

Effects of benzoyl peroxide on some properties of composites based on hemp and natural rubber

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Abstract The obtaining and characterization of polymer composites based on natural rubber and hemp, in which the elastomer crosslinking has been achieved with benzoyl peroxide, are presented. The mechanical characteristics, gel fraction, crosslink density, water uptake swelling parameters and FTIR of the composites based on natural rubber and hemp fiber vulcanized by dibenzoyl peroxide have been investigated as a function of the hemp content. The hardness, modulus at 100 % elongation, tearing strength, tensile strength and elongation at break have been improving with the increasing of fiber content in composites materials due to the better interaction of fiber in natural rubber composites. These results indicate that hemp has a reinforcing effect on natural rubber. Gel fraction value is over 95 % for all blends and varies irregularly depending on the amount of hemp in the composites. The crosslinking density (ν) of samples increases as the amount of hemp in blends increases, because hemp act as a filler in natural rubber blends and leads to reinforcement of the blends. The water uptake and swelling parameters also increases with the increasing of the amount of fiber content, because of the hemp hydrophilic characteristics.

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Introduction

Rubber–fiber composites are used in rubber industry due to the advantages they impart in processing and low cost coupled with high strength. Normally, a rubber–fiber composite can offer a set of properties that may give it the potential of entering in application areas where it is not possible with either of the components in the composite [1]. These composites combine the elastic behavior of rubber with the strength and stiffness of fiber. The aim of the present work is to study the potential of using hemp fiber as reinforcement agent in natural rubber. Hemp fiber is obtained from the bast of the plant *Cannabis sativa* L. It grows easily—to a height of 4 m—without agrochemicals and captures large quantities of carbon. Long, strong and durable, hemp fibers are about 70 % cellulose and contain low levels of lignin (around 8–10 %). The fiber diameter ranges from 16 to 50 microns. Shorter, woody core fibers (tow) contain higher levels of lignin. Hemp has been used for centuries to make rope, canvas and paper. Long hemp fibers can be spun and woven to make crisp, linen-like fabric used in clothing, home furnishing textiles and floor coverings. Hemp fibers are also used to reinforce molded thermoplastics in the automobile industry. The short core fibers go into insulation products, fiberboard and erosion control mats, while the fibrous core can be blended with lime to make strong, lightweight concrete [2]. There are few studies regarding the use and applications of hemp fibers in the development of composites based on rubber and hemp. Osabohien and Egboh [3] performed a study regarding the utilization of bowstring hemp fiber as filler in natural rubber compounds, but elastomer crosslinking was carried out using the classical method based on sulphur and vulcanization accelerators. Vulcanization with sulphur and accelerators of NR is done in general by ionic mechanism and leads to the formation of sulphur bridges between (C–S_x–C) macromolecules or cyclic combination of sulphur. At high temperatures, desulphuration takes place, determining the formation of shorter sulphur bridges. As a consequence of thermal instability of sulphur, NR vulcanized with sulphur can be devulcanized in the presence of disulphur diaryls or amines, at temperatures of over 300 °C [4]. Physical–mechanical properties of samples containing C–S_x–C crosslinking bridges exhibit better tensile strength values than those containing C–C bonds. Although vulcanization with sulphur and vulcanization accelerators leads to obtaining products with better characteristics, it also has disadvantages, such as the fact that during the process of vulcanization nitrosamines (carcinogen products) are formed and the obtained finite products are toxic, contain heavy metals (Zn), have an unpleasant odor and exudate [5, 6].

In this paper, some composites based on natural rubber and hemp, in which the elastomer crosslinking was carried out using benzoyl peroxide, were analyzed. This method of crosslinking results in a better composite resistance to aging than those obtained by the classical method of crosslinking (with sulphur and vulcanization accelerators) [7]. Vulcanisation by organic peroxides is a free radical process. The

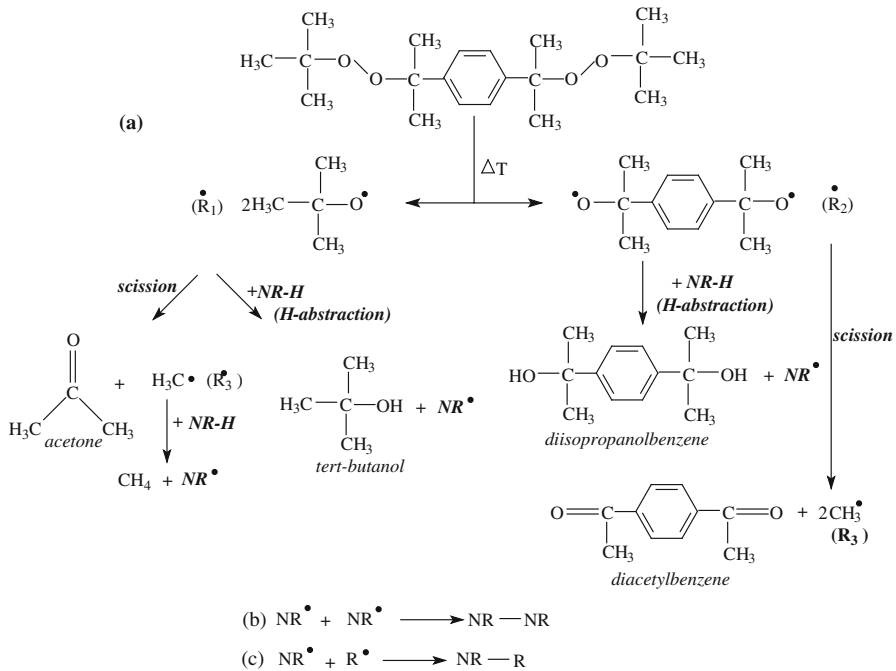
effective crosslinking can take place in the complete absence of oxygen, otherwise peroxy radicals would be formed leading to the oxidation of the rubber. Peroxide vulcanisation is, therefore, limited to products made by press molding. The structure of peroxide vulcanisate is relatively simple compared with that of a sulphur vulcanisate, as rubber chains are crosslinked by simple carbon–carbon linkages, which are highly stable towards heat. Therefore, these vulcanisates possess extremely good thermal aging characteristics, superior to those of even EV systems, and also lower compression set at elevated temperature. However, fatigue resistance and resistance to low temperature crystallization are low [8]. The mechanism of NR crosslinking by peroxide is described in Scheme 1. Vulcanization/crosslinking with peroxides [4, 9–14] is done by radicalic mechanism when bonds between C–C macromolecules are formed. Crosslinking is initiated by the thermal decomposition of a peroxide into primary radicals, R_1 and R_2 (Scheme 1a). This operation is carried out at high temperatures. Free radicals formed are very reactive chemical species which initiate “propagation” reactions. The primary radicals (R_1 and R_2) form stable species (acetone and diacetylbenzene) by scission, and the second radical ($CH_3=R_3$) continues the propagation in the presence of NR. The primary radicals formed, react with NR (NR–H) under H-abstraction and leads to the formation of NR radicals (NR·) and stable species (tert-butanol and diisopropanolbenzene). The recombination of radicals from natural rubber (NR·) and the reaction of NR· with peroxide radicals (R_1 , R_2 or R_3) represent “the end” of the radical polymerization reaction (Scheme 1b, c). Simultaneously with natural rubber crosslinking, may occur also the chemical modification of hemp fibers (Scheme 2). Therefore, free radicals may react with the hydrogen groups of cellulose or lignin fibers of hemp [15–17]. Benzoyl peroxide (BP) and dicumyl peroxide (DCP) are chemicals from the organic peroxide family that are used for the natural fiber surface modifications. In treatments with peroxides, fibers are coated with BP or DCP in acetone solution for about 30 min after an alkali pre-treatment [18–20]. As a result of peroxide treatment, the hydrophilicity of the fibers has decreased [18] and tensile properties have increased [19].

