

Aspects Regarding Ageing of Compounds Based on Natural Rubber and Plasticized Starch

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This paper presents a study on the behaviour of composites based on natural rubber and plasticized starch after aging under temperate climate conditions. Natural rubber blends containing different amounts of glycerine-plasticized starch as biodegradable filler were made. Analysis of samples after being kept for 1 year in temperate weather conditions shows a change in the surface of vulcanizates due to the influence of atmospheric factors. Surface oxidation and degradation was highlighted by: FTIR analysis (appearance of -OH, -COOH groups, etc.), SEM microscopy (appearance of cracks on the surface), immersion in water. The degradation of the materials is also highlighted by the decrease of the physical-mechanical properties, the gel fraction and crosslinking degree. The best aging behaviour was observed in the mixture containing a low amount of biodegradable starch and the worst behaviour was that of the control starch-free mixture.

Keywords: polymer composites, natural rubber, starch, degradation, properties

Products made from cured rubber undergo various physical and chemical influences over time, causing significant changes in rubber properties. These changes have led to the introduction of the notion of ageing. Vulcanizate ageing in the atmosphere is a destructive form of simultaneous action of aggressive factors such as oxygen, ozone, light, heat and mechanical stress causing degradation over time of vulcanizates if they are not provided with effective protection [1].

In order to evaluate the relative resistance of rubber to deterioration with the passing of time, accelerated ageing and heat resistance tests can be carried out. For this purpose, rubber is subjected to controlled deterioration conditions, over determined periods of time, and then characteristics are measured and compared with the properties of unaged rubber. Accelerated ageing does not reliably and under all circumstances reproduce changes caused by natural ageing [2].

This paper makes a comparison between accelerated ageing and ageing under temperate climate conditions of mixtures based on natural rubber and plasticized starch.

It is known that natural rubber (NR) aging in air affects its properties. Due to the high level of unsaturation of NR, it can be easily attacked by oxygen. It was found that the oxidation of NR is further accelerated by heat, light, impurities, and mechanical strainstress [3].

In this study, various amounts of biodegradable filler, namely starch plasticized with glycerine, were added to natural rubber mixtures. Ageing of starch-based materials leads to increased hardness, depending on their physical condition and environmental conditions. This increase in hardness may be linked to two processes. If materials are stored in a glassy state ($T_g < \text{storage temperature}$) increased rigidity is generally associated with a structural relaxation phenomenon or *physical ageing* that occurs in the material. If they are stored in an amorphous state ($T_g > \text{storage temperature}$), increased hardness is usually linked to a molecular reorganization process known as retrogradation. In 1968, Collison [4] defined retrogradation

as a crystallization process occurring due to the very strong tendency to form hydrogen bonds between hydroxyl groups on adjacent starch molecules. Retrogradation can eliminate water from the polymer network. This process is known as syneresis. Retrogradation is directly linked to the ageing of bread [5-6].

Starch introduced in the rubber mixtures was plasticized with a polyol - glycerine. Although the main functionality of these compounds is their plasticizing effect, papers were published suggesting that polyols may interact with the polymer chains of starch, reducing the retrogradation rate of these materials [7].

Several research studies have highlighted the influence of biodegradable fillers such as starch on improving rheological and physical-mechanical characteristics of some mixtures based on natural rubber [8-9]. Studies on ageing behaviour in temperate climate conditions or accelerated ageing of these types of mixtures have not been carried out yet.

Experimental part

The following materials were used in this study:

Natural rubber (NR) Crep from Sangtvon Rubber Ltd, in the form of white rubber sheets, Mooney viscosity 67.64 ML (1' + 4') 100°C, volatile matter content of 0.5%, nitrogen content 0.45%, ash content of 0.25%, impurity content of 0.026%;

Starch - produced by Lach-Ner - soluble potato starch (water insoluble substances 0.28%; loss on drying 16.9%, easily biodegradable: BOD₅ - 0.6 g/g - and COD -1.2 mg/g);

Glycerine produced by SC Chimreactiv SRL (free acidity 0.02%, density 1.26 g/cm³, purity 99.5%);

Richon IPPD antioxidant (4010 NA) N-isopropyl - N-phenyl - phenylene diamine, 98% purity, molecular mass 493.6374;

For crosslinking blends, the following were used: di(tert-butylperoxy-izopropil)benzen Perkadox 14-40B-GB (density 160 g/cm³, 3.8% active oxygen content, 40% peroxide content, pH 7) and polyfunctional monomer

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trimethylolpropane trimethacrylate Luvomaxx TMPT DL 75 (TMPT) (22 % ash, pH 9.2, density 1.36 g/cm³, 75 ± 3 % active ingredient);

Plasticizing Starch

Starch is dried at 80°C for 24 h. Starch (65%) are mixed with glycerine (35%) for 7 min at 2000 rpm and 70°C until a homogenous mixture is obtained. It is left for 16 h in a dry place for stabilization. Starch was plasticized to improve its processability and other properties [10].

