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Cellulose based micro- and nanocomposites

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ABSTRACT

Purpose: In this study, the comparative role of micro-and nano- sized cellulose powder in exploring the influence on the mechanical properties of high density polyethylene (HDPE) composites was investigated.

Design/methodology/approach: For production of alpha-cellulose and nanocrystalline cellulose, pulp was produced from Turkish pine (Pinus brutia Ten.) sapwood by Kraft pulping technique. Firstly, alpha-cellulose was isolated from Turkish pine pulp. After that, micro-cellulose and nanocrystalline cellulose were produced from this alpha-cellulose by grinding and acid hydrolysis technique, respectively. In order to compare the effect of micro-cellulose or nanocrystalline cellulose (CNC) as a filler, micro-cellulose or CNC and HDPE composites were produced with 3 different wt% cellulose containing (1.5 and 10 wt%).

Findings: The nanocrystalline cellulose-filled HDPE had a significantly higher tensile and impact strength than the micro-cellulose-filled HDPE composites.

Keywords: Alpha-cellulose; Nanocrystalline cellulose; Turkish pine; High density polyethylene; Nanocomposite

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MATERIALS

1. Introduction

Nanocomposites are new kind of composite materials and at least one dimension of reinforced material used in polymer matrix has to be smaller than 100 nanometres. Up to date nano inorganic materials such as clay, silica and TiO_2 mostly used as reinforced materials in the studies performed in nanocomposites field. Within the last decade there was an usage and significant increase on the research of the organic reinforced materials obtained from bio-based renewable resource. Nanocomposites based on cellulose are a relatively new research field and there is a growing interest on biopolymer based nanocomposites in developed and developing world and, especially if the nanocomposites are based totally on renewable raw materials.

Cellulose would appear to have great potential as a nanomaterial. Cellulose is one of the most abundant, renewable, biodegradable bio-polymer. Cellulose can be obtained from various sources, such as trees, lignocellulosic fibres, some animals (tunicates) and bacterial cellulose. Cellulose is a polydispersed linear polymer which consists of anhydro-glucose units, joined with β(1,4) glycosidic linkage (Fig. 1) [1,2].

Within the last decade there was a usage and significant increase on the research of the organic reinforced materials obtained from bio-based renewable resources. Compared to inorganic fillers, some of the advantages of using cellulose as a reinforcing phase in polymer matrix are its renewable nature, low density, relatively reactive surface due to presence of hydroxyl groups (making surface modification possible), and

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low cost. Utilisation of nanocrystalline cellulose (CNC) among the bio-based reinforcement materials is getting importance in the thermoplastic based matrices [3-6].

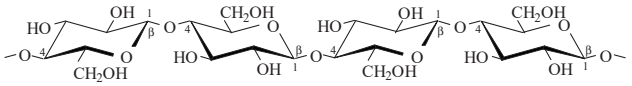

Fig. 1. Partial structure of cellulose

Nanocrystalline cellulose (CNC) is one of the most important materials of the nano-sized additives derived from renewable and natural resources. One of the well-known methods for the production of nanocrystalline cellulose is acid hydrolysis which removes the amorphous regions of the cellulose. Numerous studies have been made on this subject and nanocrystalline cellulose (CNC) from different sources was obtained (HCl, H_2SO_4) [5,7].

With dimensions in the nanoscale range, CNC can be recovered by various methods and used as reinforcing agents in nanocomposites materials. The length of the nanocrystals is dependent on the source of the sample. The size of CNC obtained from wood are 100-300 nm in length and 3-10 nm in width [8-10]. The elastic modulus of cellulose crystals has been reported as 138-167 GPa [11-13].

