

Fe₃O₄ Modification of Microcrystalline Cellulose for Composite Materials

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Abstract A new synthesis method for producing cellulose ferrite micro- and nano- composites was developed and new material properties were studied. Microcrystalline cellulose was modified with a mixture of Fe⁺²/Fe⁺³ to produce surface bonded nanoparticles magnetite (Fe₃O₄). Optimal conditions were determined. Microsized hematite (Fe₂O₃) was mixed with microcrystalline cellulose and used as a reference. The magnetite modified microcrystalline cellulose and hematite filled microcrystalline cellulose were used together with polyurethane prepolymer. New composite crosslinked conductivity materials based on the magnetite modified microcrystalline or hematite filled microcrystalline cellulose and polyurethane were developed. Morphology, crystalline properties, water absorption and electro conductivity of these materials were characterized. The physical properties of these materials were characterized by different analytical methods: SEM, XRD, water absorption and electrical resistance.

Keywords Microcrystalline cellulose, Magnetite, SEM, XRD

1. Introduction

Large amounts of magnetic particles have been produced for magnetic recording media in the past fifty years, while recently, magnetic particles have also been extensively used in a variety of applications such as ferrofluids, magnetic inks, for means of extraction and purification of biological materials and clinical diagnostics[1]. Magnetite (Fe₃O₄) particles represent a very interesting type of magnetic materials, being used among others in information storage, magnetic fluids and medical applications (i.e. drug carriers), as well as in materials for the absorption of electromagnetic radiation. Such a wide variety of possible applications has warranted a lot of attention and has resulted in a large body of research work concerning the synthesis of magnetite[2,3].

Composite materials are of interest due to the potential synergistic properties that may arise from the combination of two or more components. Two such components are wood or cellulose fibers (length 20 mm) and magnetic nanoparticles. In combination organic (fiber) and inorganic (particles) compounds forming hybrid materials possessing the inherent properties of the fiber substrate, in particular stiffness and strength, and also the magnetic properties of the nanoparticles. Superparamagnetic iron oxide nanoparticles (SPION) covered with a polymer have been used in medical research

such as devices for cell isolation, immobilization of enzymes, controlled release systems and separation of biological materials[4]. Guo et al. reported the study of inorganic adsorbents inside cellulose beads for the elimination of arsenic from aqueous solutions[5]. Thus, cellulose beads could act as a column bed, suitable for liquid chromatography. Another way of using cellulose beads is to place magnetic particles inside the structure and thus the new material could react as a magnetic actuator. Moreover, the synthesis of the magnetic cellulose[6] or polysaccharide like carboxymethyl-cellulose[7] and carrageenan[8] has generated a great attention in recent years due to their specific properties: non-toxic nature, biocompatibility, variable ionic permeability, combined with a high hydrophilic effect and considerable mechanical strength. The immobilization of α -amylase onto cellulose-coated magnetite nanoparticles has been reported in a starch degradation study[9]. Previous work describes the synthesis of cellulose beads bearing micrometric magnetite[10]. In this initial report, the covered micrometric magnetite in a cellulosic matrix leads to a net reducing effect of magnetic coercive field with consequential formation of superparamagnetic cellulose composite.

Magnetically responsive cellulose fibers will allow the investigation of new concepts in papermaking and packaging, security paper, and information storage. Potential applications are in electromagnetic shielding, magnetographic printing and magnetic filtering[6, 11-12].

Throughout the literature, there have been reports of superparamagnetic papers obtained through "in situ" synthesis of ferrites[11-13] and others concerning ferromagnetic paper

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obtained by the "lumen-loading" approach, whereby the lumen of the cellulose fiber is loaded with commercial pigments such as magnetite and maghemite.