Obtaining compounds based on natural rubber and plasticized starch

Mixtures were obtained by mixing on a roll mill. First, the NR were added into two roll mills. After mixing (ca 3'), 1 phr (parts per 100 rubber parts) antioxidant (2'); 0 phr, 15.4 phr, 30.8 phr and 46.2 phr glycerine-plasticized starch (5-15'), respectively, and lastly the vulcanizing agent: 8 phr peroxide and 3 phr TMPT are added into the compounding (2'). The mixture is homogenised and taken off the roll mill in the form of a sheet about 2 mm thick (3'). Working parameters: friction 1:1,1, temperature 55- 75°C, time 15-25 min.

Preparation of Sample: The test specimen sheets of all compounds were produced using compression moulding. The temperature of the compression moulding machine was kept constant at 165°C. The time taken to produce the specimen sheets was based on the curing time (t_{90}) from the curing testing (12-15min) [9].

Laboratory Tests

Mechanical properties of samples were measured on a Schopper tensile tester with a nominal rate of the traverse of the moving grip of 460 mm/min. Modulus at 100% strain, tensile strength, and elongation at break tests were carried out according to the conditions described in ISO 37/2012, on dumb-bell shaped specimens of type 2 (the precision and the uncertainties of the test are ±0.64 for tensile strength and ±2.95 for elongation at break). Tearing strength tests were carried out using angular test pieces (type II) according to SR EN 12771/2003. Hardness of materials was measured using the Shore A scale with samples of 6mm thickness, by using a hardener tester according to ISO 7619- 1/2011 (the precision and the uncertainties of the test are ±0.05). Elasticity was evaluated with a Schob test machine using 6 mm thick samples, according to ISO 4662/2009.

Resistance to swelling by liquids was determined according to ISO 1817/2005 by the change in mass using the following method: the test pieces of known weight were immersed in water and toluene, in diffusion test bottles and kept at room temperature for 72h. After immersion, the samples were taken out from the solvents, and the wet surfaces were quickly dried using a tissue paper and reweighed.

To calculate the percentage change in mass Δm_{100} the following formula was used:

$$\Delta m_{100} = \frac{m_i - m_0}{m_0} \times 100 \quad (1)$$

where m_0 is the initial mass of the test piece and m_i is the mass of the test piece after immersion.

Report the result as the median value for the three test pieces. The precision and the uncertainties of the test are ±0.04.

The densities of elastomer samples were measured according to ISO 2781/2010 (the precision and the uncertainties of the test are ±0.09)

Accelerated ageing trial was done according to SR ISO188/20010 using the hot air circulation oven method. Similar samples to those used for tensile testing and for hardness determination were used. Test duration was of 7 days and temperature of 70 ± 1°C. The results were compared with those from samples not subjected to ageing.

In this paper, ageing of samples was determined for a period of 1 year under temperate climate conditions. The period when samples were subjected to degradation was: 30 august 2016-30 august 2017, in Bucharest, Romania. Temperature variation was between +39 (-) 20°C. Romania has a temperate continental climate in transition, marked by some oceanic, continental, Scandinavian-Baltic and sub-Mediterranean influences, characterized by mild winters and a stronger rainfalls (particularly in autumn) [11].

Gel fraction determination

Crosslinked NR (with and without starch) was analysed to determine mass fraction of insoluble NR in the samples (gel fraction). The samples were swollen in toluene for 72 h to eliminate cleaved fragments and unreacted materials. Samples were weighed again. The gel fraction was calculated using the following relation (2):

$$Gel\ fraction = \frac{m_s}{m_i} \times 100 \quad (2)$$

where m_s and m_i are the mass of the dry sample after swelling and the mass of the sample before swelling [12-14].

