loss values after 100 cycle abrasion, respectively. This result shows that alkali treatment increased the adhesion of PPy layer on fabric surfaces. In other words, in the alkali treated fabrics, PPy deposition penetrated more deeply on fabric surface whereas in PPy coated fabric without alkali treatment, the weight loss was high, the PPy layer agglomerated on fabric surface and it was easily removed from the surface with abrasion.

Tensile strength and elongation at break values of both warp and weft yarns before and after PPy coating are given in Figure 5 and Figure 6, respectively. In general, alkali treatment and PPy coating processes both caused decline in strength and elongation for all samples because of the brittle nature of PPy structure and degradation/hydrolysis of polyester polymer chains exposed to the alkali solution. In Figure 5, it can be seen that the tensile strength value of the untreated warp yarn is about 37 cN/tex, and after PPy coating it decreased to 35 cN/tex. Considering the alkali treatment process, up to 65 % tensile strength loss was observed in 2.5 h alkali treated sample. In the 2 h alkali treated samples, the PPy coating process caused an increase in tensile strength for both warp and weft yarns in comparison with the uncoated samples because of the uniform PPy formation on the yarn surface.

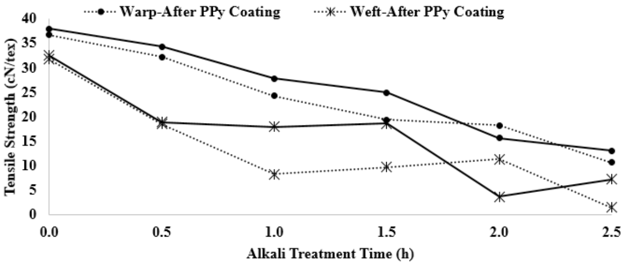


Figure 5. Tensile strength values of the polyester warp/weft yarns before and after PPy coating

The elongation at break values of weft and warp yarns before and after the PPy coating process can be seen in Figure 6. For all the samples, the elongation behavior was decreased with increasing alkali treatment time. An average 52 % elongation loss was observed in 2.5h alkali treated sample. The brittleness of PPy layer on the yarn surface prevents the elongation extension of the yarn, thus the elongation value decreased after PPy coating. Alkali treatment resulted in the deformation of polymeric chains and a decrease in the chain length. Therefore the elongation of the yarn decreases after alkali treatment.

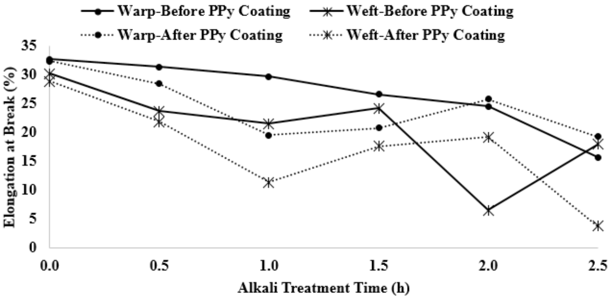


Figure 6. Elongation at break values of the polyester warp/weft yarns before and after PPy coating

4. Conclusions

Chemical oxidative polymerization of Py monomer on woven polyester fabric surfaces was performed. Fabrics were treated by alkaline solution prior to the PPy coating process. The effects of the alkali treatment time on EMSE, surface electrical resistivity, tensile properties, and abrasion resistance were investigated. The formation of PPy layer on the fabric surface was proven by FTIR and XRD analysis. Light microscopy images showed that a much more uniform PPy layer was obtained on the alkali treated fabric surface. Weight uptake value after PPy coating process increased with increasing alkali treatment time. The least surface electrical resistivity of 4.8 x 10^2 ohm/sq and the highest EMSE value of 12.06 dB were obtained in the 2 h alkali treated sample. Although the highest PPy amount was obtained in the 2.5 h alkali treated sample, the EMSE and conductivity values were not the highest in this sample because of the agglomeration of PPy on the surface. Due to the brittle nature of PPy as well as the deformation of the polymeric chains with alkali treatment, both tensile strength and elongation at break values were all decreased with the introduction of the PPy coating and increasing alkali treatment time. A greater weight loss against abrasion was recorded on the PPy coated fabric without alkali treatment. All results are in a good agreement that is alkali treatment caused a better penetration and bonding property of PPy layer to the polyester fabric surface due to the formation of strong hydrogen bonding between newly formed carboxyl groups on polyester and NH groups of PPy.

Funding

This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors.

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Organic Polymer Material Research
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ARTICLE

Rheological and MECHANICAL Performance of Asphalt Binders and Mixtures Incorporating $CaCO_3$ and LLDPE

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ARTICLE INFO

Article history
Received: 11 July 2019
Accepted: 19 August 2019
Published Online: 30 October 2019

Keywords:
Asphalt modification
Binder rheology
Mineral filler
Mixture performance
Plastic

ABSTRACT

This study was conducted to assess the performance of modified asphalt binders and engineering properties of mixtures prepared with incorporation 3 vol% and 6 vol% of calcium carbonate ($CaCO_3$), linear low-density polyethylene (LLDPE), and combinations of $CaCO_3$ and LLDPE. The rheological properties of control and modified asphalt binders were evaluated using a series of testing such as rotational viscometer (RV), multiple stress creep recovery (MSCR) and bending beam rheometer (BBR) tests. Meanwhile, four-point beam fatigue test, the dynamic modulus (E*) test and tensile strength ratio (TSR) test were conducted to assess the engineering properties of asphalt mixtures. Based on the findings, the RV and MSCR test result shows that all modified asphalt binders have improved performance in comparison to the neat asphalt binders in terms of higher viscosity and improved permanent deformation resistance. A higher amount of $CaCO_3$ and LLDPE have led modified asphalt binders to better recovery percentage, except the asphalt binders modified using a combination of $CaCO_3$ and LLDPE. However, the inclusion of LLDPE into asphalt binder has lowered the thermal cracking resistance. The incorporation of $CaCO_3$ in asphalt mixtures was found beneficial, especially in improving the ability to resist fatigue cracking of asphalt mixture. In contrast, asphalt mixtures show better moisture sensitivity through the addition of LLDPE. The addition of LLDPE has significantly enhanced the indirect tensile strength values and tensile strength ratio of asphalt mixtures.

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DOI: https://doi.org/10.30564/opmr.v1i1.1015

1. Introduction

The most critical issue and the challenge of asphalt pavement in the cold regions is thermal or low-temperature cracking. Though, the performance of asphalt pavement at high temperature is similarly crucial to take into consideration to ensure long service life. As a visco-elastic material, the performance of bituminous material heavily depends on both temperature and time [1,2]. The modulus of asphaltic concrete pavement can be varied; high during winter conditions and low in hot summer days [3]. The visco-elastics characteristics of asphalt binder enable the asphalt binder to flow at elevated temperature, and it also can withstand a long loading time. Anyhow, due to its elastic characteristics that present in the asphalt binder, the asphalt binder tends to become brittle at a reduced temperature as well as only able to sustain short loading time. The brittle characteristics of asphalt binders during low temperature could result in thermal cracking failure which would be the principal reason to the premature pavement problems. Contrarily, rutting commonly develops during the hot seasons, when the asphalt is softer. Asphalt binder consists of a complex chemical mixture, which mainly differs in size and components of hydrocarbons, as well as different elements in the functional group, such as nitrogen, hydrogen, and sulphur atoms [4]. The asphalt material also consists of organic molecules, where the molecules can react with oxygen from the surrounding area. The extent of ageing and oxidation reactions are greatly influenced by temperatures, types of modifier and concentration, which could make the binder stiffer and brittle throughout the time. Aging and oxidation reactions significantly affect the short and long-term performance of pavement materials [5-8].

Over the years, polyethylene (PE) resin had been utilized in pavement material to modify the performance of asphalt binders and mixtures [9-14]. The usage of polyethylene and polypropylene as binder modifiers could enhance the resistance to permanent deformation under traffic loading since both of this materials are characterized as plastomers, which can increase the stiffness of the modified binders [9,10]. Polacco et al. [9] reported that the PE related modifiers were strongly biphasic, where the material tended to separate into asphalt-rich and polymer-rich phases. However, LLDPE demonstrated greater compatibility with asphalt, which strongly improved the mechanical properties of modified asphalt binder in comparison to the base asphalt binder. The presence of LLDPE modifier in the asphalt binder has a substantial reaction with the asphalt through a continuum matrix of the polymer chains. The polymer continuum matrix permitted the modified asphalt to exhibit a polymer-like behaviour even though insufficient polymer content. Besides that, Drozdov and Yuan [15] specified that the morphology of polyethylene is influenced by a certain degree of stress and deformation due to the movement of chains that occurred at the nodes. Fang et al. [14] concluded that additions of LLDPE waste had improved the softening point of the modified asphalt binder from 47 °C to 76 °C, which lead to a reduction in ductility and penetration values. These results indicated that LLDPE has significantly improved the high-temperature behaviour and viscoelasticity of bitumen.