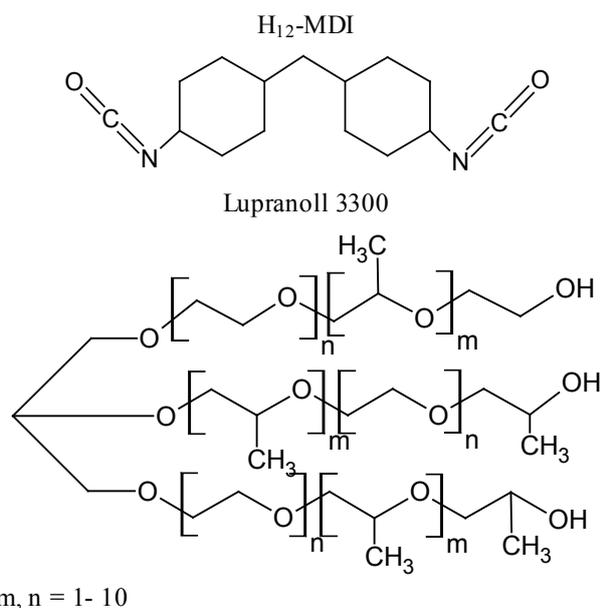
The purpose of this work is to modify microcrystalline cellulose (MCC) with two component system $\text{Fe}^{+2}/\text{Fe}^{+3}$, in order to obtain composite materials with desired properties, based on such modified MCC (mMCC) and polyurethane (PU) prepolymer. PU prepolymer served as a polymer component with active -NCO groups, which reacted with the active -OH groups from MCC.

2. Materials

For the synthesis of the composite matrix, following reagents were used:

MCC with particle size $5 \mu\text{m}$ - supplied from Sigma Aldrich Chemie GmbH, Steinheim Germany. Modifying agents used were: $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ - supplied from Malilinkrodt Baker B.V, Deventer Germany, $M=198.8 \text{ g/mol}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ - supplied from Merck KGaA, Darmstadt Germany, $M=270.3 \text{ g/mol}$. Hematite (Fe_2O_3) with particle size $5 \mu\text{m}$ was used as a referent sample, delivered from Sigma Aldrich Chemie GmbH, Steinheim Germany. 30 w% NH_3 solution - supplied from Carl Roth GmbH & Co.KG, Karlsruhe Germany, $M=17.03 \text{ g/mol}$, density 0.9 g/cm^3 .

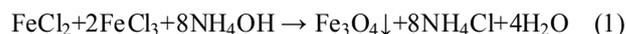
1-isocyanato-4 dicyclohexylmethan-4,4'-diisocyanate (H_{12} -MDI) under the trade name Vestanat, supplied from Performance Chemicals Handels GmbH, Hamburg, Germany, $M=262 \text{ g/mol}$, and Lupranol 3300, which is a trifunctional polyether polyol based on glycerol, were used for a prepolymer preparation. Lupranol 3300 had only secondary hydroxyl group (hydroxyl value = 400 mg KOH/g), and was supplied from BASF Polyurethanes GmbH, $M=420 \text{ g/mol}$.



3. Experimental Section

3.1. MCC Modification

The MCC (600 g) was in bulk treated with 1 mol solution (300 ml) of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and 2 mol solution (300ml) of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and a suspension was produced. The reconstituted material was left for 30 minutes to absorb ferrite solutions. After 30 minutes this suspension was treated with 30 w% NH_3 solution and was vigorously stirred for 20 min. The reconstituted material was filtrated and washed with distillate watter. The finished product should have a neutral pH. Such modified MCC was dried for 3 hours at 105°C . Fe_3O_4 was produced by the following reaction[14]:



The result was a black suspension of a mixture of MCC and magnetite.

3.2. Preparation of Polyurethane Prepolymer

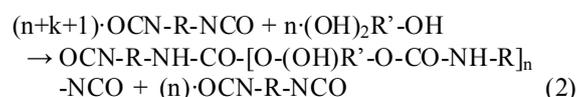
Polyurethane (PU) prepolymer was synthesized using H_{12} -MDI and Lupranol 3300. Procedure:

H_{12} -MDI was fed to a vessel and heated up to $50 - 60^\circ\text{C}$. Fresh H_{12} -MDI gives a clear colourless liquid; a slight turbidity because of beginning dimerization of H_{12} -MDI may be accepted. Lupranol 3300 was added in small portions at room temperature, stirring during the course of approximately 30 minutes. The reaction is exothermic, but the reactivity of Lupranol 3300 is very low, therefore crystallization of the H_{12} -MDI may occur in cases when the content of the vessel cools down under 40°C . The mixture is heated up to 80°C and kept at this temperature for 3 hours. After 3 hours, the NCO-content should be stable. The result is a clear, slightly yellow, viscous prepolymer. At the end of the experiments, quality control tests were performed to determine NCO-content of the product according to DIN EN ISO 11 909. Compositions and synthesis conditions are listed in Table 1.