Crosslinking density (ν) of samples was determined based on equilibrium measurements in a solvent (toluene at 23-25°C) by applying the modified Flory-Rehner equation for tetrafunctional networks. Samples (thickness of 2 mm) were initially weighed (m_i) and immersed in toluene for 72 h. Swollen samples were then carefully wiped with tissue paper to remove excess solvent before weighing (m_s) in weighing ampoules to avoid evaporation of toluene during weighing. All samples were air dried for 6 days and in a laboratory oven at 80°C for 12 h to completely remove the solvent. Finally, samples were weighed again (m_s), and volume fractions of the polymer in the samples swollen to equilibrium v_{2m} were determined from the swelling ratio, G , as follows:

$$v_{2m} = \frac{1}{1 + G} \quad (3)$$

where:

$$G = \frac{m_s - m_i}{m_i} \times \frac{\rho_r}{\rho_s} \quad (4)$$

ρ_r and ρ_s are densities of rubber samples and solvent (toluene density was 0.866 g/cm³).

Crosslinking density, ν , was determined using the Flory-Rehner equation:

$$\nu = - \frac{Lr(1 - v_{2m}) + v_{2m} + \chi_{12} v_{2m}^2}{V_1 \left(v_{2m}^{1/3} - \frac{v_{2m}}{2} \right)} \quad (5)$$

where V_1 is the molar volume of the solvent (106.5 cm³/mol for toluene), v_{2m} the volume fraction of the polymer in the sample swollen to equilibrium, and χ_{12} the Flory-Huggins polymer-solvent interaction parameter (for natural rubber - toluene χ_{12} the value is 0.393) [12-13].

Rubber-filler interactions: were analyzed using Kraus equation [15]:

$$V_{ro}/V_{rf} = 1 - m \frac{f}{1-f} \quad (6)$$

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

$$V_{rf} = \frac{[(D - FT) / \rho_r]}{[(D - FT) / \rho_r] + (A_0 / \rho_s)} \quad (7)$$

where ρ_r and ρ_s are the densities of rubber samples and solvent (0.94-1.0 g/cm³ for natural rubber and 0.866 g/cm³ for toluene), respectively, D the deswollen weight of the test specimen (dry weight), F the weight fraction of the insoluble components, T the weight of the specimen and A_0 the weight of the absorbed solvent at equilibrium swelling.

Fourier transform infrared spectroscopy (FTIR).

Changes of the chemical structure of samples were highlighted using a FTIR spectrophotometer - TENSOR 27 (Bruker, Germany) by ATR measurement method. Samples spectra are the average of 30 scans realized in absorption in the range of 4000-600 cm⁻¹, with a resolution of 4 cm⁻¹. Before analysis, samples were immersed in toluene for 72 h to eliminate uncrosslinked rubber.

Scanning Electron Microscopy (SEM).

The surface texture of the samples was examined using a scanning electron microscope (FEI/Phillips, USA). All the surfaces were placed on an aluminium mount, sputtered with gold palladium, and then scanned at an accelerating voltage up to 30 kV.

Results and discussions

Variation of physical-mechanical properties depending on the composition and method of testing ageing is presented in figures 1-6. Figure 1 shows a decrease in hardness by 3°ShA as a result of ageing for starch-free control mixtures, a decrease in hardness by 3°ShA as a result of ageing which may be due to the decreased degree of rubber crosslinking as a result of ageing. Mixture

N10 (containing 10 phr starch) shows an increased hardness, which may be due to *physical ageing* / retrogradation of starch existing in the mixture [5-7]. Mixtures N20 (containing 20 phr starch) and N30 (containing 30 phr starch), respectively, show a small variation in hardness as a result of accelerated ageing, while ageing under temperate climate conditions leads to a decrease of 7-12° ShA. This decrease may be due to the decreased crosslinking degree of mixtures that may be accelerated by the tendency of starch to biodegrade. Elasticity (fig. 2) varies irregularly with the increased amount of starch in the mixtures, for both types of ageing.