Furthermore, the author stated that the LLDPE is denoted by a multi-branching structure comprising of a long chain of linear molecules with alkyl and methyl-branched chains. These two materials are not thermodynamically incompatible; where the materials were not completely dispersed at the molecular level, due to delimitation between the materials. Through this combination, the individual components of asphalt reacted with LLDPE molecules chains causing them to swell and link together. It allowed the modified asphalt binder to absorb more energy and improve performance at high temperature [16 17].

Limestone or calcium carbonate ($CaCO_3$) is an inert material that came into regular use as an additive in asphaltic concretes in the 1980s [18]. The powder form of hydrated lime exhibits higher surface area which contributes towards rapid chemical reaction. The ions present in the interface of aggregates and asphalt binder electrically repelled each other since both the material comprises acids. In order to improve the adhesion bonding of both materials, alkali in the form of hydrated lime was added to neutralize the acidic conditions by introducing the opposite-charge ions that could strengthen the adhesion bonding [19]. Additionally, the usage of lime in asphalt mixture is not only limited as an anti-stripping agent, but it may also be used to increase the asphalt mixture stiffness, reduce plasticity index if clays exist and reduce the oxidation rate [18,19]. However, the amount of $CaCO_3$ and the proper preparation method to be used is critical to ensure the effectiveness of improving the performance of asphalt materials [20].

The two approaches that are typically used to add polymers to the asphalt binder, which are dry and wet methods. In general, the dry method can be done by adding the polymer directly into the aggregate, before incorporating the binder during the asphalt mixture preparation process. This process requires an adequate mixing duration to ensure the polymer homogeneously disperses in the asphalt mixture. However, in regards to the wet process, the polymer material is initially mixed with the asphalt binder at designated temperature prior to mixing with the aggregate.

DOI: https://doi.org/10.30564/opmr.v1i1.1015

The mixing temperature and duration as well will depend on the type of asphalt binder and polymer material [21,22].

The scope of this study covered investigations on the bitumen behavior and the engineering properties of asphalt mixtures prepared with the addition of different amounts of $CaCO_3$ powder, LLDPE plastic, and modifier contained the combination of both LLDPE and $CaCO_3$. The rheological properties of asphalt binders were evaluated based on the standard Superpave specification tests. These include volatile loss test, rotational viscometer (RV) test, dynamic shear rheometer (DSR) test and bending beam rheometer (BBR) test. Then, the asphalt mixture specimens were assessed using the four-point beam fatigue test, the dynamic modulus (E*) test, and modified Lottman test. During the sample preparation, the wet process was adopted, where the modifier was mixed with bitumen at designated temperature prior to use in the asphalt mixture preparation.

2. Materials

2.1 Asphalt Binder and Aggregate

The main materials used in this study were obtained from Payne & Dolan Inc, located in Hancock, Michigan. The PG 58-28 was selected as a control binder. The aggregate gradation adopted for the preparation of asphalt mixtures was based on the Michigan Department of Transportation (MDOT) as shown in Table 1. The course and fine aggregates used in this study were basalt and natural sand, respectively. The nominal maximum aggregate size is 12.5 mm, and the designed traffic level is less than 3 million equivalent single axles loads (ESALs) based on the current Superpave asphalt mixture design practice.

Table 1. Aggregate gradation for the preparation of asphalt mixtures

Sieve Size (mm)	Percent Passing (%)
19.00	100.0
12.50	94.0
9.50	86.3
4.75	68.2
2.360	49.2
1.18	38.4
0.60	27.8
0.30	15.0
0.15	6.7
0.075	4.5
Pan	0.0

2.2 Linear Low-Density Polyethylene

The Dow Chemical Company supplied the linear low-density polyethylene (LLDPE) pellet resin as shown in Figure 1(a) was used in this study. The physical appearance of the pellets is white in colour and odourless [23]. The density of the pellets is 0.917 g/cm^3. It was used as–received.

2.3 Calcium Carbonate

Ground calcium carbonate ($CaCO_{3,}$ uncoated) was used as a filler material in the production of asphalt modifiers. The $CaCO_3$ (Figure 1(b)) used was supplied by Specialty Minerals Inc. [24]. The material is characterized by superior brightness, and controlled particle size (mean particle size = 3.5 µm, +325 mesh = 0.004 wt%). The $CaCO_3$ consists of 97 wt% $CaCO_3$, 0.5 wt% Magnesium Carbonate ($MgCO_3$), less than 0.1 wt% Iron as (Fe_2O_3), and less than 0.2 wt% moisture content [25]. The specific gravity of this material is 2.7, which is higher compared to other modifiers used in this study. The $CaCO_3$ was used as-received and has a surface area of 3.1 m^2/g.

2.4 Polyethylene-Calcium Carbonate (PECC) Pellets

PECC pellet (Figure 1(c)) was produced by combining LLDPE resin and $CaCO_3$ powder using American Leistritz Extruder Corporation model ZSE 27 (Figure 2(a)). The extrusion equipment is equipped with a co-rotating intermeshing twin-screw extruder with numbers of heating zones. Schenck AccuRate gravimetric feeders were utilized to regulate the quantity of LLDPE accurately, and $CaCO_3$ supplied into the extruder. Then, the polymer strands enter a long water bath and cut to 3mm nominal length. Then, the pelletized composite resin was dried in an indirect heated dehumidifying oven (Figure 2(b)) at 60 ^oC for 7 hours. It was then kept in sealed moisture barrier bags before mixing with asphalt binder [26].

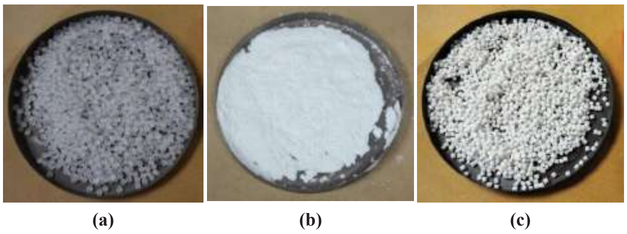
(a) (b) (c)

Figure 1. (a) LLDPE Pellets, (b) CaCO3 Powder, (c) PECC Pellets

DOI: https://doi.org/10.30564/opmr.v1i1.1015

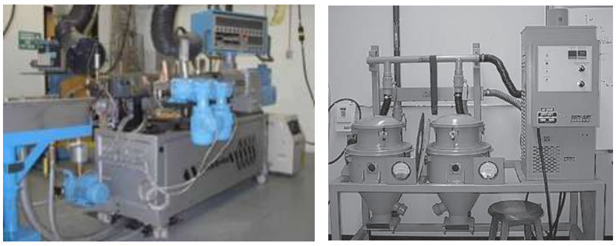

Figure 2. (a) 27mm Twin Screw American Leistritz Extruder, (b) Air Dryer dehumidifying oven

3. Specimen Preparation

3.1 Preparation of Modified Asphalt Binder

A high shear mixer was used for the preparation of modified asphalt binders. The shear mixer was used to ensure the modifiers are consistently dispersed in the asphalt binder at designated speed and time interval. The temperatures used to produce modified asphalt binders are shown in Table 2. During the production of modified asphalt binder, approximately 500g of asphalt binder PG58-28 was transferred into a one-litre metal can. Prior to the blending process of modifier with asphalt binder, the required quantity of modifier was added into the similar metal can that contain asphalt binder and was heated up in an oven at the designated temperature for two hours. Later, the asphalt binder and modifier were blended using a high shear mixer at the specified rotational speed of 5000 rpm for 45 minutes. In this study, due to great differences in density between LLDPE and $CaCO_3$, the amounts of modifiers were controlled based on the volume of asphalt binder. The quantities of modifier incorporated in the asphalt binder are summarised in Table 2.

Table 2. Temperatures used for modified asphalt preparation

Sample Designations (% is based on volume)	Modifier	Production Temperature (°C)
3 vol% LLDPE	LLDPE pellets	175
6 vol% LLDPE		
3 vol% $CaCO_3$	$CaCO_3$ powder	160
6 vol% $CaCO_3$		
3 vol% PECC	PECC pellets	170
6 vol% PECC		

3.2 Preparations of Asphalt Mixture

The asphalt mixture was mixed using a bucket mixer. The loose mixture was then compacted using gyratory compactor with 86 gyrations. In order to simulate the short-term ageing process that typically took place during the production of asphalt mixture, the loose asphalt mixture was conditioned in an oven for two hours. The compaction process takes place after the short-term simulation process. The Superpave specifications [27-29] were referred.