Table 1. Composition and synthesis condition of PU prepolymer

Sample	Lupranol 3300[mol]	H_{12} -MDI [mol]	Time of the process[min]	Temperature [$^\circ\text{C}$]
K1	0.7	1	10	< 80
K2	0.7	1.1	10	< 80
K3	0.7	1.2	10	< 80
K4	0.7	1.3	10	< 80
K5	0.7	1.4	10	< 80

The chemical reaction of polycondensation between H_{12} -MDI and the polyol for the current experimental conditions (some surplus of -NCO groups in the mixtures K2-K5 and practically equal content of very active -NCO groups and low active -OH groups in the mixture K1) and in the case of the linear product formation could be described:



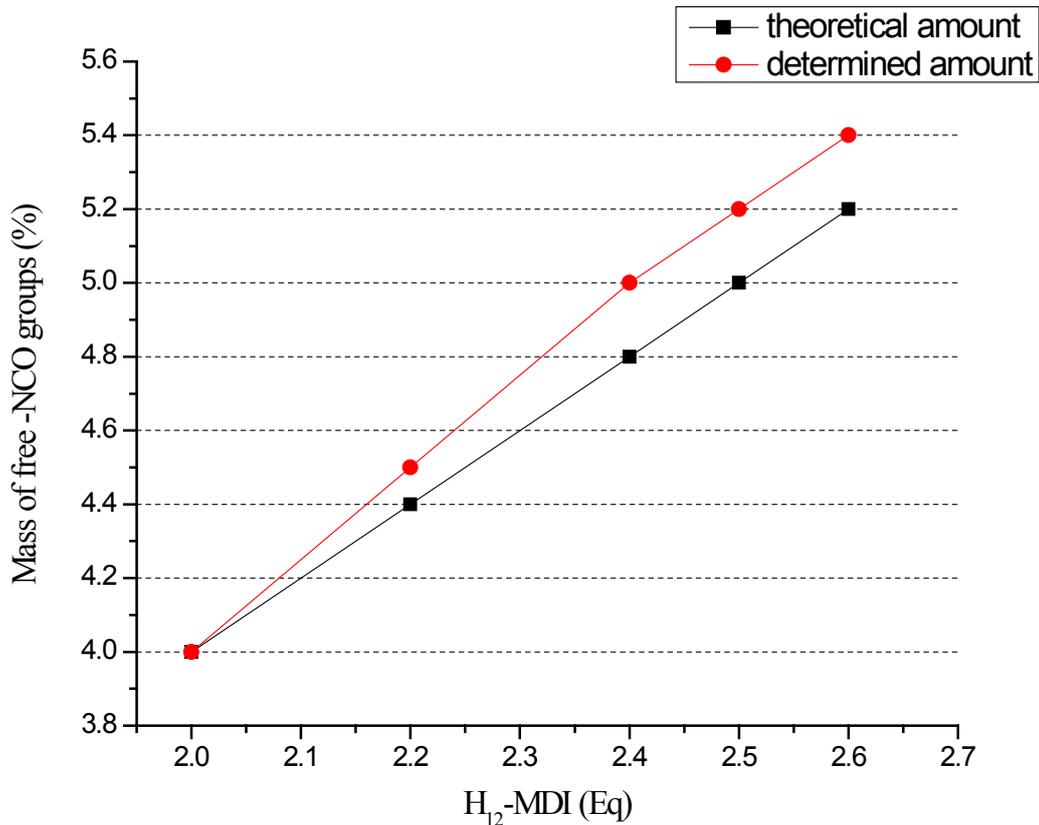


Figure 1. NCO content of PU prepolymer

Here R and R' radicals refer to H₁₂-MDI and Lupranoll 3300 correspondingly. Really, the appearance of the cross-linked PU prepolymer could be waited due to existence of a third hydroxyl group in Lupranoll molecules.

At the increasing H₁₂-MDI quantity, an increase in -NCO groups is found as expected due to incomplete reaction. Isocyanat content in prepolymers are shown in Figure 1.

Figure 1 shows the theoretical and determined content of free NCO groups of the PU prepolymers. The determination was done according to DIN EN ISO 11 909. There is a small difference between the theoretical and determined amount of free -NCO groups. The small difference can be explained with residual noncreated hydroxyl groups from Lupranol 3300.