The first studies regarding the utilisation of CNC in the polymer matrices as a reinforcing material was made in by Favier and his colleagues in 1995 [3,4]. After that, cellulose nanocrystallites were used as a reinforcing element in both natural and synthetic polymers matrices. Among the used natural polymer matrices are poly(-β-hydroxy oktanoat) (PHO) [14-16], starch [17], silk protein [18], cellulose acetate butyrate [19]. The studies performed with synthetic polymer matrices are polystyrene-co-butyl acrylate [3,20], polyvinyl chloride, polypropylene, polyoxyethylene [21]. As far as the authors known, there are limited numbers of studies the utilisation of cellulose nanocrystallites as a reinforcement materials in the thermoplastic polymer matrices by extrusion technique. Nanocrystalline cellulose (CNC) were produced from ramie fibers and characterised by de Menezes and his colleagues in 2009 [22]. The surface of CNC were modified with organic acid chlorides contains different chain lengths. Unmodified and modified CNC were extruded with low density polyethylene (LDPE) to prepare nanocomposite materials. It was reported that the homogeneity of the nanocomposites was found to increase with the length of the grafted chains [22]. In another study, cellulose nanomaterials were used as a reinforcing agent in thermoplastic (LDPE) polymers [23].

The objective of this study was to evaluate the production of cellulose based microcomposites and nanocomposites from alpha-cellulose and nanocrystalline cellulose which were produced from Turkish pine sapwood. The effect of various wt.% alpha-cellulose or nanocrystalline cellulose containing (1, 5 and 10 wt.%) on the mechanical properties of high density polyethylene micro and nanocomposites was also investigated.

2. Materials and methods

2.1. Preparation of pulp

Kraft pulping process was used for production of cellulose from Turkish pine (*Pinus brutia Ten.*). The cooking temperature was 170°C, solution / chip rate (4/1) kept constant. In cooking liquor, active alkali and sulfidity ratio were set to 16% and 25%, respectively. The cooking was performed three times. At the end of the cooking process, pulps were washed and screened on a 0.15 mm slotted screen. The moisture contents of the pulp were calculated according to TAPPI standard T210 cm-03 (2003) [24], following that dry-yields were calculated.

2.2. Preparation of alpha-cellulose and nanocrystalline cellulose

Alpha-cellulose were prepared from pulp with sodium hydroxide (17.5 wt.%) treatment. For production microcomposites, alpha-cellulose was ground using a hammer mill and sieved to a size of 140 meshes. Cellulose nanocrystallites were prepared by acid hydrolysis of cellulose pulp with sulfuric acid, hydrolysis conditions were derived from earlier publication [25].

2.3. Production of cellulose based micro- and nanocomposites

Alpha-cellulose or nanocrystalline cellulose and high density polyethylene (HDPE) were extruded using co-rotating twin screw extruder and three different compositions were prepared (Table 1). Fig. 2 shows the scheme of composite production. The temperature setting from the hopper to die was 100, 150, 170, 170 and 170°C and the screw speed was 50 rpm. Then, the extrudate was passed through a water bath and pelletized at 2 mm size,

and dried at 70 ± 2°C for 24 h. The composites were produced with the compression molding technique (9 t for 5 min at 177°C) using a tile mould [25 cm (l), 25 cm (w), and 2 mm (h)] by a Carver press (Model 12-12 H, Wabash, IN, USA) according to the American Society for Testing and Materials standards. Following that, the composites were cooled down according to Cooling Method B of the American Society for Testing and Materials standards [26].