In our study, hemp fibers having high cellulose content are used in the form of filler in a natural rubber matrix. The interface between both components (fiber and rubber matrix) influences the mechanical properties of reinforced composites. A low adhesion between both layers causes a decrease in the mechanical properties of the material, and consequently, is necessary a good adhesion to obtain a composite with high performance (good mechanical properties). The hydrophilic nature of natural fibers, due to the existence of many hydroxyl groups in cellulose, presents a major problem for their use in composites, because it results in low compatibility with hydrophobic polyolefin matrices [21, 22].

Experimental

Materials

For preparing the above polymer composites, the following materials were used: natural rubber (NR) Crep 1× (74 ML₁ + 4 Mooney viscosity at 100 °C, 0.32 %

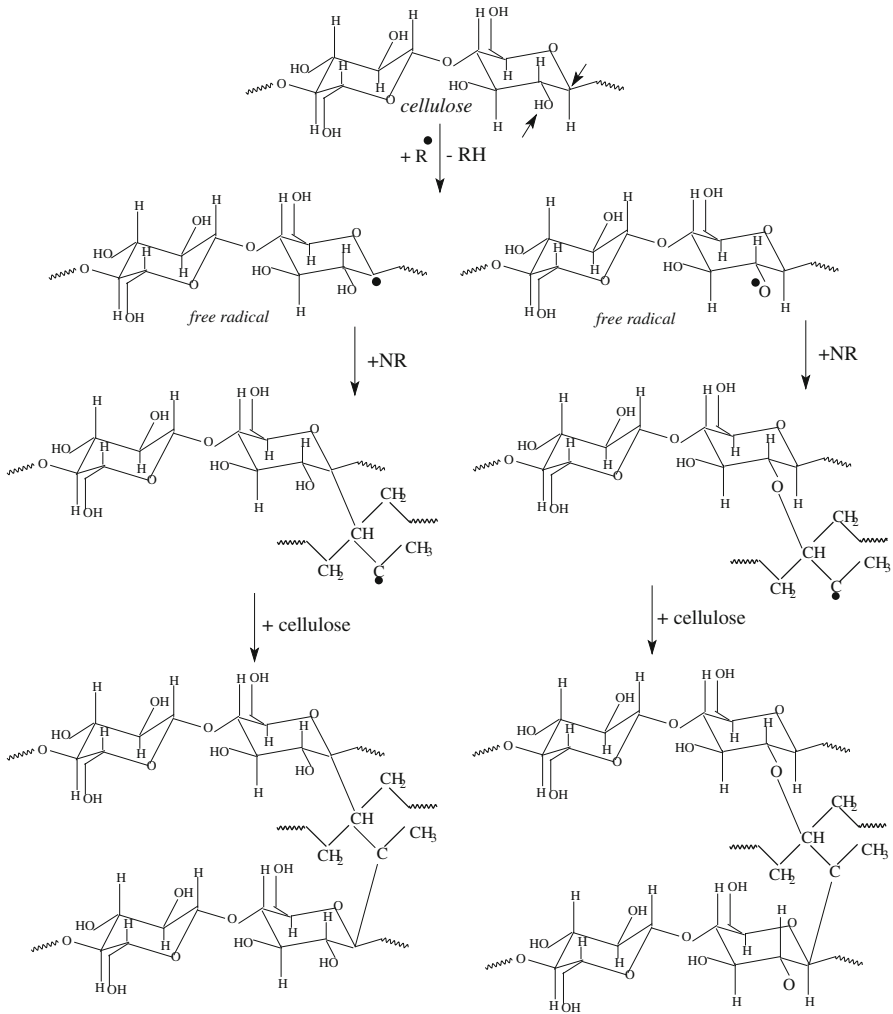


Scheme 1 Mechanism of NR crosslinking by peroxide: **a** decomposition of the peroxide and propagation reaction—the primary radicals formed react with NR by addition and H-abstraction; **b, c** termination reaction by combination

volatile materials, 0.38 % nitrogen, 0.22 % ash, 0.021 % impurities) from Almar Trading Co(Pte) Ltd, Sri Lanka, antioxidant pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate Irganox 1010 from CIBA-BASF, Germania, polyethylene glycol PEG 4000 from Bayer, Germania, (1,128 g/cm³ density, 4–8 °C melting point range), ground hemp (thread length of max 3 mm) and dibenzoyl peroxide Perkadox 14-40B (1,60 g/cm³ density, 3.8 % active oxygen, 40 % peroxide, pH 7) from AkzoNobel Polymer Chemicals, USA, as vulcanizing agent.

Sample preparation

The blends were prepared in an electrically heated laboratory roller. For preparation of the polymeric composites, the blend constituents were added in the following sequences and amounts: 100 parts natural rubber (NR) roll binding (2'), embedding 3 phr (parts to 100 parts rubber) PEG 4000 and 1 phr Irganox 1010 antioxidant (2'), adding 5, 10, 15 and 20 phr ground hemp (2-4'), respectively, 8 phr of dibenzoyl peroxide Perkadox 14-4B (2') as vulcanizing agent was added, homogenisation of blends and removing from the roll in the form of sheet (4'). The process variables were temperature 25–50 ± 5 °C, friction 1:1.1 and total blending time 8–14'. The plates required for physico-mechanical tests with sizes of 150 × 150 × 2 mm³ were obtained by pressing in a hydraulic press at 160 °C and 150 MPa; the curing time was 19'.