Modulus at 100% elongation and tensile strength (figs. 3-4) decrease significantly both by accelerated ageing and by ageing under temperate climate conditions for 1 year, and the best values after ageing are those obtained for mixture N20 (decreases of 74.6%). These results may indicate a degradation of vulcanizates due to meteorological conditions. Similar effects for natural rubber vulcanizates were reported by R.P. Brown and T. Butler. [16]. Elongation at break (fig. 5) decreases by max 23% for accelerated ageing and by 23-77% for ageing under atmospheric conditions, indicating either an increased crosslinking degree as a result of accelerated ageing at high temperature, or a degradation of elastomers under the action of atmospheric factors. Tear strength (fig. 6) for mixtures subjected to accelerated ageing varied irregularly [+37.5 - (-) 51.5%], as a result of increased crosslinking

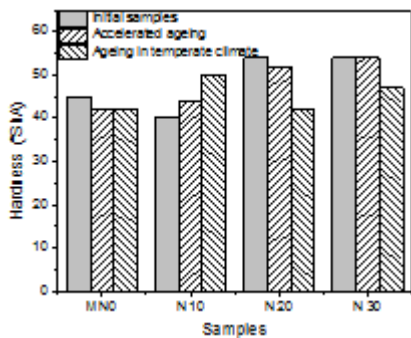


Fig. 1. Hardness variation

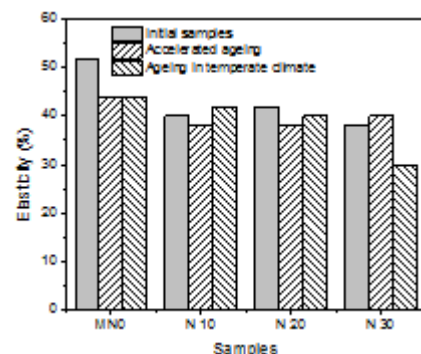


Fig. 2. Elasticity variation

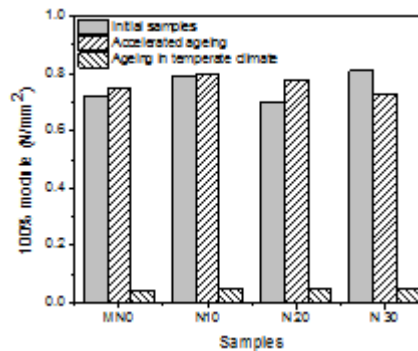


Fig. 3. 100% modulus variation

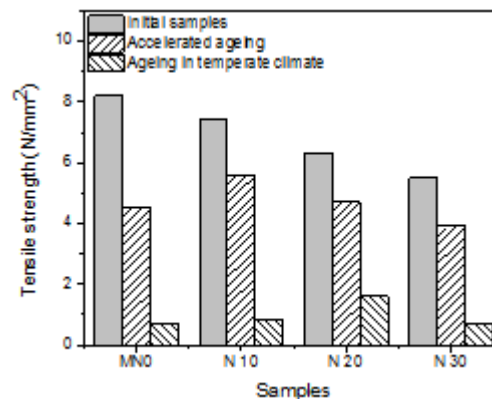


Fig. 4. Tensile strength variation

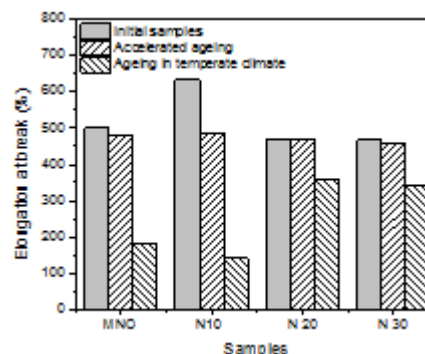


Fig. 5. Elongation at break variation

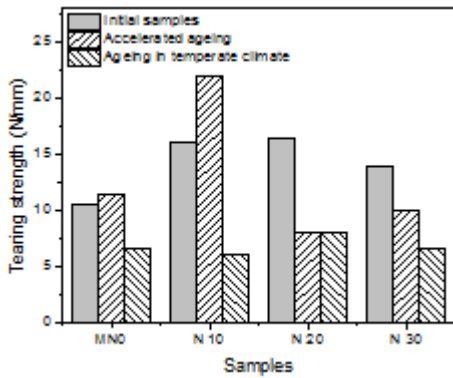


Fig. 6. Tear strength variation

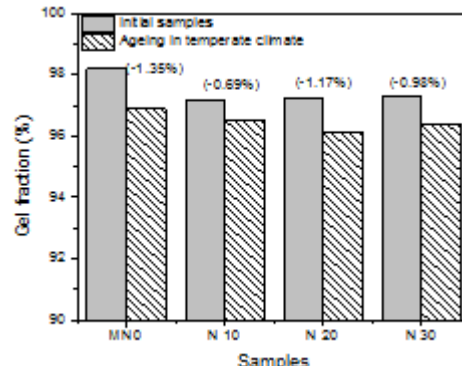


Fig. 7. Gel fraction variation

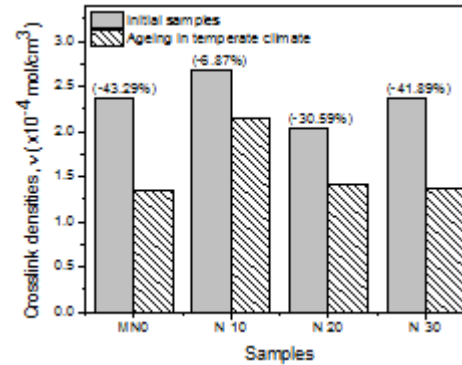


Fig. 8. Crosslink density variation

degree by heating, and has decreased by 38.1-62.5% respectively for mixtures aged under temperate climate conditions for 1 year, as a result of the degradation action of atmospheric factors (low/high temperatures, humidity, impurities, wind, etc.).

Resistance to swelling by liquids

Mass variation in toluene (table 1) increases by 37.3% for the control mixture (without starch) and by 2.9-23.7% for starch mixtures, indicating a better behaviour of mixtures with starch after maintaining under temperate climate conditions for 1 year.

Mass variation in water (table 1) for the control mixture (without starch) has a significant increase (by 657% mass variation), indicating that the surface was oxidized under the influence of atmospheric factors, forming various groups (aldehydes, ketones, carboxylated acids, alcohols) that absorb water. On the other hand, mixtures with 10, 20, 30 and 40 phr starch, after 1 year, show only small increases from 5.7 to 51.3% compared to the initial state, indicating a better behaviour to ageing.