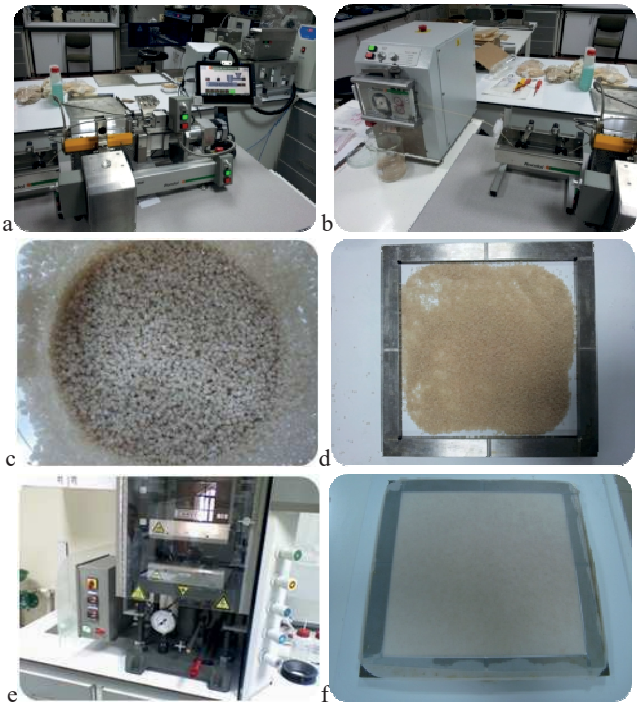

Fig. 2. Scheme of composite production: a) Twin screw extruder, b) Pelletizer, c) Nanocrystalline cellulose (CNC) mixed HDPE pellets, d) Tile mould, e) Hot press, f) CNC reinforced HDPE sample

2.4. Determination of mechanical properties of the composites

The composites were then cut into dumbbell shape and bar shapes and conditioned at 23 ± 2°C with relative humidity of 65 ± 5% for 7 days. Tensile, flexural, and impact strength tests were performed according to ASTM D638, ASTM D6109 and ASTM D256, respectively [27-29].

3. Results and discussion

For production of alpha-cellulose and nanocrystalline cellulose based composites, Turkish pine sapwood was chosen as a raw material. Cellulose pulp was produced by Kraft pulping method, then alpha-cellulose was obtained from this pulp (Fig. 3). Alpha-cellulose and nanocrystalline cellulose were produced by 17.5% sodium hydroxide treatment and acid hydrolysis technique from the pulp, respectively. The yields of the compounds obtained from starting raw material Turkish pine are shown in Figure 4. As can be seen from Fig. 4, 46% pulp, 42% holocellulose, 34% alpha-cellulose and 13% nanocrystalline cellulose were obtained from wood chips as a starting raw material.

Fig. 3. Produced pulp (left) and alpha-cellulose (right) from Turkish pine sapwoods

Table 1.
The compositions used for production of micro-cellulose or CNC based composites

	HDPE	Micro-cellulose	CNC
C_0	100	-	-
C_1	99	1	-
C_5	95	5	-
C_{10}	90	10	-
W_1	99	-	1
W_5	95	-	5
W_{10}	90	-	10

In this study, alpha-cellulose and nanocrystalline cellulose were used as thermoplastic filler in the production of cellulose based micro and nanocomposites. Firstly, the effect of various cellulose wt% containing (1 wt.% to 10 w.t%) on the properties of composites was determined.

Effect of cellulose wt.% containing levels on the tensile strength values are shown in Figure 5. As can be seen from Fig. 5, the tensile strength values of nanocrystalline cellulose reinforced composites were better than that of alpha-cellulose reinforced composites in all studied filler ratios.

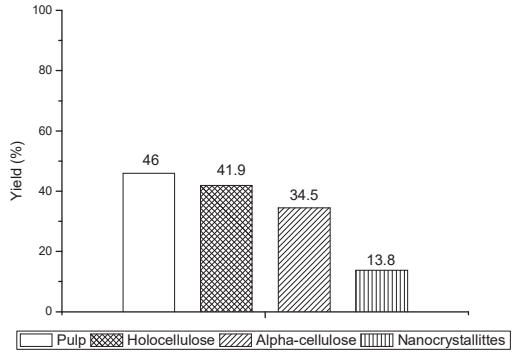

Fig. 4. Percentage yields of nanocrystalline cellulose, alpha-cellulose, holocellulose and pulp were obtained from Turkish pine wood chips