Scheme 2 Proposed mechanism for chemical modification of hemp fibers and for the interaction between cellulose and natural rubber and NR/hemp composites obtained

Laboratory tests

Mechanical characteristics

Tensile strength tests were carried out with a Schopper strength tester with testing speed of 460 mm/min, using dumb-bell shaped specimens according to ISO 37/2012. The hardness was measured using a hardener tester according to ISO 7619-1/2011 on samples having the thickness of 6 mm. The elasticity was evaluated with a Schob type test machine also on samples of 6 mm thick, according to ISO 4662/2009.

The sol–gel analysis

The sol–gel analysis was performed on crosslinked NR rubber (with and without hmp) to determine the mass fraction of insoluble NR (the network material resulting from network-forming crosslinking process) from samples (gel fraction). The samples were swollen in toluene and extracted after 72 h to remove any scissioned fragments and unreacted materials. The networks were then dried in air for 6 days and in a laboratory oven at 80 °C for 3 h, and reweighed. The gel fraction was calculated as:

$$\text{Gelfraction} = \frac{m_s}{m_i} \times 100 \quad (1)$$

where m_s and m_i are the weight of the dried sample after extraction and the weight of the sample before extraction, respectively [23, 24].

The crosslink density

The crosslink density (ν) of the samples was determined on the basis of equilibrium solvent-swelling measurements (in toluene at 23–25 °C) by application of the well-known modified Flory–Rehner equation for tetra functional networks. The samples (2 mm thick) were initially weighed (m_i) and immersed in toluene for 72 h. The swollen samples were removed and cautiously dried to remove the excess solvent before being weighed (m_g) and, during this operation, the samples were covered to avoid toluene evaporation during weighing. The solvent traces and other small molecules were then eliminated by drying in air for 6 days and in a laboratory oven at 80 °C for 3 h. Finally, the samples were weighed for the last time (m_s), and volume fractions of polymer in the samples at equilibrium swelling ν_{2m} were determined from swelling ratio G as follows:

$$\nu_{2m} = \frac{1}{1 + G} \quad (2)$$

where

$$G = \frac{m_g - m_s}{m_s} \times \frac{\rho_r}{\rho_s}; \quad (3)$$

ρ_r and ρ_s are the densities of rubber samples and solvent (0.866 g/cm³ for toluene), respectively. The densities of elastomer samples were determined by hydrostatic weighing method, according to the SR ISO 2781/2010. By this method, the volume of a solid sample is determined by comparing the weight of the sample in air with the weight of the sample immersed in a liquid of a known density. The volume of the sample is equal to the difference in the two weights divided by the density of the liquid. The crosslink densities of the samples, ν , were determined from measurements in a solvent, using the Flory–Rehner relationship:

$$\nu = - \frac{\text{Ln}(1 - \nu_{2m}) + \nu_{2m} + \chi_{12} \nu_{2m}^2}{V_1 \left(\nu_{2m}^{1/3} - \frac{\nu_{2m}}{2} \right)} \quad (4)$$

where V_1 is the molar volume of solvent ($106.5 \text{ cm}^3/\text{mol}$ for toluene), v_{2m} is the volume fraction of polymer in the sample at equilibrium swelling, and χ_{12} is the Flory–Huggins polymer–solvent interaction term (the values of χ_{12} are 0.393 for toluene [23, 24]).

Rubber–fiber interactions

The extent of interaction between rubber and fiber can be analyzed using Kraus equation. The Kraus theory and Kraus equation [25] have been successfully used by some researchers to assess the interfacial interaction in fiber-reinforced rubber composites [26–30]. The Kraus equation is as follows:

$$V_{ro}/V_{rf} = 1 - m \frac{f}{1-f} \quad (5)$$

where V_{ro} and V_{rf} are the volume fractions of rubber in the gum vulcanizate and in fiber-filled swollen sample, respectively; f is the volume fraction of fiber, and m is the fiber polymer interaction parameter. The volume fraction of rubber in the swollen sample V_{rf} , was calculated by the expression:

$$V_{rf} = \frac{[(D - FT)/\rho_r]}{[(D - FT)/\rho_r] + [A_0/\rho_s]} \quad (6)$$

where ρ_r and ρ_s are the densities of rubber samples and solvent (0.98 g/cm^3 for natural rubber and 0.866 g/cm^3 for toluene), respectively; D is the deswollen weight of the test specimen (dry weight), F is the weight fraction of the insoluble components, T is the weight of the specimen and A_0 is the weight of the absorbed solvent at equilibrium swelling.

Water uptake test

The effect of water absorption on fiber-reinforced natural rubber composites is investigated in accordance with SR EN ISO 20344/2004. The samples were dried in an oven at $80 \text{ }^\circ\text{C}$ for 2 h and then are allowed to cool at room temperature in desiccators before weighing. Water absorption tests were conducted by immersing the samples in distilled water in bottles and kept at room temperature $23 \pm 2 \text{ }^\circ\text{C}$ and in a laboratory oven at $70 \pm 1 \text{ }^\circ\text{C}$. Samples were removed from the bottles at periodic intervals, and the wet surfaces were quickly wiped using a clean dry cloth or tissue paper and weights of the specimen after swelling were determined at regular intervals until no further increase in solvent uptake was detected. The moisture absorption was calculated by the weight difference. The percentage weight gain of the samples was measured at different time intervals. The water uptake was calculated as:

$$\text{Water uptake (\%)} = \frac{m_s - m_1}{m_1} \times 100 \quad (7)$$

where, m_s is the weight of the sample saturated with water, determined at periodic intervals and m_1 is the initial weight of the oven-dried sample.

Swelling parameters

The swelling studies provide information about the strength of interface, dispersion degree of fibers, and their alignment in the elastomer matrix. Swelling behavior was determined by the change in mass using the following method. For cured rubber blends, the test pieces of known weight (m_1) were immersed in water in diffusion test bottles and kept at room temperature for 49 days (until no further increase in water uptake was detected). After immersion, the samples were taken out from the solvents and the wet surfaces were quickly dried using a tissue paper and reweighed (m_2). The test samples of the blends were further dried in air for 6 days and in a laboratory oven at 100 °C for 6 h, cooled in a desiccator and immediately weighed (m_3). The swelling parameters [30] of blends were calculated as follows:

(a) Calculation of Q_t (mol% uptake of the solvent): the mol% uptake of the solvent, Q_t , for the composite samples was determined using the equation:

$$Q_t = \frac{(m_2 - m_1)/M_s}{m_1} \times 100 \quad (8)$$

(b) Swelling index (SI %) was calculated by the equation:

$$SI (\%) = \frac{m_2 - m_1}{m_1} \times 100 \quad (9)$$

(c) Soluble fraction (SF %) was determined by the following relation:

$$SF (\%) = \frac{m_1 - m_3}{m_1} \times 100 \quad (10)$$

Fourier transform infrared (FTIR) spectroscopy

Changes of the chemical structure of natural rubber/hemp fiber composites vulcanized with dibenzoyl peroxide were highlighted using a FTIR spectrophotometer—JASCO FT/IR 4200, by ATR measurement method. Samples spectra are the average of 30 scans realized in absorption in the range of 4,000–600 cm^{-1} with a resolution of 4 cm^{-1} .