Gel fraction and crosslink density

Figures 7-8 present values of gel fraction and crosslink density for normal state and after 1 year of ageing under temperate climate conditions. In both cases, the best values were obtained for the mixtures with 10 phr starch (N10), and the highest decreases were obtained for the control mixtures, while the other values range between these two.

Gel fraction values are good (over 95%), but there is a decrease after 1 year, by 1.35% for the control mixture (without starch), by 0.69% for the mixture with 10phr starch (N10), and the other values are found between these two. Similarly, the crosslinking density decreased after ageing

for 1 year under temperate climate conditions, only in this case there are much higher decreases of values: MN0 < N30 < N20 < N10 .

In conclusion, the best behaviour to ageing was seen in the mixture containing a low amount of biodegradable filler such as starch and the worst behaviour was that of the control mixture without starch. As a result, starch has led to an improved behaviour to ageing of rubber mixtures, and the best results were obtained for the mixture containing a lower amount of starch.

Rubber-filler interactions

The rubber-filler interaction degree determined according to the Kraus equation [15] is presented in table 2. The V_{r0}/V_{rf} ratio is the swelling restriction degree of rubber due to the presence of starch. The lower and lower values of the V_{r0}/V_{rf} ratio are associated with an increased adherence between filler (starch) and rubber, according to the Kraus theory and equation. Samples aged for 1 year under temperate climate conditions show decreases of V_{rf} compared to initial samples, indicating a higher degree of restrictions. In the case of N10 samples, V_{rf} decreases by 2.74% and the V_{r0}/V_{rf} ratio decreases by 21.86 % after

Mixture symbol	TOLUENE		WATER	
	Mass variation %	Initial/degraded variation	Mass variation, %	Initial/degraded variation
MN-0	252	+37.30%	0.56	+657.14%
MN-0 / 1 year	346		4.24	
N10	239	+2.94%	5.56	+5.76%
N10 / 1 year	246		5.88	
N20	258	+19.77%	7.63	+15.99%
N20 / 1 year	309		8.85	
N30	236	+23.73%	7.79	+51.35%
N30 / 1 year	292		11.79	

Table 1
MASS VARIATION AFTER 72 h OF IMMERSION IN TOLUENE AND WATER, RESPECTIVELY

Samples	V_{rf}		V_{r0}/V_{rf}	
	initial	after 1 year	initial	after 1 year
N10	0.2515	0.2446	1.0632	0.8308
N20	0.2286	0.1959	1.1696	1.0375
N30	0.2352	0.2022	1.1371	1.0052