3.3. Preparation of Composite Materials

In present work, the K5 prepolymer was used to synthesize all samples described in Table 2. The composite synthesis is based on the physical mixing and chemical bonding of MCC and PU prepolymer. Mixing was carried out in Brabender-Plasti[®] Corder Lab Station, equipped with Mixer 350 E. Calculated amounts (200 g) of both the components were added to the apparatus and mixed for 15 min at 180° C with rotation speeds of 20 min⁻¹. Then the material was pressed at 4 MPa in the laboratory press

Servitec/Polystat 300 S. Table 2 represents the contents of the composite materials.

Table 2. Composition and synthesis condition of PU prepolymer

Sample	Prepolymer[%]	MCC[%]	Fe ₃ O ₄ mMCC[%]	Fe ₂ O ₃ [%]
KD 1.1	30	70	-	-
KD 1.2	20	80	-	-
KD 1.3	10	90	-	-
KD 2.1	30	-	70	-
KD 2.2	20	-	80	-
KD 2.3	10	-	90	-
KD 3.1	30	60	-	10
KD 3.2	20	70	-	10
KD 3.3	10	80	-	10
KD 4.1	30	50	-	20
KD 4.2	20	60	-	20
KD 4.3	10	70	-	20

MCC acts as chain extender and active component. The -NCO groups of PU prepolymer react with -OH groups of cellulose molecules. The reduction of free isocyanate groups

is described by the following scheme:



where R and R' radical refer to cellulose and PU prepolymer respectively.

4. Analysis Methods

4.1. Scanning Electron Microscopy (SEM)

For the SEM investigation, specimens with surface areas of about 5x5 mm and thickness about 0,1 mm were taken from modified MCC. The samples were coated with gold by argon sputtering. Subsequently surface morphology of the materials was investigated by SEM - JSM-6400 (voltage = 20.0 kV and magnification 500-17000).

4.2. X-ray Diffraction (XRD)

XRD investigation of composites was performed using D-8Advance from Bruker AXS, equipped with a Ge(111)-Johansson monochromator Cuka ($\lambda=1.540598 \text{ \AA}$). The measurements were performed in the range of scattering angles 2θ from 10° to 80° , with a step width of 0.01° .

XRD was used for structural phase identification Figure 3, 4. Coherently diffracting domain size (d_{xrd}) was calculated from the width of the XRD peak under the Scherrer approximation (which assumes the small crystallite size to be the cause of line broadening) after correcting for instrumental broadening.

4.3. Water Absorption

Water absorption of composites was used to determine the amount of water absorbed under specified conditions. This research was done according DIN 53 496 The measurement was done at samples with a length of 2 cm, width of 1 cm and thickness from 2.4 mm to 2.9 mm were immersed in a glass of water for 24, 48 and 72 hours at $\approx 25^\circ\text{C}$.

4.4. Electrical Resistance

This measurement was done using Agilent N9320B RF Spectrum Analyzer, with scanning frequency in the range 1 MHz to 3 GHz. The samples thickness ranged from 2,4 mm to 2,9 mm. The step of frequency was 20 Hz. The test was performed at room temperature $\approx 25^\circ\text{C}$.

5. Results and Discussion

The prepared composite materials were characterized by SEM, XRD, water absorption, mechanical properties and electro conductivity.

Figure 2. (A, B, C) represents SEM micrographs of Fe_3O_4 mMCC powder scanned with different resolutions. The micrographs show MCC particles covered with magnetite with different size (nano- and micro- size), thus some of the particles agglomerate during the modification process.