4. Asphalt Binder Behaviour

4.1 Volatile Loss

The quantification of asphalt binder volatiles lost (mass loss) during the short-term ageing process was conducted through the rolling thin film oven (RTFO) test. In this test, the light molecules from binder were driven off, increasing the asphalt's viscosity. The process was done by inducing the occurrence of heat and flowing air on a thin film of asphaltic material. Table 3 shows the mean mass loss test results. Most of the binders have low volatiles lost during the ageing process, where the values are less than one wt% of asphalt binder based on the Superpave Specification. The 6 vol% LLDPE sample has exhibited the highest volatile loss, which is about 0.116 wt% of asphalt binder. This indicates the modification process using LLDPE and $CaCO_3$ are not results in changes of the chemical structure of the asphalt binder. According to a study conducted by Fang et al. [14], the asphalt binder modified with a higher percentage of modifier has higher mean mass loss value, except the PECC's modified asphalt binder that presented the opposite trend.

Table 3. Mean mass loss values using RTFO aging process

Sample (% is based on volume of asphalt binder)	Results (Mean Mass Loss ± Std Dev, n=3)
PG58-28	0.097±0.0010 wt%
3 vol% $CaCO_3$	0.095±0.0030 wt%
6 vol% $CaCO_3$	0.105±0.0005 wt%
3 vol% LLDPE	0.097±0.0005 wt%
6 vol% LLDPE	0.116±0.0040 wt%
3 vol% PECC	0.105±0.0020 wt%
6 vol% PECC	0.094±0.0030 wt%
*Requirement: Percent loss should be less than 1 wt%	

4.2 Rotational Viscosity

The rotational viscometer with #27 spindle was used to evaluate the viscosity of asphalt binders at service temperature. It is essential to ensure the asphalt binder

DOI: https://doi.org/10.30564/opmr.v1i1.1015

is pump-able and ease to handle prior to use in the mixture production stage, and in an ideal condition for the compaction in the field. This test examines the torque value needed to uphold a constant rotational speed (20 rpm) of a cylindrical spindle under a consistent temperature. The recorded torque value is then presented as viscosity.

The mean rotational viscosity test results are presented in Figures 3 to 5. The addition of modifier in asphalt binder results in higher viscosity compared to the neat binder (PG58-28). Higher percentages of modifiers have led to higher viscosity values. Adding LLDPE to asphalt binders has considerably increased the asphalt binders' viscosity and stiffness, which can be contributed to better resistance to rutting. The asphalt binder prepared with 6 vol% LLDPE indicates the highest viscosity compared to other modified asphalt binders. Whereas it has been translated into proportionally higher mixing and compaction temperature compared to PG 58-28 (Table 4). All samples are found to fulfil the Superpave requirement on rotational viscosity's value, whereas the RV readings should be lower than 3 Pa·s at 135 °C.

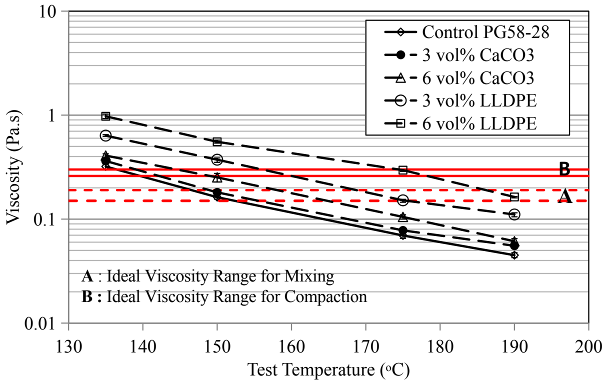

Figure 3. Effects of $CaCO_3$ and LLDPE modifiers on asphalt viscosity

Referring to Figure 3, addition of $CaCO_3$ into asphalt binders has escalated the binder viscosity, which is in a range of 13 – 23.1% and 27.3 – 55.1% for the asphalt binders modified with 3 vol% $CaCO_3$ and 6 vol% $CaCO_3$, respectively. A higher amount of $CaCO_3$ has led to a higher viscosity as a result of the presence of lime powder that increase the stiffness of binders. The presence of LLDPE molecules in asphalt binders has further increased the viscosity of the asphalt binders. The 3 vol% LLDPE's modified asphalt binder has doubled the neat asphalt binder's (PG 58-28) viscosity. Meanwhile, the modified asphalt binder prepared with 6 vol% LLDPE was found to have the highest viscosity compared to other modified asphalt binders, and three times greater compared to the neat asphalt binder.

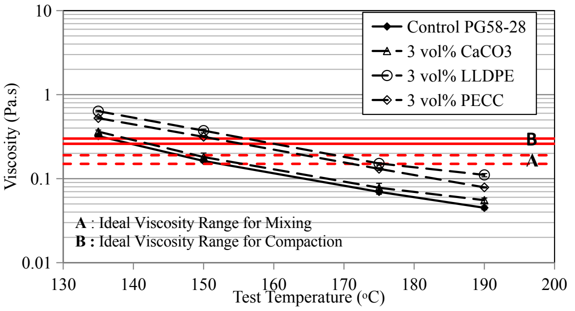

Figure 4. The viscosity of modified asphalt binders at 3 vol% of asphalt binder

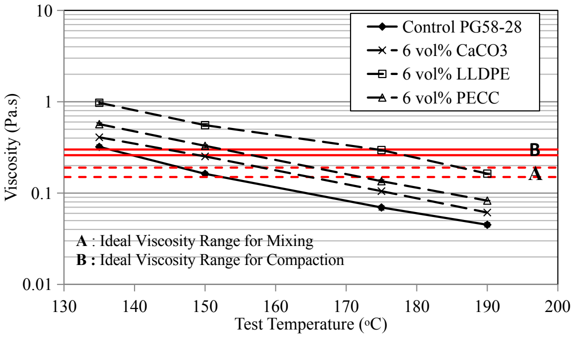

Figure 5. The viscosity of modified asphalt binders at 6 vol% of asphalt binder

Figures 4 and 5 illustrate the outcomes of asphalt binders modified using LLDPE, $CaCO_3$, and PECC modifiers. Modified asphalt binders prepared using a combination of LLDPE and $CaCO_3$ (PECC modifier) have lower viscosity value compared to LLDPE's modified asphalt binder. The presence of $CaCO_3$ in PECC's modified asphalt binder has tuned down its viscosity compared to LLDPE's modified asphalt binders. This result could be correlated to a research conducted by Zhou et al. [30].

The optimal mixing and compaction temperatures for an asphalt mixture as stated by the Asphalt Institute are at a viscosity of 0.17 ± 0.02 Pa·s and 0.28 ± 0.03 Pa·s, respectively. The ideal mixing and compaction temperatures were obtained, and the results are shown in Table 4.

Table 4. Mixing and compaction temperatures of asphalt mixture based on the ideal viscosity ranges

Sample (% is based on the volume of asphalt binder)	**Temperature (°C), n=3**	
	Mixing	**Compaction**
PG 58-28	150	140
3 vol% $CaCO_3$	150	140
6 vol% $CaCO_3$	160	150
3 vol% LLDPE	175	160
6 vol% LLDPE	185	175
3 vol% PECC	170	155
6 vol% PECC	170	155

DOI: https://doi.org/10.30564/opmr.v1i1.1015

4.3 Multiple Stress Creep Recovery

The dynamic shear rheometer test was conducted on asphalt binders at different ageing levels: un-ageing, short-term ageing and long-term ageing. The short-term ageing (STA) procedure is used to simulate ageing during mixing and construction processes. The STA ageing process was performed conforming to AASHTO T 240. While, the long-term ageing (LTA) was carried out conforming to AASHTO R 28 to simulate the ageing thru the pavement service life, approximately five to ten years period. The Multiple Stress Creep Recovery (MSCR) test was conducted using Bohlin CVO 120 high-resolution DSR.