Table 2
 V_{rf} AND V_{r0}/V_{rf} OF NR/PLASTICIZED STARCH COMPOSITES DETERMINED IN TOLUENE

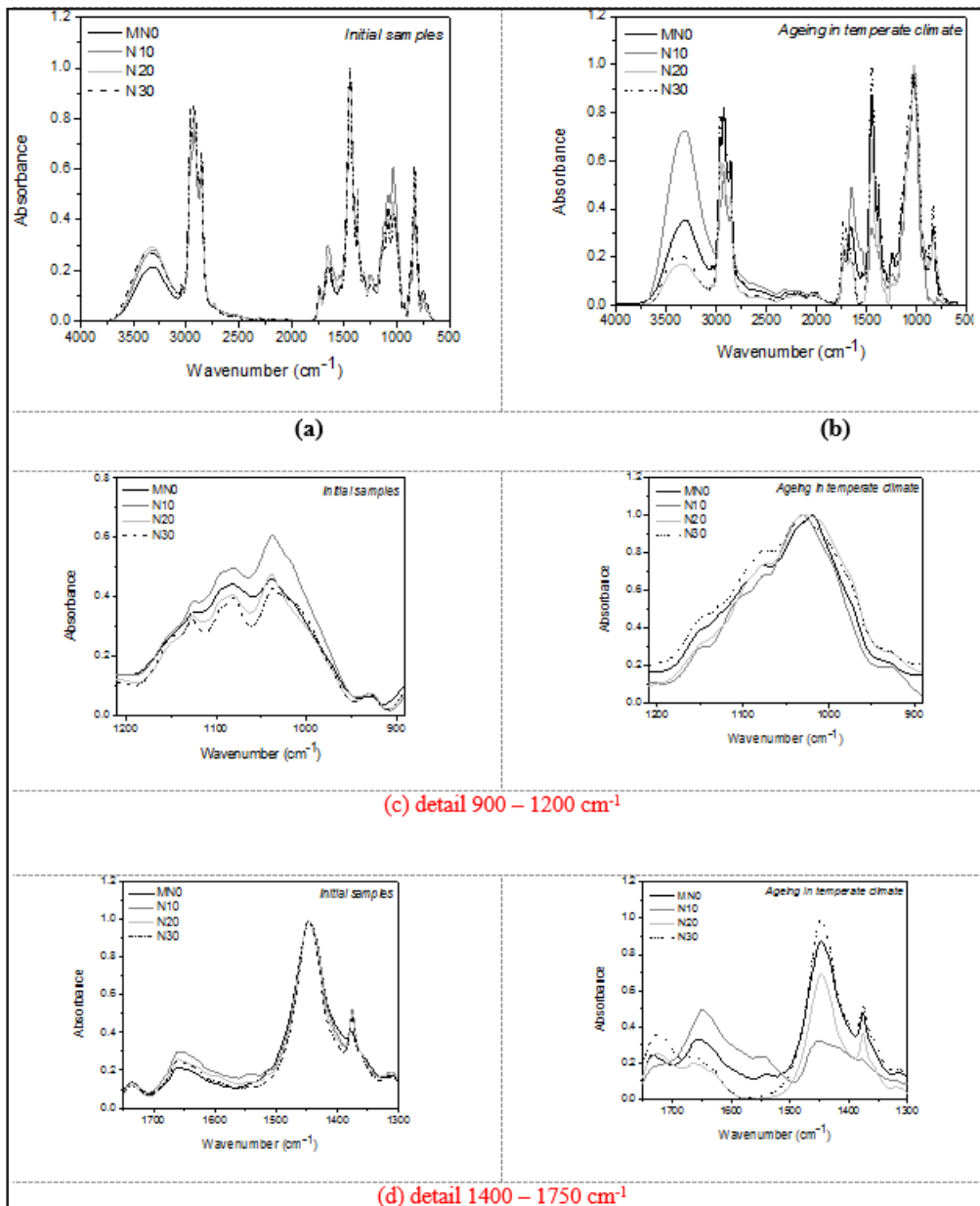


Fig. 9. Infrared spectra in a range of 4000-500 cm^{-1} , a) initial samples; b) ageing in temperate climate, (c) detail 900 - 1200 cm^{-1} , (d) detail 1400 - 1750 cm^{-1}

ageing for 1 year, while for samples N20 and N30, V_{10}^f/V_{170}^f decreases by 14.3 and 14.03%, respectively, and the V_{10}^f/V_{170}^f ratio decreases by 11.29 % and 11.6 %, respectively.