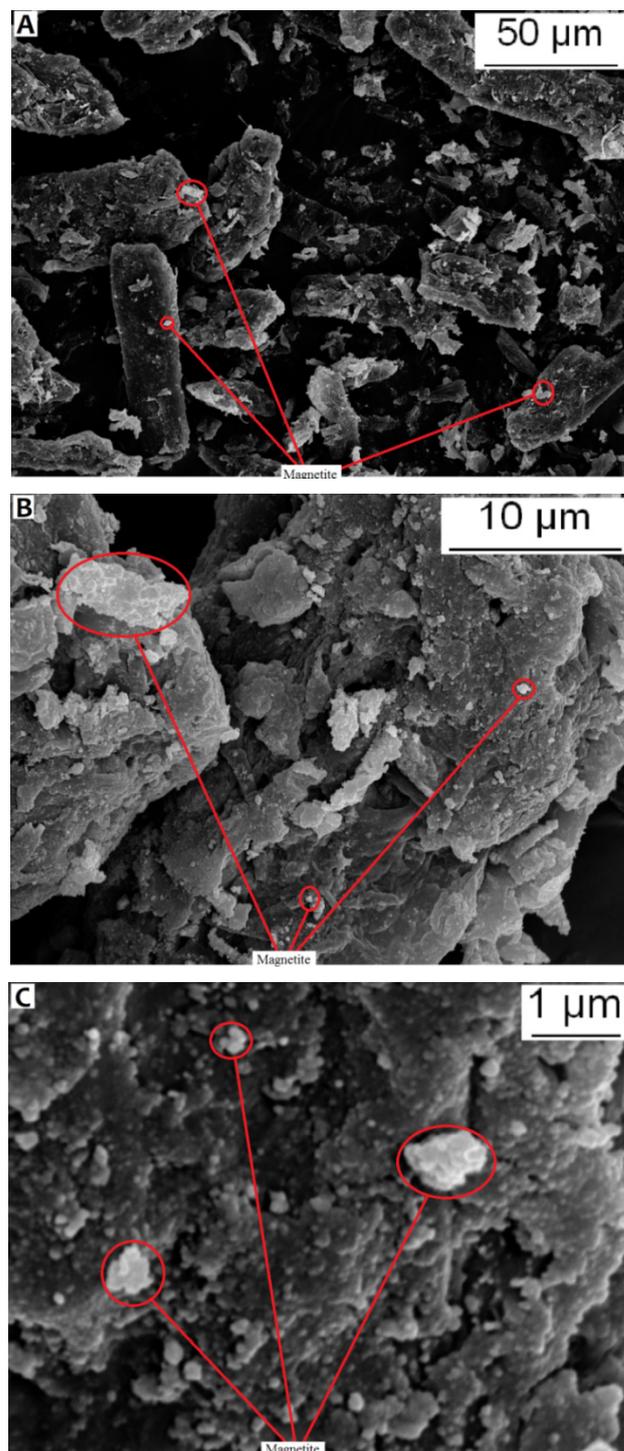


Figure 2. SEM of Fe_3O_4 mMCC

Figure 3. represents an X-ray measurement of Fe_3O_4 mMCC composite. The reflections at $2\theta = 14.8, 16.6$ and 22.4° corresponding to the crystalline part of cellulose. On the second diffractogram (Figure 4.) the broader reflection at $2\theta = 32^\circ$ belongs to the hematite structure and $2\theta = 30, 35.8, 57.3, 62.8^\circ$ are typical for the magnetite and have an inverse cubic spinel structure[15, 16]. From the Scheerer equation, assuming ideal spherical shape the crystallite size was estimated to be 70 nm for magnetite phase. However, the

particle diameters from SEM measurements are slightly larger than the observed crystal sizes from XRD, due to the presence of noncrystalline surface layers [17].

Figure 5 shows water absorption of series KD 1, KD 3 and KD 4. Samples of KD 2 series undergo destruction process after 24 h, thus they are omitted from Fig. 5. The lowest

water absorption was achieved by the samples KD 1.2, KD 3.2 and KD 4.2 with 20 % prepolymer. Samples of series KD 2 were destroyed in water test. This may be due the fact that Fe₃O₄ mMCC has only weak reacted with the PU prepolymer.