The DSR with G*/sin δ (AASHTO M320) is the representative criterion for rutting projection of asphalt roadway. However, this technique has been appraised to deliver an improved estimation of the rutting performance of the modified asphalt binder, called multiple stress creep recovery (MSCR). This revised method computes the permanent strain concentrated in the binder after designated cycles of shear loading and unloading. In which, better resistance to rutting of the roadway are indicated by lower permanent shear strain value. In this study, the MSCR test was carried out by exposing the RTFO aged asphalt binder sample to repetitive creep and recovery process at elevated temperature. The test has been carried out in compliance with AASHTO TP 70-08 at 58 °C, which is the high-temperature grade of PG 58-28. The sample for MSCR testing was prepared in circular shaped asphalt binders with diameter of 25 mm and thickness of 1 mm. Two stress levels were assigned to the sample, which was 0.1 kPa and 3.2 kPa at one second loading time and nine seconds recovery time [31,32]. The test was initiated with 0.1 kPa stress for ten cycles without time lags and continued with 3.2 kPa stress under the same number of cycles.

Non-recoverable compliance (J_{nr}) is the best method to substitute the existing Superpave method, G*/sin δ ($\omega = 10$ rad/s). Due to that, the resistance to rutting of asphalt binder is indicated by using non-recoverable compliance [32,33]. Furthermore, in order to figure out the high-temperature viscoelastic deformation properties, the value of percentage recovery (R) was also determined [32]. Where a better permanent deformation resistance is illustrated through lower J_{nr} value. Meanwhile, greater R-value specifies an improved rutting resistance.

Figure 6 shows the mean J_{nr} of specimens (n=3) tested under the 0.1 kPa and 3.2 kPa stresses respectively. Based on both figures, all the modified binders demonstrate lower mean J_{nr} values compared to control asphalt binder (PG 58-28), which directs a better resistance to rutting. Besides that, a higher percentage of modifiers added to the control asphalt binders have resulted in better resistance to rutting. It was also found that the asphalt binder modified with 6 vol% LLDPE gave the lowest J_{nr} value compared to other asphalt binders, which indicates a better resistance to rutting. Theoretically, the lowest J_{nr} value indicates a better resistance to rutting under the respective stress.

Referring to Figure 6, $CaCO_3$ has successfully reduced the J_{nr} value of a neat asphalt binder at both stress levels, with higher amounts of $CaCO_3$ have resulted in lower J_{nr} values. The specimens prepared with 3 vol%, and 6 vol% $CaCO_3$ have better rutting resistance, which is about 9 % and 25 % higher compared to the control asphalt binder (PG 58-28). This result is consistent with previous studies which claimed the $CaCO_3$ could be used to reduce the susceptibility to rutting, due to an increase in stiffness [34,35]. The $CaCO_3$ is typically incorporated into the asphalt mixture using a dry process, which enhances adhesive bonding between aggregates and asphalt binder. Based on the previous study conducted by Button and Epps [36], asphalt mixture prepared using lime through a dry process has a better performance regarding resilient modulus, tensile strength, and Marshall stability compared to asphalt mixtures prepared using lime through a wet process.

Asphalt binder modified using 3 vol% LLDPE exhibits the best resistance to rutting. However, the combination of $CaCO_3$ and LLDPE, which was denoted as 3 vol% PECC has reduced the material response to loading or recovery. It is due to the application of $CaCO_3$ in the modifier has slightly reduced the J_{nr} value compared to the modified binder that was prepared using LLDPE. Whereas, the $CaCO_3$ particles had resulted in a polymer-island effect that enlarged the distance between LLDPE molecules, which undermined the interaction force or bonding between material interface molecules [15,30]. The 6 vol% LLDPE modified asphalt binder was found to have an improved rutting resistance compared to the mixture prepared using other modifiers. Bahia et al. [37] mentioned that permanent deformation or creep is a repeated mechanism developed under sinusoidal loading pulses. However, some of the deformation will be recovered due to elastic stored energy in the materials, which dissipated in damping and permanent flow. The damping energy is recoverable if given enough time, and also believed to be the principal mechanism to improve the resistance to rutting of asphalt material. However, based on Lu and Isacsson [38], although the thermoplastic modifiers have enhanced the stiffness and viscosity of asphalt binder, it does not sufficiently help regarding elastic behaviour, which is crucial to improving the elastic behaviour of the modified binder.

DOI: https://doi.org/10.30564/opmr.v1i1.1015

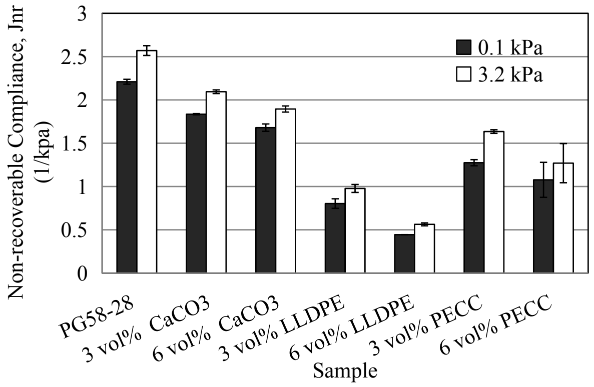

Figure 6. Results of MSCR at 0.1 kPa and 3.2 kPa

The mean percent recovery of the tested asphalt binders is presented in Figure 7. In general, the figure shows a positive trend of asphalt recovery with the increases of asphalt modifiers, excluding for the samples prepared using PECC modifier. The 6 vol% LLDPE has the highest percent recovery, which is about five times better compared to the control sample when tested at stress levels, 0.1 kPa and 3.2 kPa. It is also found that the percent recovery of 6 vol% $CaCO_3$ is comparable to 3 vol% $CaCO_3$ and control binder (PG58-28) at both stress levels.

Based on Figure 7, higher amounts of LLDPE have resulted in better R values that indicate a better resistance to rutting at both stress levels. The combination of LLDPE and $CaCO_3$ shows a negative effect on the recovery of asphalt binders. The highest reduction can be clearly spotted on the R-value results conducted on the 6 vol% PECC samples tested at 3.2kPa. This decrease is almost three times lower compared to specimen prepared using 6 vol% LLDPE.

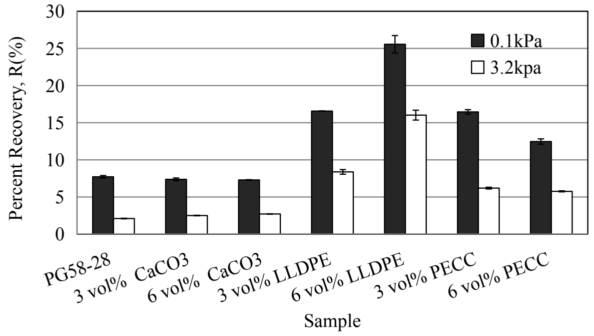

Figure 7. Results of percent recovery at 0.1 kPa and 3.2 kPa

4.4 Bending Beam Rheometer

The bending beam rheometer test was carried out to assess the low-temperature stiffness and relaxation properties of asphalt binders. It was assessed depending on the function of load and duration. An asphalt binder's ability to withstand low-temperature cracking was portrayed through this testing. The test was completed in accordance with AASHTO T 313. A simply supported beam of asphalt binder was subjected to a constant load of 980 mN for a duration of four minutes. Over time, the creep stiffness and m-value of the sample were documented at three low temperatures. The test was conducted at three different temperature of -12 °C, -18 °C and -24 °C to outline the critical cracking temperature of control and modified binders.

Figure 8 shows the low limiting temperature or T_{cr} for each binder. Generally, all the modified asphalt binders have revealed comparable performance on resistance to low-temperature cracking, except for the sample prepared using the LLDPE modifier. It can be deduced that integrating the LLDPE modifier had remarkably reduced the low-temperature grade of the asphalt binder. Whereas the thermal cracking might occur at -22 °C (3 vol% LLDPE) and -27.8°C (6 vol% LLDPE), compared to the control asphalt binder that could withstand the thermal cracking as low as -30.5 °C based on the BBR test.

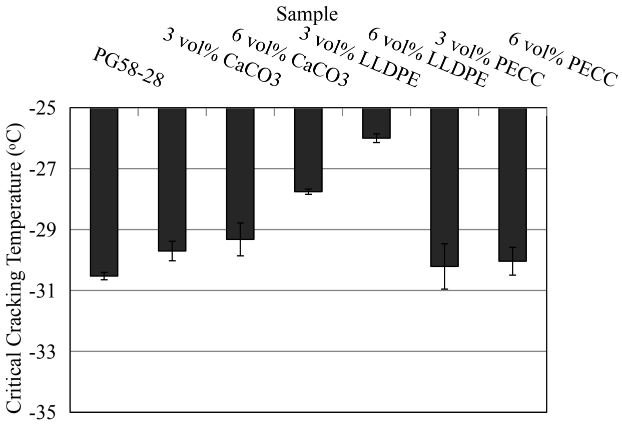

Figure 8. The critical cracking temperature of control binder and modified asphalt binder

Figures 9 (a) to (c) show the equipment used for the characterization of asphalt binders based on the viscosity, binder recovery, and the critical cracking temperature, respectively.