FTIR study

Figure 9 shows the infrared spectra and characteristic infrared bands observed (in the region of 4,000–560 cm^{-1}) of samples before and after ageing for 1 year under temperate climate conditions. Absorption bands specific to natural rubber are seen: at 830-834 cm^{-1} corresponding to chemical groups cis C=C, at 860-885 cm^{-1} corresponding to 3,4 addition products of isoprene, at 1370-1375 cm^{-1} for $-\text{CH}_3$, at 1635 - 1665 cm^{-1} corresponding to $-\text{C}=\text{C}$ [17]. Mixtures containing starch show the common signals for these kinds of polysaccharides, with glucopyranose rings such as OH bands at 3300-3400 cm^{-1} , C-H stretching vibrations of aliphatic groups at 2918-2928 cm^{-1} , adsorbed water signals at 1648-1662 cm^{-1} , C-C and C-O stretching at 1120 - 1160 cm^{-1} , and C-O-H bending vibration at 1005 cm^{-1} [18-19].

After degradation by maintaining for 1 year under temperate climate conditions the following are noticed: intensification of bands specific to aldehydes and ketones (1750-1725 cm^{-1}), organic acids (1550-1610 cm^{-1}), ethers

(1050-1150 cm^{-1}), alcohols (3200-3400 cm^{-1}), etc. These results indicate that the ageing process of elastomer samples is accompanied by an oxidative degradation activated by ultraviolet light and heat in the presence of atmospheric oxygen. These oxidative effects occur when oxygen attacks the unsaturated bond from the macromolecular chain of natural rubber as a result of rubber ageing under temperate climate conditions, also reported by other researchers [1, 20-21].

SEM

To correlate the influence of degradation under temperate climate conditions on the mechanical properties, the morphological aspect of the natural rubber/plasticized starch composites required evaluation by SEM technique. For SEM analysis, the samples were initially immersed in toluene for 72 h to remove unvulcanized natural rubber. SEM micrographs of the samples MNO and N10 in initial state and after 1 year, are shown in figures 10a, 10b, 10c and 10d. The SEM micrographs also revealed that the filler - plasticized starch - is uniformly distributed in the natural rubber matrix (figs. a and c). After ageing for 1 year in temperate climate, due to the degradation phenomenon, changes have occurred on the surface of

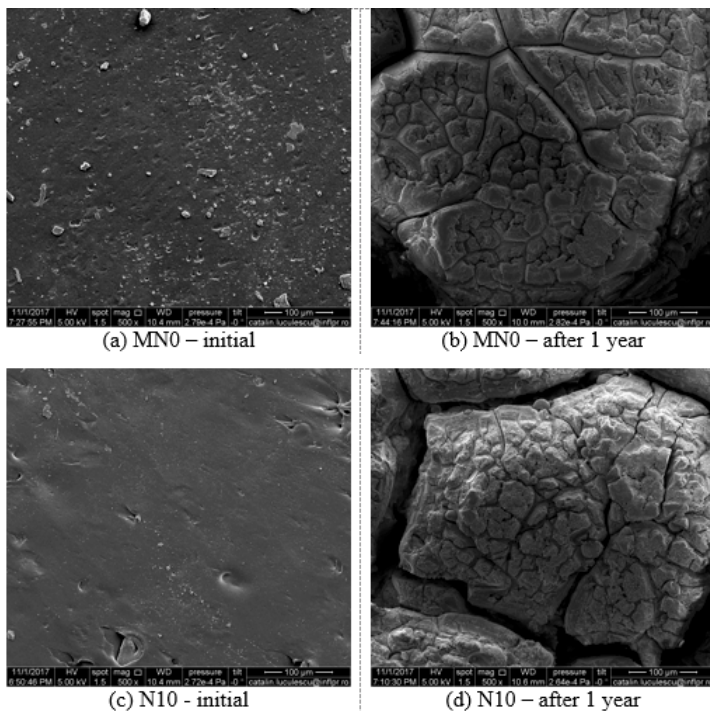


Fig.10. SEM micrographs

vulcanizates - cracks and breaks of varied sizes and depths appeared on the surface of the material (figs.10 b and 10d). According to existing research, these have occurred primarily due to the ozone in the atmosphere. At first only the surface of the object is affected by the attack, then degradation progresses, causing a change in physical-mechanical properties, and ultimately leading to a complete break in the object. [1, 21].