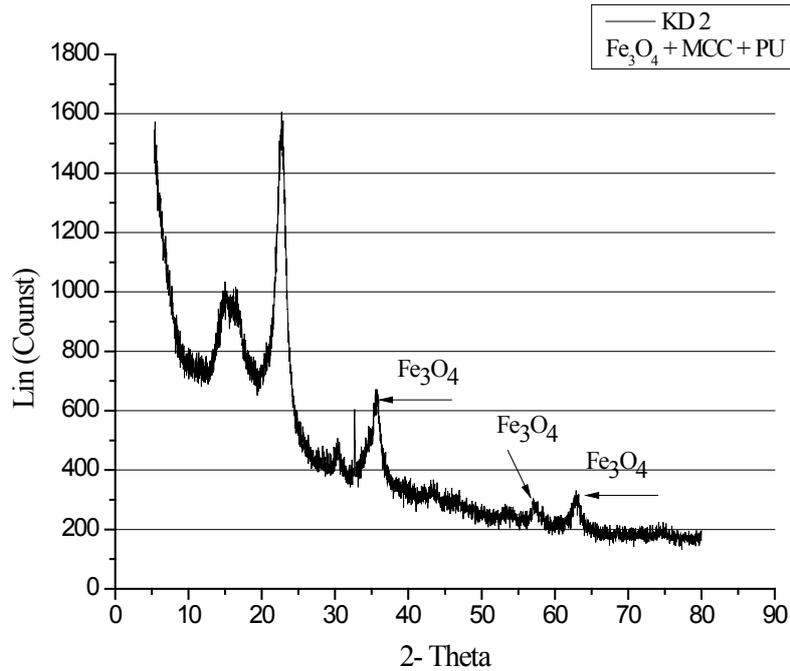


Figure 3. X-ray structure of composite materials with Fe₃O₄ mMCC

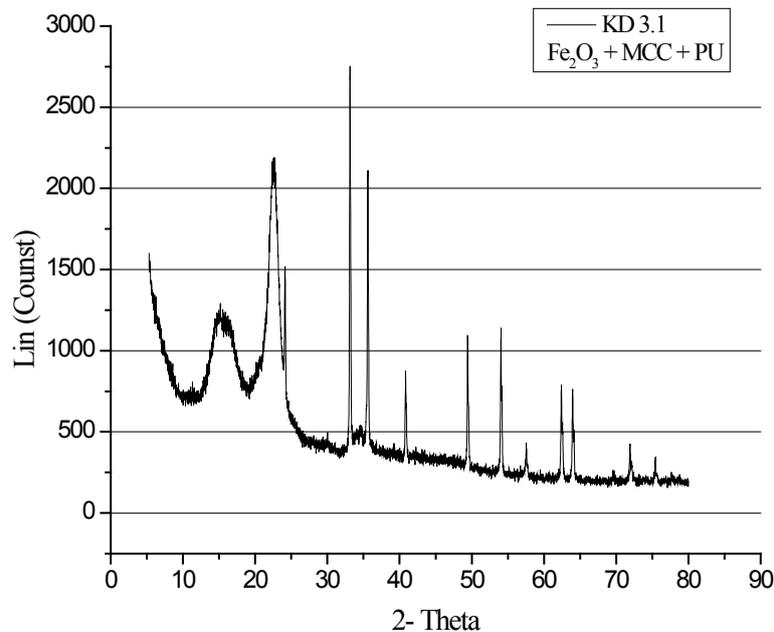


Figure 4. X-ray structure analysis of composite materials with MCC and hematite

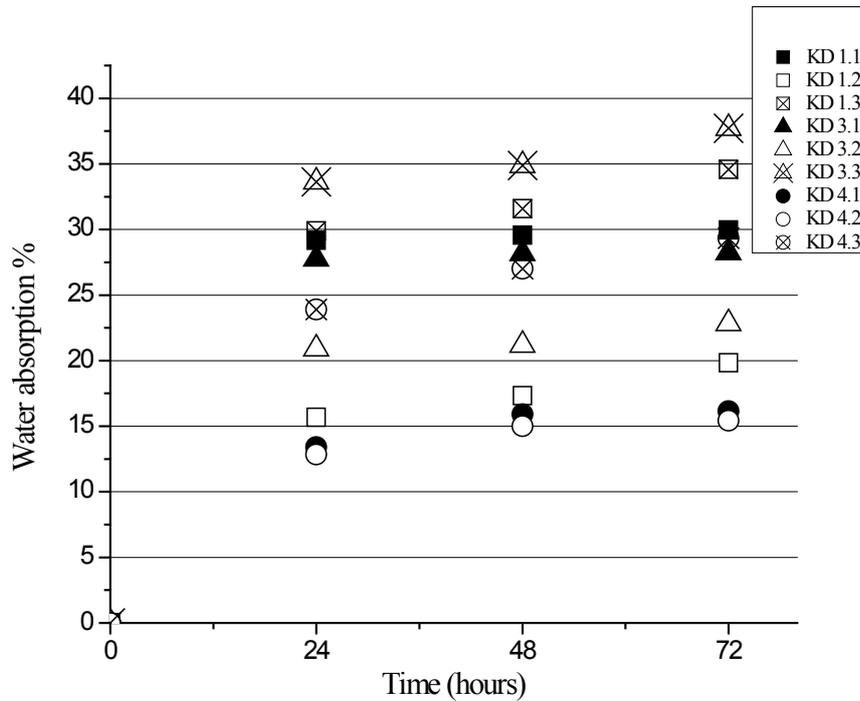


Figure 5. Dependence on water absorption of time

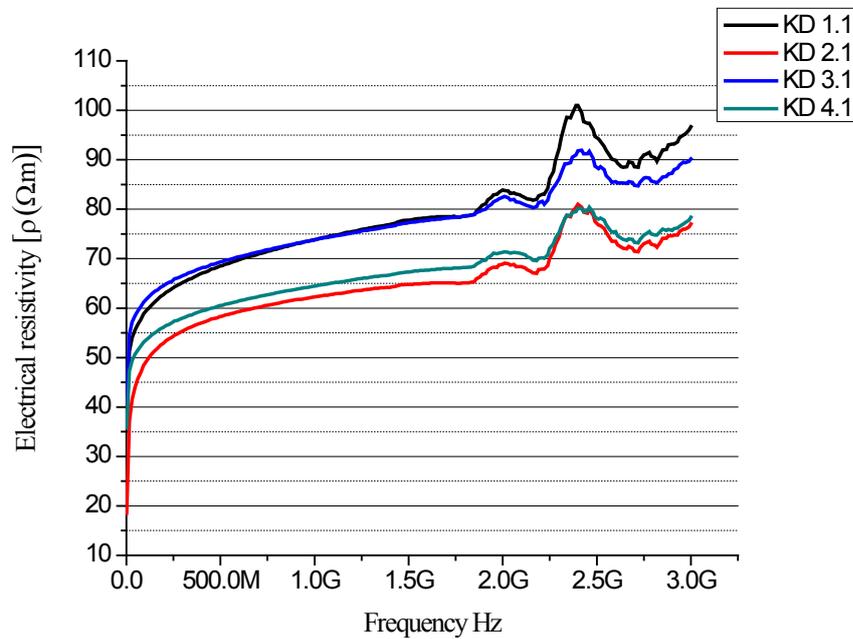


Figure 6. Electrical resistivity as a function of frequency (composites with 30 % PU prepolymer)

The values of the water absorption in percentage were calculated equation 4.

$$WA(t) = (W(t) - W_0) / W_0 \times 100 \quad (4)$$

Where WA (t) is the water absorption at the time t, W₀ is oven dried weight and W (t) is the weight of specimen at a given immersion time t.

Figures 6 - 8 show the dependence of electrical resistivity

of the composite materials on the amount of PU prepolymer used. Sample KD 2.1 has the lowest values of electrical resistivity and highest values of electro conductivity respectively. The effect is due to the magnetite nanoparticles on the mMCC surface. As it can be seen from the figures the values of electrical resistivity and conductivity of KD 4.1 are close to the sample KD 2.1 values.

The conductivity was calculated equation 5. Conductivity

σ was defined as the inverse of resistivity.

$$\sigma = \frac{1}{\rho} \tag{5}$$

As can be seen from figure 7. sample KD 2.2 has the lowest values of el. resistivity and highest values of el. conductivity respectively. Sample KD 4.2 and sample KD 4.1 show no considerable difference in the values of el. resistivity. The amount of PU prepolymer used does not appreciable affect the electrical properties.

Figure 8. shows that sample KD 2.3 has higher values of el. resistivity and lower values of el. conductivity compared to samples KD 2.1 and KD 2.2 due to the lower amount of PU prepolymer.

The measurements of electrical resistivity show that the materials have properties similar to composites with CuS[18].