Results and discussion

Physical–mechanical characteristics

The variations of mechanical properties with the increasing of the fiber amount in composites based on NR/fiber are provided in Figs. 1, 2, 3, 4 and 5. The hardness (Fig. 1) and modulus at 100 % elongation (Fig. 2) were increased with the increasing of fiber amount in blends. The hardness exhibits an increase of about 27 % for 5 phr hemp and 60 % for 20 phr hemp, while modulus at 100 % elongation exhibited an increase of 5.5 and 105 % with the same fiber loading. It can be seen from the Fig. 3 that the tensile strength decreased with the increasing of filler (hemp) loading. The decrease in tensile strength is due to the poor adhesion of

the filler–matrix and the agglomeration of filler particles. It has been shown that for irregularly shaped fillers, the strength of the composites can decrease due to the inability of the filler to support stresses transferred from polymer matrix [31]. On the other hand, poor interfacial bonding causes partially separated micro-spaces between the filler particles and the polymer matrix [32]. The elongation at break (Fig. 4) decreased with increasing of fiber content in composites. The decreasing of elongation at break with the fiber content increasing in the composite is the result of the high crosslinking. The elongation at break shows a decrease of 16 % for 5 phr hemp and of 33.4 % for blend with 15-phr fiber content. The tearing strength (Fig. 5) follows the same trend, as the hardness and modulus at 100 % elongation have increased with increase of fiber content in composite. The tearing strength shows an increase of about 26 % for 10 phr hemp and with 60 % for 20 phr hemp content in composite. The values of hardness and modulus at 100 % elongation have increased due to a better interaction of fiber with NR. These results indicate that hemp has a reinforcing effect on natural rubber.

Gel fraction and crosslink density of the blends

Table 1 shows the gel fraction (mass fraction of the network material resulting from a network-forming polymerization or crosslinking process; the gel fraction comprises a single molecule spanning the entire volume of the material sample) and crosslink density (number of crosslinks per unit volume in a polymer network) of the samples vulcanized with dibenzoyl peroxide as a function of the hemp content. Gel fraction value is over 95 % for all blends and varies irregularly depending on the amount of hemp in the composites. The crosslinking density (ν) of samples increases as the amount of hemp in blends increases, because hemp acts as a filler in natural rubber blends and leads to its reinforcement of blends. The experimental results confirmed by other works [24, 33] showed that with the increasing in crosslink density, hardness and modulus at 100 % elongation were increased, whereas the elongation at break decreased. Analyzing the results presented in Figs. 1, 2, 3, 4 and 5, it can be noticed that hardness and modulus at 100 % elongation of blends have higher values and elongation at break has lower values, compared to the control sample. Those results are in accordance with the values of crosslink density in Table 1 and literature data [4, 16, 17].

Rubber–fiber interactions

The extent of interaction between rubber and fiber was analyzed using Kraus equation, and the results are listed in Table 2 and Fig. 6. Samples of NR with 5, 10, 15 and 20 phr content of hemp fiber were swollen in toluene for 72 h. The results of V_{r0} and V_{rf} calculated according to Eqs. 5 and 6 are presented in Table 2 and Fig. 6. From the results in Table 2, it is observed that the equilibrium solvent uptake of the samples decreased as the fiber content increased, which caused an increase in V_{rf} . Therefore, the ratio V_{r0}/V_{rf} decreases since V_{r0} is a constant. This is due to the increased hindrance exerted by the hemp fibers at higher loadings. The diffusion mechanism in the composite is strongly connected with the ability of rubber to

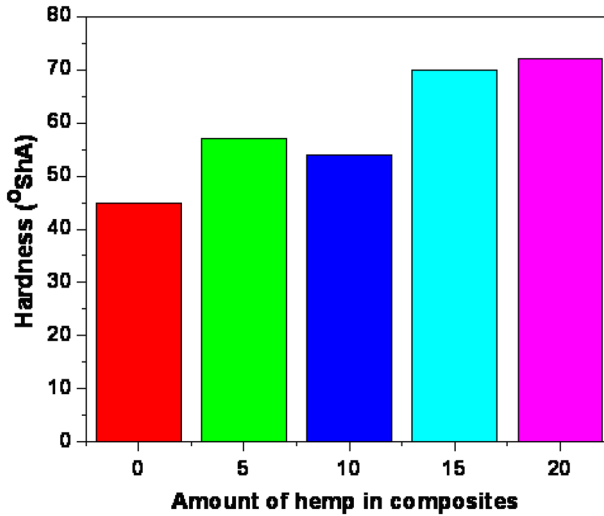


Fig. 1 Hardness according to the amount of hemp in composites

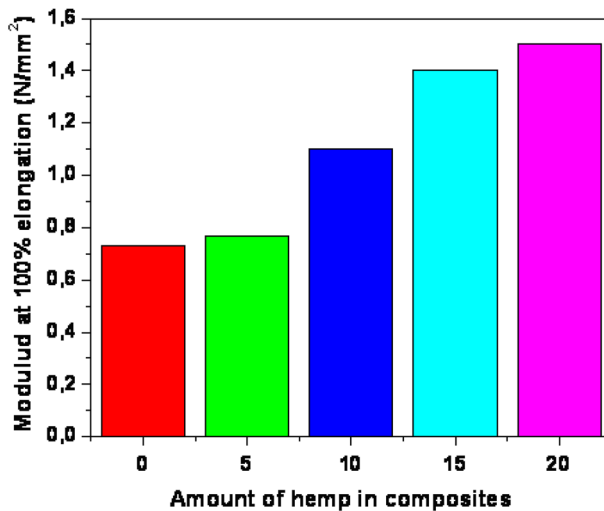


Fig. 2 Modulus at 100 % elongation according to the amount of hemp in composites

provide pathways for the solvent to progress in the form of randomly generated voids. As the void formation decreases with fiber content, the solvent uptake also decreases. The ratio V_{r0}/V_{rf} is the degree of restriction of swelling of the rubber matrix due to the presence of fibers [29]. The more and more reduced values of V_{r0}/V_{rf} ratio are associated with the enhanced adhesion between fiber and rubber, according to the Kraus theory and Kraus equation. The decreased values of V_{r0}/V_{rf} values at higher loadings indicate the reinforcement effect of the fibers. The