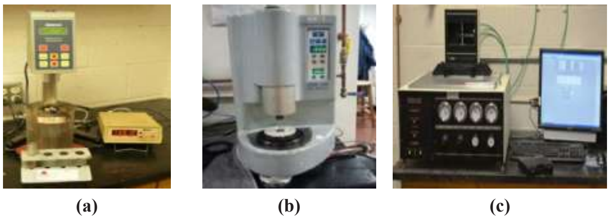
(a) (b) (c)

Figure 9. Equipment used for the binder test (a) Rotational viscometer, (b) Dynamic shear rheometer, (c) Bending beam rheometer

5. Asphalt Mixture Performance

5.1 Four-Point Beam Fatigue

The four-point beam fatigue test was utilized to evaluate the fatigue life of the asphalt mixture subjected to the repetitive bending till failure. The fatigue failure of the asphalt mixture was defined as a 50 % reduction of initial stiffness. In this test, a frequency of 10 Hz and 400 micro-strains (constant strain) was used for all samples. The test was conducted following AASHTO T321.

Figure 10 shows the mean values (n=3) from the four-point beam fatigue test. Based on the result, the specimen prepared with $CaCO_3$ is discovered to have the highest fatigue life compared to other samples, including the control sample. A higher proportion of $CaCO_3$ has led to better resistance to fatigue cracking. The fatigue life of the asphalt mixture prepared using 6 vol% $CaCO_3$ is 1.5 times greater compared to the control sample (PG58-28). Based on the previous studies, application of $CaCO_3$ also has successfully improved the ageing resistance, resistance to fracture adhesive bonding, and dynamic and residual stability which all contribute to the fatigue life of asphalt mixture [18,39]. However, the incorporation of LLDPE has weakened the fatigue life of asphalt mixtures. The lowest fatigue life value was found in 6 vol% LLDPE, which is 7.5 times lower compared to the control asphalt mixture. This result can be linked to an earlier study conducted by Lu and Isacsson [38], whereas although the thermoplastic modifiers have enhanced the stiffness and viscosity of asphalt binder, it does not sufficiently help regarding elastic behaviour, which is crucial to improving the elastic behaviour of the modified binder.

Furthermore, the combination of LLDPE and $CaCO_3$ has slightly improved the fatigue life of asphalt mixture compared to specimen prepared using LLDPE. It is due to the appearance of $CaCO_3$ that has reduced the stiffness of the asphalt binder (based on the RV test results), which can be seen in Figures 4 and 5. However, higher amounts of PECC modifier incorporated into asphalt mixtures have resulted in lower resistance to fatigue cracking. The inconsistent results could be due to the inadequate time of mixing during the preparation of modified asphalt binder or asphalt mixture. It is essential to limit the amount of LLDPE modifier in the asphalt binder to ensure excellent resistance to fatigue cracking.

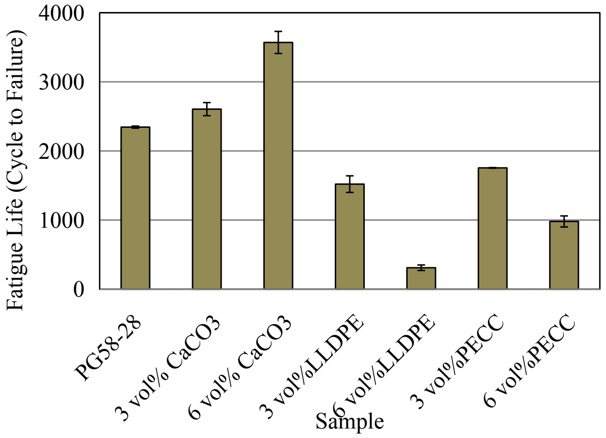

Figure 10. Comparison of fatigue life cycle values between $CaCO_3$, LLDPE and PECC

5.2 Moisture Damage

The tensile strength ratio (TSR) was used to assess the moisture susceptibility of asphalt mixture via tensile strength of specimens. Indirect tensile strength (ITS) of asphalt mixtures under two different condition, namely dry and wet conditions were compared in order to evaluate the moisture susceptibility as shown in Figure 11. In this evaluation, the test was done following AASHTO T283. The asphalt mixtures were tested at the room temperature with constant loading speed at the rate of 0.085 mm/s. The asphalt mixtures were subjected to compression loads which act parallel to the vertical diameter plane. From Figure 11, only one type of trend can be observed where the addition of modifier improved the strength of asphalt mixture under both dry and wet condition compared to control specimens. However, PECC modified asphalt mixture tensile strength is much lower compared to LLDPE and $CaCO_3$ modified asphalt mixture.

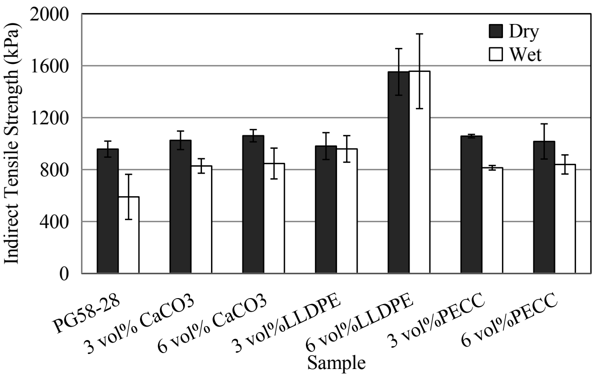

Figure 11. Comparison of ITS values between CaCO3, LLDPE and PECC

DOI: https://doi.org/10.30564/opmr.v1i1.1015

Figure 12 shows the mean TSR results (n=3) for the control and modified asphalt mixtures prepared at two different percentages of each modifier. In general, most asphalt mixtures' TSR values are higher than 0.8, except the specimen prepared with 3 vol% PECC, which approximately 0.770. In this study, the $CaCO_3$ powder has been incorporated into the asphalt mixture using a wet process to ensure a similar preparation protocol for all samples. Through the wet process, the $CaCO_3$ powder (also other modifiers) was formerly blended with the asphalt binder using a high shear mixture before blending with the aggregates. This process is slightly different compared to the dry process, which is the typical approach of adding $CaCO_3$ into the asphalt mix. In the dry process, the $CaCO_3$ powder directly combines with the aggregates instead of blending it with asphalt binder. It is used to allow direct contact between $CaCO_3$ particles with aggregates and asphalt binder to improve the adhesive bonding in the mixture, hence better resistance to moisture damage. According to the result, the TSR values of 3 vol% $CaCO_3$ and 6 vol% $CaCO_3$ are not much different compared to the control sample because the $CaCO_3$ particles have been completely coated by the asphalt binder and not directly reacted with the aggregate surface.

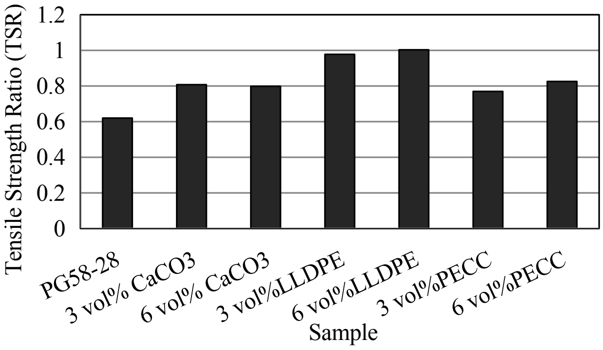

Figure 12. Mean tensile strength ratio results

Moreover, the incorporation of LLDPE has increased the TSR of asphalt mixtures as presented in Figure 12. This is particularly the case for the specimen prepared with 6 vol% LLDPE which has the highest ITS values in both conditions, dry and wet, as shown in Figure 11. This indicates the presence of LLDPE in asphalt mixture has altered the bonding between materials and prevents the HMA failure due to moisture damage through the freeze-thaw cycle. However, application of PECC modifier (a combination of LLDPE and $CaCO_3$) greatly undermined the resistance to moisture damage of asphalt mixtures with TSR values less than 0.8, and lower ITS values compared to specimens prepared with either LLDPE and $CaCO_3$ separately (Figure 11). The possible explanations of this condition have been cited from Zhou et al. [30], where incorporation of $CaCO_3$ into polyethylene (PE) has reduced the specimen tensile strength. Zhou et al. further mentioned that $CaCO_3$ particles had enlarged the distance between LLDPE molecules, which undermined the interaction force or bonding between material interface molecules [30].