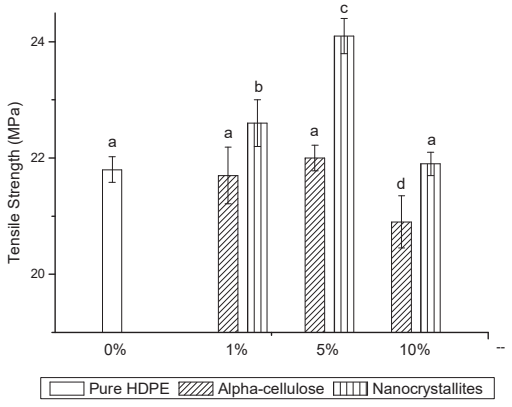

Fig. 5. Effect of alpha-cellulose or nanocrystalline cellulose (wt% addition) on the tensile strength values of HDPE composites (Bars with the same letter are not significantly different)

Tensile strength values of alpha-cellulose based composites was initially similar with pure HDPE composites, after that the tensile values slightly reduced when alpha-cellulose wt.% containing was reached at 10 wt.% (from 22 MPa to 21 MPa). According to the Tukey test result, there was no significant difference between pure HDPE composites and low level alpha-cellulose wt.% containing (1 wt.% and 5 wt.%) micro-composites. Higher tensile strength properties of the composites were achieved using the nanocrystalline cellulose (1 w.t% and 5 w.t%) as a filler. The best tensile strength values were obtained with 5 wt.% nanocrystalline cellulose loaded composites, which were 9% and 10% better than alpha-cellulose-HDPE (5 wt.%) and pure HDPE composites, respectively.

It was reported that when the surface interaction is not strong enough in the soft fillers such as wood flour reduce the tensile strength [30]. In earlier studies [31,32], it was reported that the increasing the lignocellulosic based filler wt% containing, the filler was not homogenously distributed in HDPE polymer matrix and also some aggregations were occurred. As a result of this, surface area of the filler reduced and interaction between cellulose and HDPE matrix decreased. This might also be the reason of the tensile strength reduction in 10 wt.% alpha-cellulose or nanocrystalline cellulose filled HDPE composites.

The pure HDPE composites showed 1.4 GPa flexural modulus value, although 1 wt.% alpha-cellulose or nanocrystalline cellulose containing in HDPE composites did not make any changes in the flexural modulus value. From this point, the flexural modulus of the composites showed an increase with the increasing with alpha-cellulose or nanocrystalline cellulose containing (Fig. 6). The highest flexural modulus value was obtained as 1.7 GPa at 10 wt.% alpha-cellulose containing.

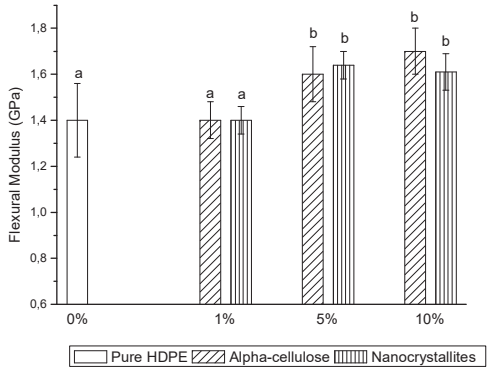

Fig. 6. Effect of alpha-cellulose and nanocrystalline cellulose (wt.% addition) on the flexural modulus values of HDPE (Bars with the same letter are not significantly different)

Fig. 7 shows the variations of impact strength of micro and nano-composites as a function of the alpha-cellulose or nanocrystalline cellulose containing. Impact strength dramatically decreased with the alpha-cellulose containing than nanocrystalline cellulose containing, reaching a minimum at 5 wt.% or above alpha-cellulose containing.