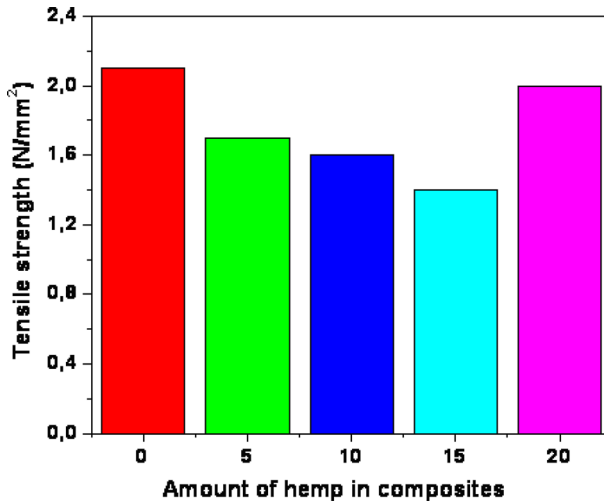


Fig. 3 Tensile strength according to the amount of hemp in composites

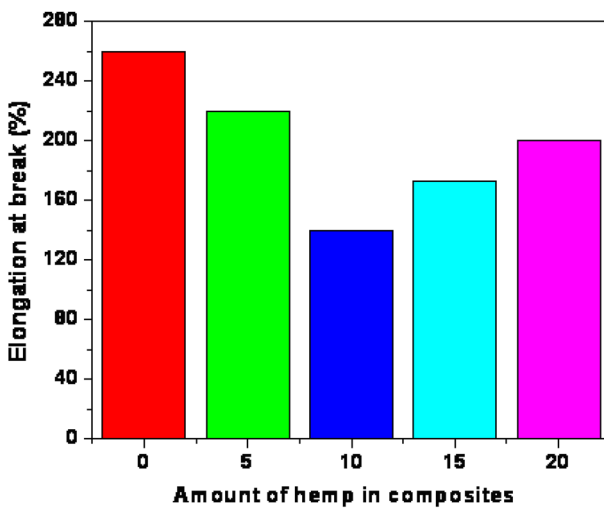


Fig. 4 Elongation at break according to the amount of hemp in composites

compatibilized composites based on NR and hemp fiber have a negative slope as shown in Fig. 6 [29].

Swelling parameters

The swelling parameters and water uptake of samples are presented in Tables 3, 4, 5, 6 and Figs. 7 and 8. Figure 7 shows the water uptake according to the amount of

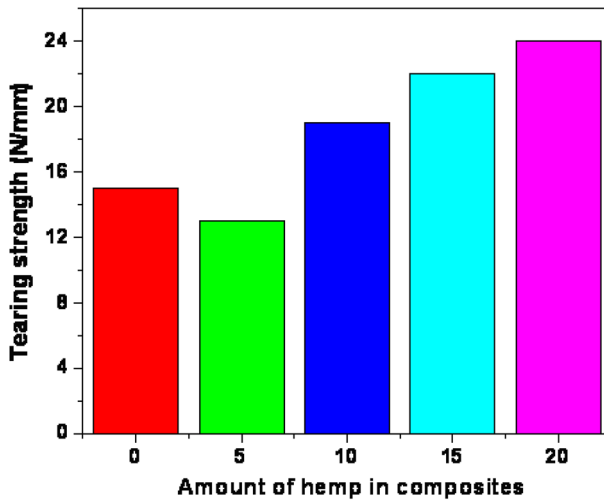


Fig. 5 Tearing strength according to the amount of hemp in composites

Table 1 Gel fraction and crosslink density of samples

Sample	Gel fraction (%)	ν (10^{-4} mol/cm ³)
NR	95.17	2.3458
NR/5 phr hemp	96.62	3.0240
NR/10 phr hemp	96.68	3.2264
NR/15 phr hemp	96.19	3.5515
NR/20 phr hemp	96.65	4.0724

hemp in composites: (a) at 25 °C and (b) at 70 °C. It can be observed that water uptake increased with increasing fiber content and temperature. Thus, (a) after 24 h in water at room temperature water uptake values were: 0.8 % for the sample without hemp, 1.75 % for 5 phr hemp, 2.56 % for 10 phr hemp, 3.2 % for 15 phr hemp and 3.92 % for 20 phr hemp; (b) after 24 h in water at 70 °C water uptake values were: 3.13 % for the sample without hemp, 4.41 % for 5 phr hemp, 5.31 % for 10 phr hemp, 6.57 % for 15 phr hemp and 6.88 % for 20 phr hemp; (c) after 216 h in water at room temperature water uptake values were: 1.8 % for the sample without hemp, 5.11 % for 5 phr hemp, 8.35 % for 10 phr hemp, 9.27 % for 15 phr hemp and 10.97 % for 20 phr hemp; (d) after 216 h in water at 70 °C water uptake values were: 7.78 % for the sample without hemp, 10.06 % for 5 phr hemp, 11.34 % for 10 phr hemp, 11.9 % for 15 phr hemp and 12.76 % for 20 phr hemp. It can be seen that the composites absorb water very fast initially (in the first 24 h), the amount of water absorbed then being increasingly smaller (after 216 h). The temperature of 70 °C seems to accelerate the moisture water uptake behavior. By increasing the amount of hemp in composite the water absorption increases also. This can be explained by the fact that the diffusion of water in elastomers is not

Table 2 V_{rf} and V_{ro}/V_{rf} of NR/hemp fiber composites in toluene

Samples	V_{rf}	V_{ro}/V_{rf}
NR/5 phr hemp	0.2720	0.9161
NR/10 phr hemp	0.2767	0.9005
NR/15 phr hemp	0.2818	0.8845
NR/20 phr hemp	0.2944	0.8465

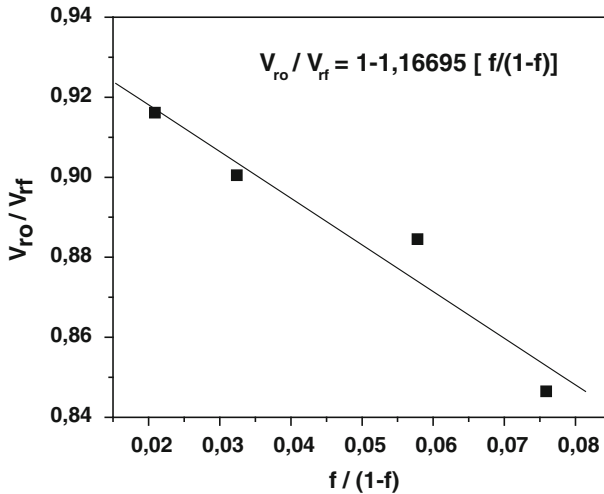


Fig. 6 V_{ro}/V_{rf} versus $f/(1 - f)$ relation curves (Kraus plot) of the NR/hemp fiber composites

straightforward due to the presence of hydrophilic materials (such as the hemp). In the case of NR it is mainly proteinaceous. When water diffuses into the rubber, the water-soluble hydrophilic materials dissolve, forming droplets of solution within the rubber. An osmotic pressure gradient would exist between watery domains in the rubber and that of the external solution immersing the rubber. This results in more water diffusing into the internal solution droplet. Water absorption reaches equilibrium when the elastic stresses acting on the droplets balance the osmotic pressure difference [34].