5.3 Dynamic Modulus

The dynamic modulus test (Figure 13) was done using UTM 100 from IPC as stated in AASHTO TP62-03 at different temperatures of -10 °C, 4 °C, 21.3 °C and 39.4 °C. Different frequencies ranging from 0.1 Hz to 25 Hz was used to conduct this test. The recoverable axial micro-strain was controlled within 75, and 125 microstrains to confirm the material was in a viscoelastic spectrum [40, 41]. This test is a response established under sinusoidal loading conditions, and the asphalt mixture sample is loaded under the compressive test. The applied stress and the subsequent recoverable axial strain response of the asphalt mixture sample have been measured continuously. The software automatically computed the dynamic modulus and phase angle of the asphalt mixture sample. The dynamic modulus is defined as the ratio of the amplitude stress (σ) and amplitude of the sinusoidal strain (ε) that results in a steady-state response at the same time and frequency.

Master curve technique had been used to analyze and compare the dynamic modulus (E*) test results. The technique that was used to shift all E* values at various frequencies and temperatures into one single curve is known as the sigmoidal fitting model. Through this method, the numbers of curves have been associated to form a single master curve which is based on a reference temperature of -10 °C.

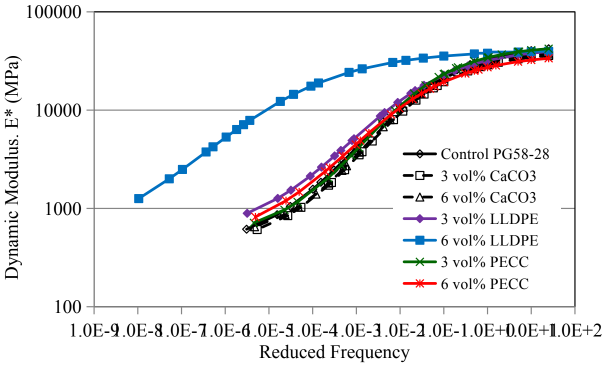

Figure 13. Mean dynamic modulus results of control and modified asphalt mixtures

DOI: https://doi.org/10.30564/opmr.v1i1.1015

6. Conclusions

Based on the results and analysis of this research, the conclusions can be drawn as follows:

(1) All modified asphalt binders have a low volatile loss during the short-term ageing process (less than 1 wt%). This indicates the modification process using LLDPE, $CaCO_3$, and their combination does not result in the changes of the chemical structure and chemical reaction in the asphalt binder. Referring to MSCR test results, the modified asphalt binders have better performance regarding high-temperature behaviour, at least 15 % higher compared to control binder.

(2) The viscosity of asphalt binder increases by incorporating the modifier, which significantly improved the mixing and compaction temperature compared to control asphalt binder. The highest viscosity values are produced by the modified asphalt binder prepared using 6 vol% LLDPE.

(3) Incorporation of 6 vol% LLDPE has remarkably reduced the low-temperature grade of the asphalt binder, where the thermal cracking could happen at -26 °C, compared to control asphalt binder that may withstand the thermal cracking at -30.5 °C based on the bending beam rheological testing results.

(4) In general, the results indicate that a higher percentage of modifier content has reduced the mixture air voids, hence lowered the optimum binder content required for the sample preparation. The decreases in air voids with increases of modifier content may be attributed to the modifier particles filling the voids.

(5) The decrease in fatigue life can be observed based on the four-point beam fatigue test where asphalt mixture prepared using LLDPE-related modifiers has the lowest fatigue life. However, the specimen prepared with $CaCO_3$ was discovered to have the highest fatigue life compared to control and other modified samples. $CaCO_3$ has significantly improved the fatigue performance of asphaltic mixtures, which were higher by about 11.1 % and 52.2 % for the specimen prepared using 3 vol% $CaCO_3$ and 6 vol% $CaCO_3$, respectively compared to control mixture.

Acknowledgments

The authors grateful to express their appreciation to Specialty Minerals Inc. (Bethlehem, PA, USA), Payne & Dolan Inc. (Waukesha, WI, USA), and Dow Chemical Company (Midland, MI, USA) for donating test materials. The authors would like to acknowledge the research assistantships to Mohd Rosli Mohd Hasan, Mohd Khairul Idham Mohd Satar, Muhammad Naqiuddin Mohd Warid, and Nurul Hidayah Mohd Kamaruddin. The authors also want to acknowledge Julia A. King from the Department of Chemical Engineering of Michigan Technological University for her significant contributions in materials preparation, test design, and paper revision. It is impossible for the authors to complete the work without her effort. Any opinions, findings and conclusions expressed in this paper are those of the authors' and do not necessarily reflect the views of the official views and policies of any institution or company.

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ARTICLE

Optimal Method for Production of Amorphous Cellulose with Increased Enzymatic Digestibility

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ARTICLE INFO

Article history
Received: 11 September 2019
Accepted: 21 September 2019
Published Online: 30 October 2019

Keywords:
Cellulose
Mixed waste paper
NaOH/Urea solvent
Treatment
Amorphous cellulose
Enzymatic saccharification

ABSTRACT

In this paper, a simple and cheap method for producing of amorphous cellulose was studied by treating the initial cellulosic material (MCC and waste paper) with a cold solvent, such as aqueous solution of 7% NaOH/12% Urea, at the various ratios of the solvent to cellulose (v/w) (R). If was found that after treatment of cellulose materials with the solvent at $R \geq 5$, a completely amorphous cellulose (AC) is formed. Due to high digestibility, the AC with concentration of 50 g/L is converted to glucose almost completely for 48 h under the action of cellulolytic enzyme CTec-3 with a dose of 30 mg/g solid sample. Such sample can be used as an amorphous standard in the study of crystallinity degree and enzymatic hydrolysis of various types of cellulose and lignocellulose. It was found that enzymatic saccharification is most advantageous to carry out at elevated concentrations of AC, 150 g /L. Due to high cost of MCC, it is preferable to use a cheap cellulose raw material, such as mixed waste paper (MWP), for the commercial production of AC and glucose. The resulting glucose can find application in biotechnology as a promising nutrient for various microorganisms.

1. Introduction

As is known, the conventional method for production of amorphous cellulose (AC) is regeneration from dilute solution (2.3 wt. % or 40 g/L) of microcrystalline cellulose (MCC) in 85% phosphoric acid (PhA) [1,2]. This type of AC, called PhA-Swollen Cellulose (PASC), is characterized by low crystallinity and high saccharification ability under action of cellulolytic enzymes [3,4]. However, the known method for preparation of AC has two main shortcomings. The first problem is low productivity of the process due to use of too dilute cellulose solution, and the second problem is high cost of even commercial grade PhA, estimated at $1 per kg.

The same problems arise if instead of phosphoric acid expensive organic solvents are used, such as ionic liquids (IL) [5], NMMO [6], DMSO/PFA [7], DMSO/DEA/SO_2 [8], DMAA/$LiCl_2$ [9], etc. So according to Alibaba catalog, the average price of DMSO, DEA and DMAA is $1.5-2 per kg, NMMO $10-20 per kg and IL $100-150 per kg.

The traditional cellulose solvents, CS_2/NaOH system and Cuproxam, used in XX century for production of artificial cellulose fibers and films, are currently prohibited due to high toxicity and environmental hazard.

The cheapest solvent for cellulose is probably aqueous solution of 7% NaOH/12% Urea [10-12], having cost of $0.05 per kg due to low price of commercial chemicals. The problem is that only the dilute 3-4 wt. % solution of

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DOI: https://doi.org/10.30564/opmr.v1i1.1301

MCC in this solvent can be obtained, which complicates the regeneration process and reduces the productivity of AC obtaining. The purpose of this study was to optimize the production of AC using the lowest ratio of the solvent to cellulose.

2. Experimental

2.1 Materials and Chemicals

MCC Avicel PH-101 (FMC Co., Princeton, USA) and mixed waste paper (MWP), containing waste of paper towels, paper wipes and blotting/absorbing paper (Amnir Recycling, Hadera, Israel), were used as initial cellulose materials. Sodium hydroxide and urea were supplied from Sigma-Aldrich Co. These chemicals were used to prepare an N/U - solvent, such as aqueous solution containing 7% NaOH and 12% Urea.

2.2 Treatment

Approximately 10 g of initial cellulosic material (MCC powder or 10-15 mm MWP pieces) was placed in a glass beaker cooled with ice/salt mixture having temperature of -15°C. Then, a cold N/U - solvent, was added at the ratio of the solvent to cellulose material (R) from 3 to 10 (v/w) while periodically stirred for 1 h, and after which left overnight in a freezer at -15^{o}C. The treated samples were removed from the freezer and mixed with a 10-fold volume of tap water. The gel-like samples were separated from a liquid medium by means of vacuum Glass filter No1, washed with tap water, neutralized with 1% HCl to pH 6-7 and then washed with distilled water, which was suctioned off under vacuum to obtain 20-25 wt. % solid content.