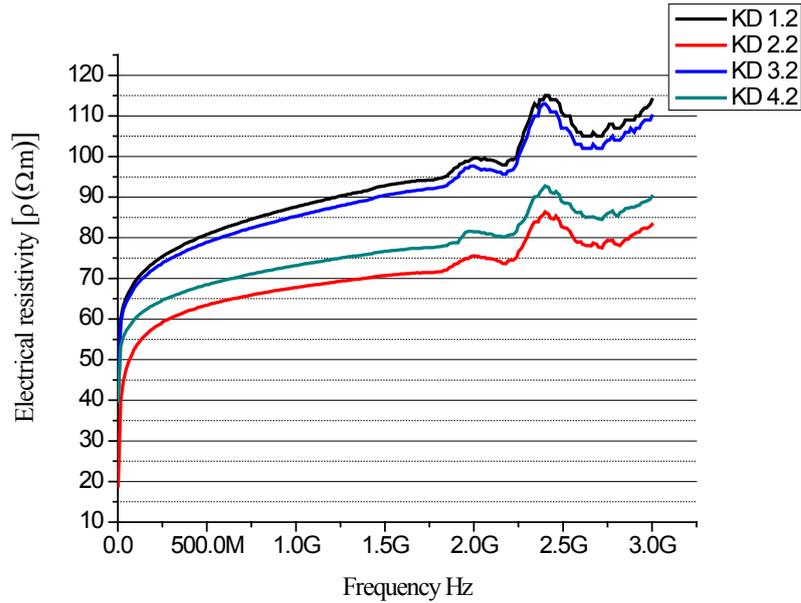


Figure 7. Electrical resistivity as a function of frequency (composites with 20 % PU prepolymer)

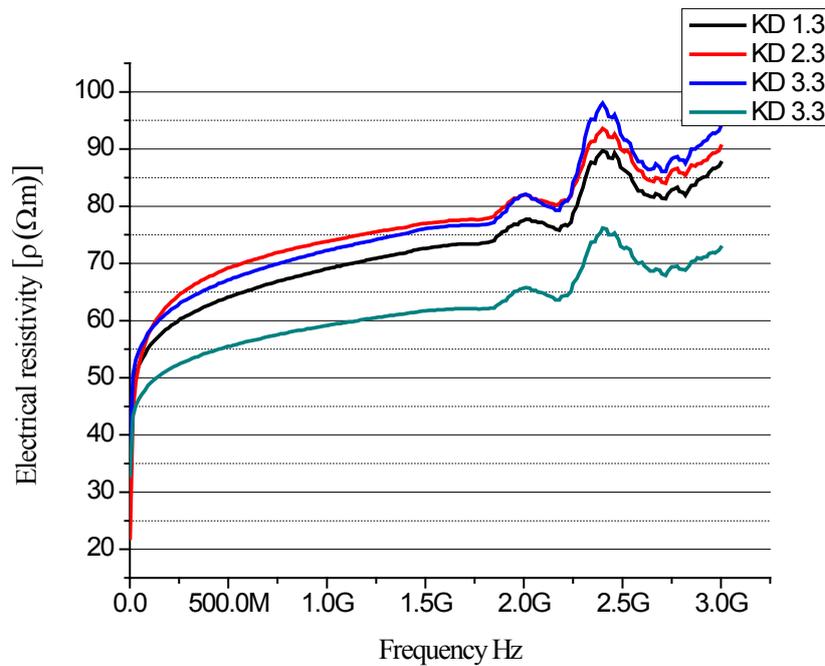


Figure 8. Electrical resistivity as a function of frequency (composites with 10 % PU prepolymer)

6. Conclusions

SEM and XRD investigation show successful MCC – magnetite modification by magnetite. Both investigations show the presence of nano-sized magnetite. As can be seen from SEM micrographs, the micro-sized magnetite particles coexist with nano-sized ones. This fact could be explained by the agglomeration process during the modification of MCC. XRD investigation confirms that the particles are magnetite.

The water absorption degree is an indication that the hematite-filled cellulose composites are more suitable for use in water environment compared to the Fe₃O₄ mMCC composite materials.

Electrical resistivity measurements show that the samples with Fe₃O₄ mMCC have higher values of electrical conductivity than the composite with pure MCC. This can be an indication for successful modification of MCC also. These kinds of materials are possible to have electromagnetic absorption properties and can be used for electromagnetic shielding.

The whole investigation shows that modification of MCC with two-component system of Fe⁺² and Fe⁺³ followed by its chemical transformation in nano- and micro-sized magnetite particles is possible and provides the possibility for further investigation in this direction.

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