The water absorption at 23 ± 2 °C becomes constant after 1,176 h (Fig. 8). In these composites, water is absorbed mainly by the hemp. The maximum percentages of water uptake for NR with 5, 10, 15 and 20 phr content of hemp fiber, immersed at room temperature for 1,176 h were 8.09, 12.70, 13.70 and 15.11 %, respectively. The water uptake for all blends, except NR without other additions (which absorbed a low percentage of water, 1.85 % after 1,176 h), is linear at the beginning, then slows and reaches saturation after prolonged time. Both the initial rate of water absorption and the maximum water uptake grow for all composites samples because of the fiber volume fraction growth. This phenomenon can be explained by

Table 3 Q_t (mol% uptake of the solvent)

Time (h)	Q_t (%)										
	24	48	72	96	120	216	336	480	720	888	1.176
NR	0.04	0.07	0.08	0.09	0.09	0.09	0.11	0.11	0.11	0.11	0.11
NR/5 phr hemp	0.09	0.14	0.16	0.17	0.21	0.28	0.35	0.35	0.39	0.39	0.50
NR/10 phr hemp	0.14	0.19	0.24	0.27	0.34	0.46	0.53	0.56	0.61	0.64	0.70
NR/15 phr hemp	0.18	0.23	0.25	0.29	0.38	0.51	0.59	0.61	0.68	0.71	0.76
NR/20 phr hemp	0.22	0.30	0.34	0.39	0.49	0.61	0.69	0.73	0.80	0.81	0.84

Table 4 Swelling index of samples

Time (h)	Swelling index (%)										
	24	48	72	96	120	216	336	480	720	888	1.176
NR	0.79	1.25	1.43	1.75	1.76	1.80	1.81	1.85	1.85	1.85	1.85
NR/5 phr hemp	1.75	2.43	2.79	3.08	3.72	5.11	6.21	6.34	6.96	7.17	8.08
NR/10 phr hemp	2.56	3.57	4.37	4.92	6.09	8.35	9.56	10.04	10.99	11.59	12.70
NR/15 phr hemp	3.20	4.07	4.54	5.34	6.91	9.27	10.72	11.01	12.26	12.78	13.70
NR/20 phr hemp	3.92	5.38	6.07	6.98	8.77	10.97	12.58	13.12	14.40	14.65	15.11

Table 5 Swelling coefficient of samples

Time (h)	Swelling coefficient										
	24	48	72	96	120	216	336	480	720	888	1.176
NR	0.008	0.012	0.014	0.017	0.0176	0.018	0.018	0.018	0.018	0.018	0.018
NR/5 phr hemp	0.018	0.024	0.028	0.031	0.037	0.051	0.062	0.063	0.069	0.072	0.081
NR/10 phr hemp	0.025	0.035	0.043	0.049	0.061	0.083	0.095	0.101	0.101	0.116	0.127
NR/15 phr hemp	0.032	0.041	0.045	0.053	0.069	0.092	0.107	0.110	0.123	0.127	0.137
NR/20 phr hemp	0.039	0.054	0.061	0.069	0.087	0.109	0.126	0.131	0.144	0.146	0.151

Table 6 Solubility (soluble fraction) % of samples

	Solubility (%)
NR	1.0674
NR/5 phr hemp	0.6903
NR/10 phr hemp	0.7479
NR/15 phr hemp	0.9718
NR/20 phr hemp	1.4689

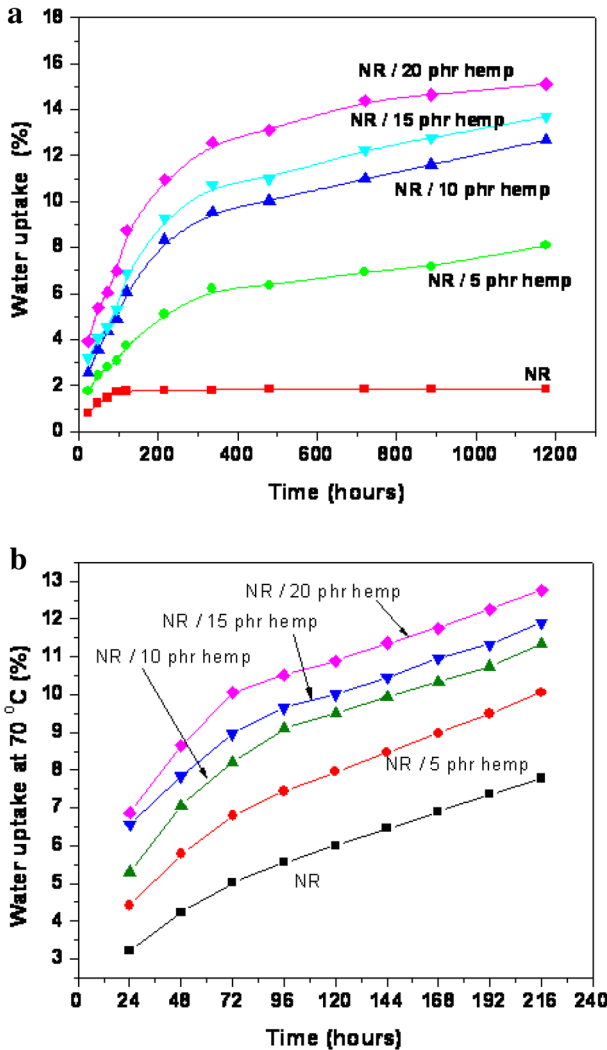


Fig. 7 Water uptake according to the amount of hemp in composites: **a** at $23 \pm 2 \text{ }^\circ\text{C}$, **b** at $70 \pm 1 \text{ }^\circ\text{C}$

considering the water uptake characteristics of the hemp fibers. When the NR/hemp composite is exposed to moisture, the hemp fibers suffer swelling. The high cellulose content in hemp fiber (approximately 75 %) further contributes to more water penetrating into the interface of composites materials [35]. The natural rubber is a hydrophobic material and its water absorbability can be neglected [36]. For the same absorption time, composites having a high fiber content exhibit high water absorption because one of the properties of these natural fibers (hemp) is the hydrophilic characteristic. The obtained composites can be used in manufacturing products with applications in the automotive industry, in the furniture industry, etc.