2.3 Enzymatic Hydrolysis

The initial and treated samples were hydrolyzed with a commercial cellulolytic enzyme Cellic CTec-3 (Novozymes A/S, Bagsvaerd, Denmark). The dose of enzyme was 30 mg per 1 g of solid sample. Hydrolysis of the samples was carried out in 50-mL polypropylene tubes. The samples containing 1 g of the solid matter and 1 ml of 50 mM acetate buffer (pH=4.8) were put into the tubes. Then needed amount of the enzyme was added. Further, an additional amount of the buffer was supplemented to obtain concentration of the cellulosic substrate (C_o) from 50 to 150 g/L. The tubes closed with covers were placed in a shaker incubator at 50^{o}C and shaken for 48 h.

2.4 Analysis

Structural state of the samples was studied by method of X-ray diffraction [13]. Concentration of glucose (C_g, g/L) in the hydrolyzate was determined by the by HPLC-apparatus of Agilent Technologies 1200 Infinity Series. The Amines HPX-87H column was used. Main conditions of the analysis were temperature 45^{o}C; mobile phase 0.005 M sulfuric acid; flow rate 0.6 ml/min. The hydrolyzate was preliminary filtered through 0.45 µm Nylon filter. Degree of digestibility (DD, %) of samples after enzymatic hydrolysis was calculated by the equation:

$$DD = 90\ (C_g/C_o) \qquad (1)$$

3. Results and Discussion

X-ray study of the initial MCC Avicel showed that this cellulose type is a crystalline matter having crystallinity degree (DCr) of 75% (Figure 1, Table 1). After processing of MCC with N/U solvent at R =3, the CI allomorph of the initial cellulose is transformed into CII allomorph with a low DCr of 28% (Figure 2). However, when MCC is treated with the solvent at R ≥ 5, a completely amorphous cellulose (AC) is formed. Thus, the minimum R required for preparation of AC after cellulose processing with solvent is about 5. The same minimum R is required to obtain AC by treatment of mixed waste paper (MWP) (Table 1).

Table 1. Degree of crystallinity (DCr), degree of amorphicity (DAm) and crystalline allomorph (AL) of cellulose samples

Sample	DCr, %	DAm, %	AL
Initial MCC Avicel	75	25	CI
Initial MWP	60	40	CI
MCC treated with solvent at R=3	28	72	CII
MCC treated with solvent at R=5	0	100	no
MCC treated with solvent at R=10	0	100	no
MWP treated with solvent at R=5	0	100	no

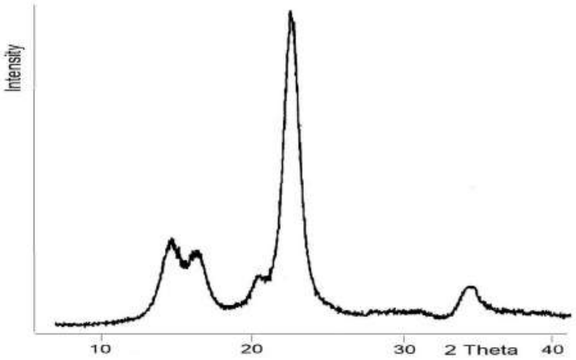

Figure 1. X-ray diffractogram of MCC

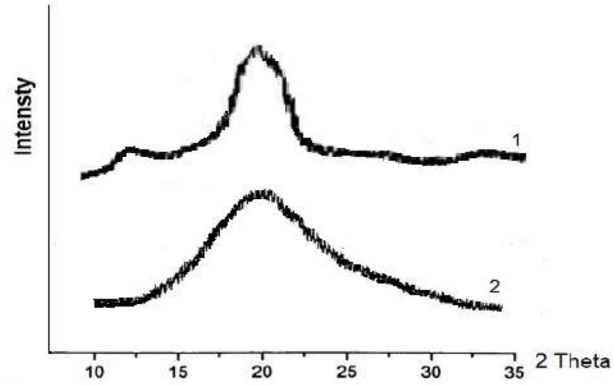

Figure 2. X-ray diffractograms of MCC treated with solvent at R=3 (1) and R=5 (2)

The X-ray findings are confirmed by the results of enzymatic hydrolysis of cellulose samples. As shown in Figure 3, after enzymatic hydrolysis at cellulose concentration C_o=50 g/L, the degree of digestibility (DD) of initial MCC Avicel is relatively low, with DD=40% only. The enzymatic digestibility of CII sample reaches 80% due to low DCr of this sample, whereas samples of amorphous cellulose, AC1 and AC2, are hydrolyzed almost completely.

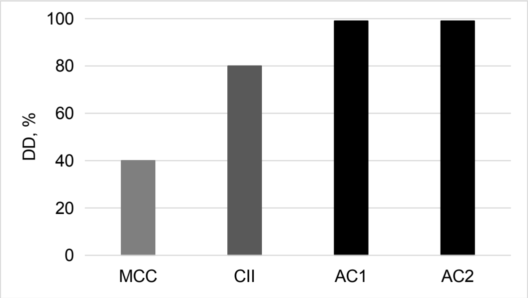

Figure 3. Degree of enzymatic digestibility (DD) of MCC samples at C_o=50 g/L: initial sample (MCC) and samples treated with solvent at R=3 (CII), R=5 (AC_1), and R=10 (AC_2)

As is known, the crystallinity of cellulose is the main factor impeding the enzymatic hydrolysis [14,15]. Therefore, decrease in DCr or increase in DAm facilitate the enzymatic digestibility of cellulose samples (Figure 4).

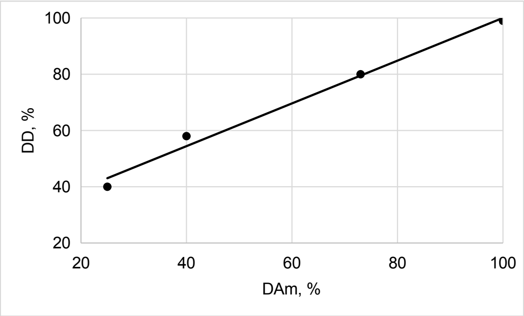

Figure 4. Effect of amorphicity degree (DAm) on enzymatic digestibility (DD) of cellulose samples at C_o= 50 g/L

Thus, if the AC concentration at enzymatic hydrolysis is 50 g/L, then the enzymatic digestibility of this sample reaches 100% for 48 h at enzyme dose of 30 mg/g solid cellulose. Such sample can be used as an amorphous standard, instead of expensive PASC, in the study of enzymatic hydrolysis of various types of cellulose and lignocellulose.

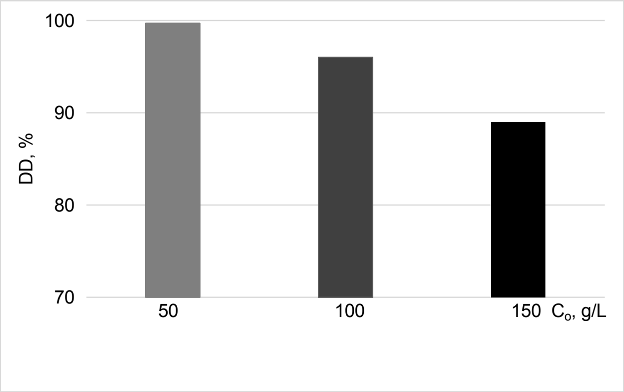

Figure 5. Dependence of enzymatic digestibility (DD) of AC_1 on concentration of cellulosic substrate (C_o)

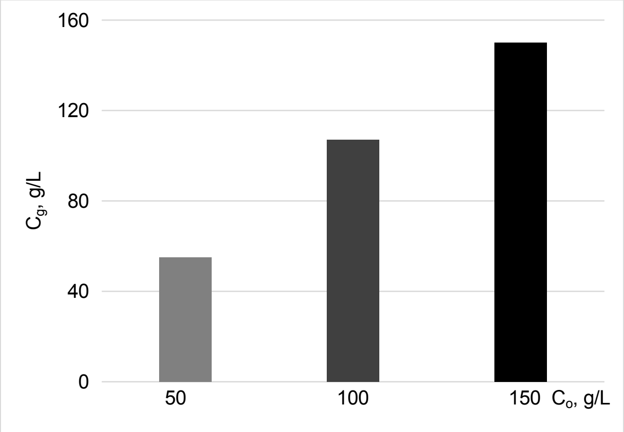

Figure 6. Dependence of glucose concentration (C_g) formed after enzymatic hydrolysis of AC_1 on concentration of cellulosic substrate (C_o)

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Although an increase in the concentration of AC at enzymatic hydrolysis leads to a decrease in the degree of digestibility (Figure 5), the concentration of obtained sugar (glucose) increases in this case (Figure 6).