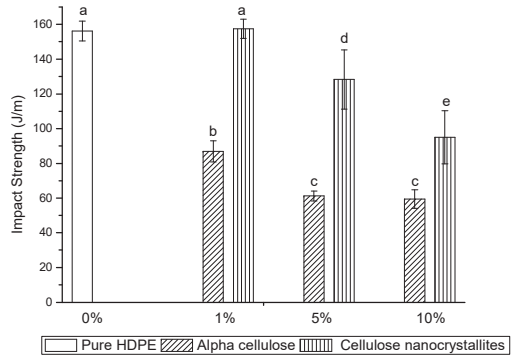

Fig. 7. Alpha-cellulose and nanocrystalline cellulose wt% addition effects on the impact strength values of the HDPE composites (bars with the same letter are not significantly different)

4. Conclusions

In conclusion, the nanocrystalline cellulose yield of Turkish pine wood chips was 13%. When 5 wt.% nanorystalline cellulose was used as a reinforced material in a polymer matrix resulted in improvement in tensile strength and flexural modulus properties compared to pure HDPE composite. 1 wt.% addition of nanocrystalline cellulose had no effect on the impact strength and gave similar values with pure HDPE composites. With further increase in nanocrystalline cellulose addition (5 wt.% and above) gradually reduced the impact strength compared to pure HDPE composites. Addition of up to 5 wt.% micro-cellulose had no effect on the tensile strength values, whereas significantly reduced the impact strength values compared to pure HDPE composites.

Acknowledgements

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References

[1] M.M.D.S. Lima, R. Borsali, Rod like cellulose microcrystal's: Structure, properties, and applications, Macromolecular Rapid Communications 25 (2004) 771-787.
[2] C.A.S. Hill, Wood Modification. Chemical, Thermal and Other Processes, Published by John Wiley & Sons, Chichester, 2006.
[3] V. Favier, H. Chanzy, J.Y. Cavaillé, Polymer nanocomposites reinforced by cellulose whisker, Macromolecules 28 (1995) 6365-6367.
[4] V. Favier, G. Canova, J.Y. Cavaillé, H. Chanzy, A. Dufresne, C. Gauthier, Nanocomposite materials from latex and cellulose whiskers, Polymers for Advanced Technologies 6 (1995) 351-355.
[5] M.A.S. Azizi Samir, F. Alloin, J.Y. Sanchez, N. El Kissi, A. Dufresne, Preparation of cellulose whiskers reinforced nanocomposites from an organic medium suspension, Macromolecules 37 (2004) 1386-1393.
[6] M.A.S. Azizi Samir, F. Alloin, A. Dufresne, Review of recent research into cellulosic whiskers, their properties and their application in nanocomposite field, Biomacromolecules 6 (2005) 612-626.
[7] D. Bondeson, A. Mathew, K. Oksman, Optimization of the isolation of nanocrystals from microcrystalline cellulose by acid hydrolysis, Cellulose 13 (2006) 171-180.
[8] H. Chanzy, Aspects of cellulose structure, in Cellulose Sources and Exploitation, J.F. Kennedy, G.O. Phillips, P.A., Williams, Published by Ellis Horwood, New York, 1990.
[9] J.F. Revol, L. Godbout, X.M. Dong, D.G. Gray, H. Chanzy, G. Maret, Chiral nematic suspensions of cellulose crystallites phase separation and magnetic field orientation, Liquid Crystals 16 (1994) 127-134.
[10] J. Sugiyama, H. Chanzy, J.F. Revol, On the polarity of cellulose in the cell wall of Valonia, Planta 193 (1994) 260-265.
[11] T. Nishino, K. Takano, K Nakamae, Elastic modulus of the crystalline regions of cellulose polymorphs, Journal of Polymer Science Part B: Polymer Physics 33 (1995) 1647-1651.
[12] A. Strucova, G.R. Davies, S.J. Eichorn, Elastic modulus and stress-transfer properties of tunicate cellulose, Biomacromolecules 6 (2005) 1055-1061.
[13] K. Tashiro, M. Kobayashi, Theoretical evaluation of three-dimensional elastic constants of native and regenerated celluloses: role of hydrogen bonds, Polymer 32 (1991) 1516-1526.