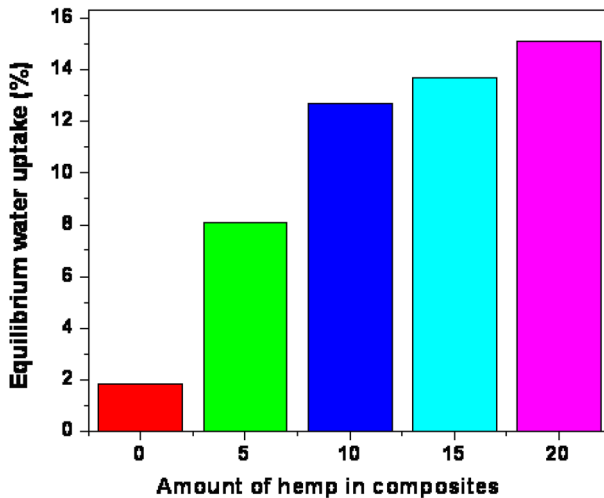


Fig. 8 Equilibrium water uptake according to the amount of hemp in composites at 23 ± 2 °C

FTIR study

Fourier transform infrared spectroscopy is one of the most widely employed techniques for analyzing polymeric materials. The natural rubber/hemp fiber composites vulcanized with dibenzoyl are analyzed by FTIR to know the various chemicals constituents present in them. The natural rubber is composed of hydrocarbons (89.3–92.4 wt%), proteins (2.5–3.5 wt%), and other ingredients (4.1–8.2 wt%). The main component of NR is cis-1, 4-polyisoprene with a high degree of long chain branching generally associated with the presence of non-hydrocarbon groups distributed along the chains. Natural fibers can be considered as naturally occurring composites consisting mainly of cellulose fibrils embedded in lignin matrix. The cellulose fibrils are aligned along the length of the fiber, which render maximum tensile and flexural strengths, in addition to providing rigidity. The reinforcing efficiency of natural fiber is related to the nature of cellulose and its crystallinity. The main components of natural fibers are cellulose (α -cellulose), hemicellulose, lignin, pectins and waxes [37].

Figures 9, 10a–c and Table 7 show the infrared spectra and the characteristic bands observed one by one in natural rubber, hemp fibers and natural rubber/hemp fiber composites vulcanized with dibenzoyl peroxide, in the range of the $4,000\text{--}650\text{ cm}^{-1}$. The broadband in the $3,340\text{--}3,334\text{ cm}^{-1}$ region, which can be due to the OH-stretching vibration, gives considerable information concerning the hydrogen bonds from the amorphous celluloses [38]. The presence of amorphous cellulosic samples can be confirmed by the band from $2,940\text{ to }2,840\text{ cm}^{-1}$, corresponding to the C–H stretching vibration in methyl and methylene groups [39]. The absorption located in the region $1,740\text{--}1,730\text{ cm}^{-1}$ corresponds to the C=O stretch in non-conjugated ketones, carbonyls and in ester groups [39]. Absorption bands in the region

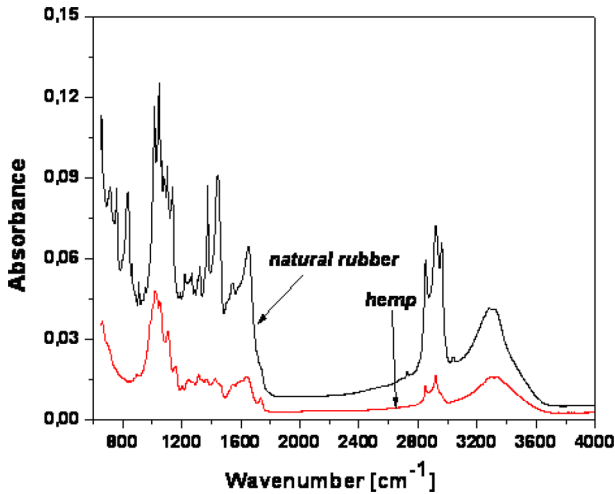


Fig. 9 FTIR spectra of hemp and natural rubber

1,635–1,623 cm^{-1} were due to absorbed water in cellulose [40]. or are caused by lignin (aromatic skeletal vibrations) [39]. In addition, the absorption band in the region 1,432–1,430 cm^{-1} is assigned to a symmetric CH_2 -bending vibration. This band is also known as the “crystallinity band” [38]. The characteristic peak which appeared in the range of 1,320–1,305 cm^{-1} is assigned to the cellulose component: bending vibration of C–H and C–O groups of aromatic rings [39, 40]. The absorption located in the region 1,165–1,150 cm^{-1} corresponds to the anti-symmetrical deformation of the C–O–C bond, and absorption located in the region 1,070–1,020 cm^{-1} is due to the C–O, alcohol, O–H or aliphatic ethers [39, 40].

The presence of absorption bands in the spectrum of natural rubber in the spectral region located between 1,664 and 1,658 cm^{-1} is due to valence vibration of homogeneous double bonds (C=C) in the NR structure. Their intensity decreases for vulcanized samples compared with non-vulcanized samples. The specific absorption bands of $\text{R}_2\text{C}=\text{CH}-\text{R}$ group are observed at 836–838 cm^{-1} . These changes occur as a result of elastomer crosslinking and the consumption of double bonds. The absorption band of CH_2 deformation occurs at 1,430–1,460 cm^{-1} and of CH_3 asymmetric stretching at 1,360–1,380 cm^{-1} [16, 17, 41]. It is known that the NR contains also other compounds such as lipids, neutral glycolipids and phospholipids, etc. Absorption bands with maxima at 3,035–3,036 cm^{-1} corresponding to CH stretching in the $-\text{CH}=\text{CH}_2$ group are observed. Vulcanization of the polymeric compositions results in consumption of the double bonds in NR molecules, so that the intensities of these absorption bands decrease. The characteristic bands of the saturated aliphatic sp^3 C–H bonds are observed in the region 2,970–2,830 cm^{-1} which are assigned to $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{as}}(\text{CH}_2)$, and $\nu_{\text{s}}(\text{CH}_2)$, respectively (as three corresponding bends) [42]. These bands are specific to natural rubber and cellulose, lignin or hemicellulose, from the hemp fibers existing in the mixture [43]. It can be noticed that with the hemp amount increasing in the mixture, the intensity bands