Since MCC is an expensive cellulose material (cca $4-5 per kg), it cannot be applied for preparation of AC and glucose on the pilot or industrial scale. For commercial production of AC and its enzymatic saccharification purposes, it is advisable to use a cheap raw material, such as mixed waste paper, which can be supplied by price of $50 per ton. As can be seen from obtained results, AC produced by treatment of MWP with N/U - solvent at R=5 is highly digestible and produces an increased amount of glucose after enzymatic hydrolysis at Co=50 g/L (Figures 7, 8).

Increase in the concentration (C_o) of AC reduces the degree of enzymatic digestibility. On the other hand, increase in Co of AC during enzymatic hydrolysis leads to enhance in concentration of obtained glucose. Thus, to increase the concentration of glucose, it is most advantageous to carry out enzymatic saccharification at an increased concentration of AC, 150 g/L (Figure 8). This conclusion is consistent with literature data [16].

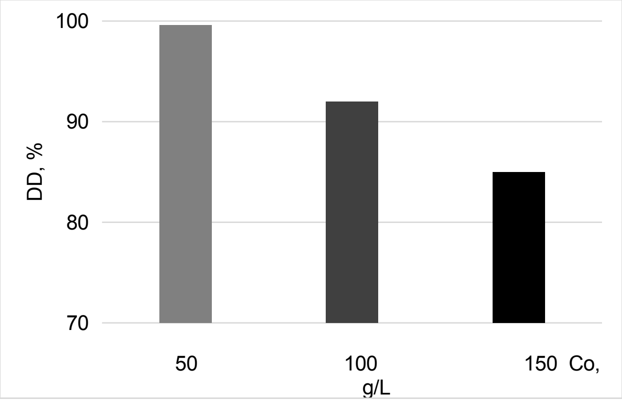

Figure 7. Dependence of digestibility (DD) of AC from MWP on concentration of cellulosic substrate (C_o)

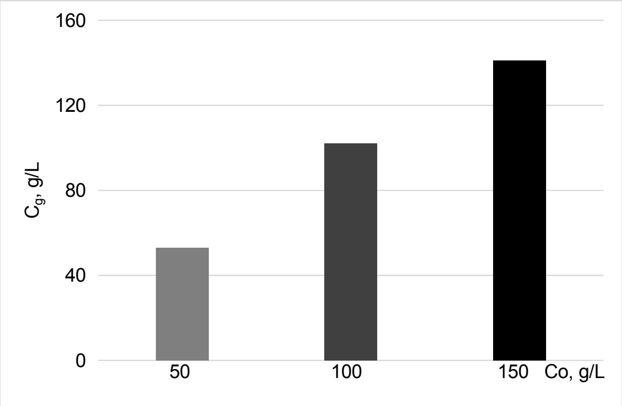

Figure 8. Dependence of glucose concentration (C_g) formed after enzymatic hydrolysis of AC from MWP on concentration of cellulosic substrate (C_o)

The resulting glucose can find application in biotechnology as a promising nutrient for various microorganisms in the production of ethanol [17]; acetic, lactic and citric acids [18]; feed proteins, yeasts and enzymes [19-21]; bacterial cellulose [22] and polyhydroxyalkanoates (biopols) [23], and other valuable products. The biotechnological application of cellulosic glucose obtained by enzymatic hydrolysis of AC from waste paper, instead of food glucose, can reduce the area of energy crops, decrease the consumption of agrochemicals and water, which ultimately can prevent an increase in food prices and its shortage.

4. Conclusions

The optimal method for producing of amorphous cellulose (AC) was developed by treating the initial cellulosic material with a cold solvent, such as aqueous solution of 7% NaOH/12% Urea, at ratio of the solvent to cellulose (v/w) R=5. Due to high digestibility, the AC with concentration of 50 g/L is converted to glucose almost completely for 48 h under the action of cellulolytic enzyme CTec-3 with a dose of 30 mg/g solid sample. Such sample can be used as an amorphous standard in the study of crystallinity degree and enzymatic digestibility of various types of cellulose and lignocellulose. The decrease in crystallinity or increase in amorphicity of cellulose samples facilitate their enzymatic digestibility. It was found that enzymatic saccharification is most advantageous to carry out at elevated concentrations of AC, 150 g /L. Due to high cost of MCC, it is preferable to use a cheap cellulose raw material, such as mixed waste paper (MWP), for the commercial production of AC and glucose. The resulting glucose can find application in biotechnology as a promising nutrient for various microorganisms.

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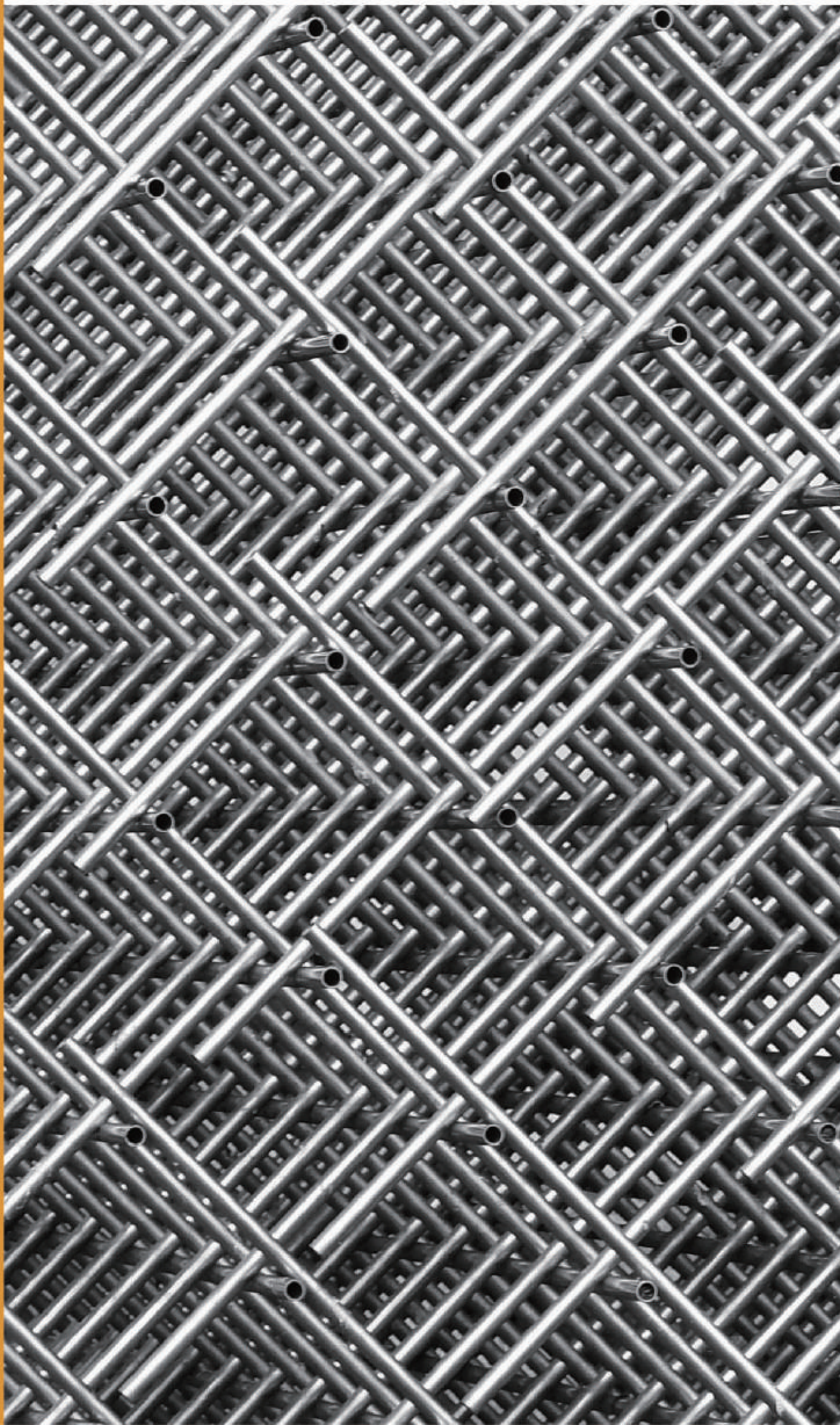

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