Acknowledgements: This research was financed through Nucleu Program 2016-2017 PN 16 34 01 01: Development of biodegradable nanocomposites based on natural rubber, starch and OMMT with applications in the food and pharmaceutical industries supported by Romanian Ministry of Research and Innovation.

Conclusions

Analysis of characteristics of mixtures based on natural rubber and plasticized starch after maintaining under temperate climate meteorological conditions for 1 year indicates a change in the surface of vulcanizates as a result of atmospheric factors. Oxidation and degradation of surfaces was highlighted by FTIR analysis (presence of -COOH groups, etc.), SEM microscopy (presence of cracks on the surface), immersion in water highlighting the existence of polar groups on the surface of vulcanizates. Degradation of materials is also highlighted by the decrease in physical-mechanical properties, gel fraction and crosslinking degree. The best ageing behaviour was seen in the mixture containing a low amount of biodegradable filler such as starch and the worst behaviour was that of the control mixture, while the best results were obtained in the case of the mixture containing a lower amount of starch.

References

1. VOLINTIRU, T., IVAN, GH., Technological Bases for Processing Elastomers, Technical Press, Bucharest,1974.
2. *** ISO 188:2010
4. M. E. ABU-ZEID, Y. A. YOUSSEF, F. A. ABDUGRASQUL, J Appl Polym Sci., **32**, 1986, p. 3345.

4. COLLISON, R., Starch retrogradation. In J. A. Radley, Starch and its derivatives (p. 198-202). London: Chapman and Hall. 1968.
5. SHUJUN W., CAILI L., LES C., QING N., SHUO W. (2015-09-01), Comp Rev Food Sci Food Safety.ens **14**, nr.5, 2015, p. 568.
6. ELIASSON A.-C., LARSSON K., Cereals in breadmaking: a molecular colloidal approach, CRC Press, 1993, p.126.
7. ENRIONE J., Mechanical Stability Of Intermediate Moisture Starch Glycerol Systems, Thesis Of Doctor of Philosophy, Biosciences University of Nottingham Sutton Bonington, 2005.
8. ORAVEC J., PRETO J., JURKOVIE P., MATYASOVSKY J., CHODAK I., ORAVCOVÁ A., Ann. WULS - SGGW, For. and Wood Technol., **83**, 2013, p.317
9. STELESCU M.D., GEORGESCU M., ALEXANDRESCU L., SONMEZ M., NITUICA M., The 17th International Multidisciplinary Scientific GeoConference SGEM 2017, Nano, Bio, Green and Space - Technologies for a Sustainable Future, Issue 62, Section: 26., 2017, p. 105.
10. SHEY J., IMAM S.H., GLENN G.M., ORTS W.J., Ind Crops Prod., **24**, no. 1, 2006, p. 34.
11. *** <http://www.meteoromania.ro>
12. LOPEZ-MANCHADO M.A., HERRERO B., ARROYO M., Polym Int **52**, no.7, 2003, p. 1070.
13. CHENAL JM, CHAZEAU L, GUY L, BOMAL Y, GAUTHIER C, Polymer, **48**, no.4, 2007, p. 1042.
14. STELESCU, M. D., Leather Footwear J. **10**, no. 3, 2010, p. 51.
15. G. KRAUS, J Appl Polym Sci, **7**, no.3, 1963, p. 861.
16. R.P. BROWN, T. BUTLER, Natural Ageing of Rubber, Changes in Physical Properties Over 40 Years, Rapra Technology Limited, Shawbury, Shrewsbury, United Kingdom, 2000.
17. ROY S., DE PP, Polymer Testing, **11**, no. 1, 1992, p. 3.
18. M. G. LOMELI-RAMIREZ, A. J. BARRIOS-GUZMÁN, S. GARCIA-ENRIQUEZ, J. RIVERA-PRADO, R. MANRÍQUEZ-GONZÁLEZ, BioResources, **9**, no. 2, 2014, p. 2960.
19. KIZIL R., IRUDAYARAJ J., SEETHARAMAN K. J., Agric Food Chem, **50**, no. 40, 2002, p. 3912.
20. MATHEW N. M., Chapitol 2, Natural Rubber, Rubber Technologist's Handbook, Edited by Sadhan K. De and Jim R. White, Rapra Technology Limited, 2001
21. HAMED G. R., Engineering with Rubber, A. N. Gent (Ed.), 2nd edition, 2001, Hanser, p. 27

Manuscript received: 10.11.2017