Fig. 10 FTIR spectra for NR/hemp composites: **a** in range of $650\text{--}1,400\text{ cm}^{-1}$; **b** in range of $1,300\text{--}1,800\text{ cm}^{-1}$; **c** in range of $2,250\text{--}3,750\text{ cm}^{-1}$

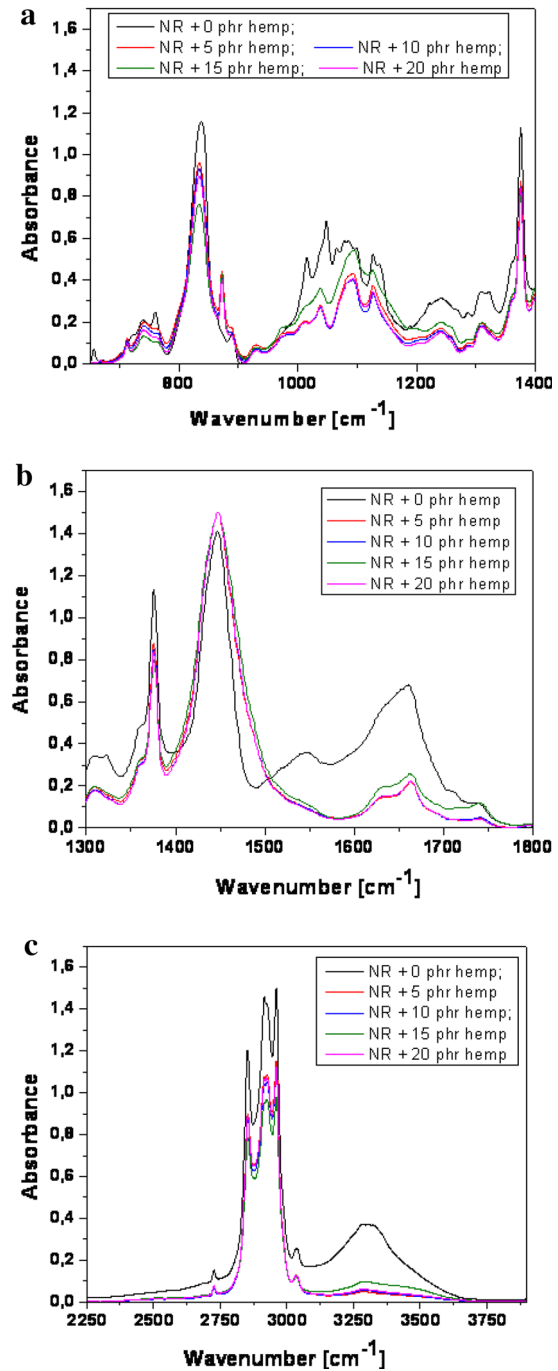


Table 7 Characteristic infrared bands observed in NR/hemp composites

Wave number (cm ⁻¹)	Assignment
3,340–3,334	OH-stretching vibration from the amorphous cellulose
3,280–3,290	N–H stretching vibration of amide groups from the existing proteins in NR
3,035–3,036	CH stretching of–CH=CH ₂ group from NR
2,940–	C–H stretching vibration in methyl and methylene groups (from cellulose)
2,964–2,957	–CH ₃ asymmetric-stretching vibration of NR
2,930–2,910	–CH ₂ asymmetric-stretching vibration of NR
2,860–2,847	–CH ₂ – symmetric-stretching vibration of NR
1,740–1,730	C=O stretch in non-conjugated ketones, carbonyls and in ester groups (from cellulose)
1,740–1,720	The fatty add ester groups existing in NR
1,635–1,623	C=C alkene or absorbed water in cellulose
1,432–1,430	CH ₂ symmetric bending vibration (cellulose, lignin)
1,430–1,460	Deformation vibration –CH ₃ – group from NR
1,360–1,380	–CH ₃ symmetric deformation of NR
1,320–1,305	Bending vibration of C–H and C–O groups of aromatic rings (cellulose, lignin)
1,165–1,150	Anti-symmetrical deformation of the C–O–C bond (cellulose, lignin)
1,664–1,658	R ₂ C=CR ₂ stretching vibration of homogeneous double bonds from NR
1,070–1,020	O–H alcohols (primary and secondary) and aliphatic ethers (cellulose, lignin)
836–838	Deformation vibration of R ₂ C=CH–R groups from NR

vary out of uniformity. The absorption bands at 3,280–3,290 cm⁻¹ were identified in the proteins and in both mono-peptides and di-peptides present in natural rubber [44]. This band is specific for NR and cellulose, lignin and hemicellulose from the hemp fibers existing in the mixture [43]. Band intensity significantly decreases for vulcanized samples with the amount of fiber hemp increasing in the mixture. These are the consequences of proteins and peptides degradation. The absorption band around 1,740–1,727 cm⁻¹ was identified to the fatty acid ester groups in NR [45]. In fingerprint region, there are some specific single bands for cellulose, lignin and hemicellulose from hemp fibers but also for NR, some of them mentioned above. With the hemp fiber amount increasing, significant changes occur in the specific absorption bands of hemp fiber fingerprint.

Conclusions

Our investigation of the basic mechanical and some physical chemical parameters as a function of hemp content in peroxide-vulcanized NR proved the reinforcing effect of the hemp fibers. The mechanical characteristics, gel fraction, crosslink density, water uptake and swelling parameters of composites based on natural rubber and hemp vulcanized by dibenzoyl peroxide, have been investigated as a function of the hemp content. The mechanical characteristics (hardness, modulus at 100 %

elongation, tearing strength, tensile strength and elongation at break) were improved depending on the level of filling by hemp fibers in composite. These results indicate that hemp has a reinforcing effect on natural rubber. Gel fraction value is over 95 % for all blends and varies irregularly depending on the amount of hemp in the composite. The crosslinking density (ν) of samples increases as the amount of hemp in blends increases, because hemp acts as a filler in natural rubber blends and leads to the reinforcement of blends. The water uptake and swelling parameters increases also with increasing the amount of fiber content due to the hydrophilic characteristics of hemp. The water absorption becomes constant after 1,176 h. In these composites, the water is absorbed mainly by the hemp. Obtaining polymeric composites based on hemp and natural rubber is an efficient method of exploiting hemp waste from the textile industry. The use of natural fibers in composites has increased due to their relative cheapness, their ability to be recycled and for the fact that they can compete well in terms of strength per weight of material.

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