[14] D. Dubief, E. Samain, A. Dufresne, Polysaccharide microcrystals reinforced amorphous poly(â-hydroxyoctanoate) nanocomposite materials, Macromolecules 32 (1999) 5765-5771.
[15] A. Dufresne, M. Kellerhals, B. Witholt, Transcrystallization in mcl-PHAs/cellulose whiskers composites Macromolecules 32 (1999) 7396-7401.
[16] A. Dufresne, Interfacial phenomena in nanocomposites based on polysaccharide nanocrystals, Composite Interfaces 10 (2003) 369-388.
[17] M.N. Angles, A. Dufresne, Plasticized starch/tunicin whiskers nanocomposites: 1. Structural analysis, Macromolecules 33 (2000) 8344-8353.
[18] Y. Noshiki, Y. Nishiyama, M. Wada, S. Kuga, J. Magoshi, Mechanical properties of silk fibroin-microcrystalline cellulose composite films Journal of Applied Polymer Science 86 (2002), 3425-3429.
[19] M. Grunert, W.T. Winter, Nanocomposites of cellulose acetate butyrate reinforced with cellulose nanocrystals. Journal of Polymers and the Environments 10 (2002), 27-30.
[20] W. Helbert, J.Y. Cavaillé, A. Dufresne, Thermoplastic nanocomposites filled with wheat straw cellulose whiskers. Part I: Processing and mechanical behaviour, Polymer Composites 17 (1996) 604-611.
[21] M. Matos Ruiz, J.Y. Cavaille´, A. Dufresne, C. Graillat, J.F. Ge´rard, New waterborne epoxy coatings based on cellulose nanofillers, Macromolecular Symposia 169 (2001) 211-222.
[22] A.J. de Menezes, G. Siqueira, A.A.S. Curvelo, A. Dufresne, Extrusion and characterization of functionalized cellulose whiskers reinforced polyethylene nanocomposites, Polymer 50 (2009) 4552-4563.
[23] H Farahbakhsh Cotton-based cellulose nanomaterials for applications in composites and electronics, PhD thesis, North Carolina State University, 2015.
[24] Tappi T 210 cm-03, Sampling and testing wood pulp shipments for moisture, Tappi Test Methods, Tappi Pres, Atlanta, 2003.
[25] N.S. Çetin, P. Tingaut, N. ÖzmenHenry, D. Harper, M. Dadmun, G. Sebe, Acetylation of Cellulose Nanowhiskers with Vinyl Acetate under Moderate Conditions, Macromolecular Bioscience 9 (2009) 997-1003.
[26] American Society for Testing and Materials (2010), Standard Practice for Compression Molding Thermoplastic Materials into test Specimens, Plaques, or Sheets. ASTM D4703-10. West Conshohocken, PA, USA: ASTM.
[27] American Society for Testing and Materials (2001). ASTM D638, Standard Test Method for Tensile Properties of Plastics. West Conshohocken, PA, USA: ASTM.
[28] American Society for Testing and Materials (2005). ASTM D6109, Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastic Lumber and Related Products. West Conshohocken, PA, USA: ASTM.
[29] American Society for Testing and Materials. ASTM D256 (2005). Standard Test Methods for Impact Resistance of Plastics and Electrical Insulating Materials. West Conshohocken, PA, USA: ASTM.
[30] N. Özmen, N.S. Çetin, F. Mengeloğlu, E. Birinci, K. Karakuş Effect of vinyl acetate modification on the properties of woodplastic composites, Bio Resources 8 (2013) 753-767.
[31] N.S. Çetin, N. Özmen, N. Narlıoğlu, V. Çavuş, Effect of bark flour on the mechanical properties of HDPE composites, II. Ulusal Ege Kompozit Malzemeler Sempozyumu, 2013, 452-463 (in Turkish).
[32] N.S. Çetin, N. Özmen, D.P. Harper, Vinyl acetate-modified microcrystalline cellulose-reinforced HDPE composites prepared by twin-screw extrusion, Turkish Journal of Agriculture and Forestry 39 (2015) 39-47.