EPDM vulcanizes · thermoplastic starch · corn starch · filler · physical-mechanical properties

In recent years, chemical industry is focused on research and utilization of natural resources, for example lignin, cellulose and starch. The main issue of rubber product is caused by constant increase of rubber waste, their landfilling and lack of reduction ability. This work is focused on the application of corn starch and thermoplastic starch as a filler in EPDM rubber. The influence of natural filler on the curing process and physical-mechanical properties of EPDM blends was observed. The main goal was to find suitable amount of used corn and thermoplastic starch in combinations with other additives of rubber compounds in order to support biodegradability and to reduce the costs of the final products. The corn starch was applied in natural form, and also after modification as a thermoplastic starch.

EPDM Komposite, gefüllt mit Getreidestärke und thermoplastischer Stärke

EPDM Vulcanisate · thermoplastische Stärke · Getreidestärke · Füllstoffe · Physikalisch-mechanische Eigenschaften


EPDM Composites filled with Corn Starch and thermoplastic Starch

1. Introduction

Starch is a polysaccharide which can be found in various parts of plants reservoir. Starch is polymer consisted of two forms of α-D-glucose - linear polysaccharide-amylose which is made up of essentially α-(1→4) D-glucopyranosyl units and a highly branched polysaccharide-amylopectin which is made up of a large number of short chains linked together at their reducing end side by a α-(1→6) linkage. Corn starch usually contains approximately 20–30% of amylose and 70–80% of amylopectin. Size of corn starch granules is 15 µm and gelatization temperature is ranging from 62 to 71 °C.

Starches are used in many kinds of industry. For example in the field of paper, pharmaceutical and textile industry, also in alcohol-based fuels and adhesives. Native starch does not have high thermal stability and tend to easily retrogradation. Therefore, modification of native starch is used to overcome its weaknesses. [2,3]

Thermoplastic starch can be produced from native starch using a swelling or plasticizing agent while applying a dry starch in compound extruders without adding water. When a starch with content higher than 5% of water is plastified or pasted under pressure and temperature, a de-structured starch is always formed. In the production procedure of thermoplastic starch, the mainly water-free raw material is homogenized and melted in an extrusion process at 155 °C and after cooling was granulated.

2. Experimental

Tested rubber composites were made from ethylene propylene diene rubber EPDM (DUTRAL TER 4049 Polimery, Italy), and various amount of corn starch in natural and thermoplastic form. The content of processing additives, fillers (carbon black N550 and kaoline) and components of sulfur curing system was kept constant in all experiments. Corn starch, (Meritena 100) with moisture content 11% and pH 6.7 was supplied by AMY-LUM SLOVAKIA, Boleráz. Thermoplastic starch was applied in two forms. One (TPS 1) contains of starch 72,1 %, water 25,24 %, glycerol 2,51 % and modifier 0,15 % and second type (TPS) contains of starch 72,2 %, water 25,27 %, glycerol 2,53 % but does do not content modifier 0 %. The content of corn starch in rubber blends varied from 10 to 40 phr. The tested starches were applied into the rubber blends, which in itself already contains of filler as carbon black and kaoline.

2.1. The methods and procedures

The EPDM rubber batch consisted of rubber matrice Dutral ter 4049, carbon black N 550 and oil was prepared in 2 kg laboratory mixer.

Thermoplastic starch was prepared in two form. TPS compound was contained of native starch Meritena 100 and as a plasticizing agent was used glycerol and water. In TPS1 was included modifier of organic origin. All components of mixture were mechanically blended and subsequently were dosing into twin-screw extruder. The starch compound was homogenized and melted in an extrusion process at 155 °C and after cooling was granulated.

The rubber compounds were prepared in laboratory mixer Brabender in two mixing steps. In the first step, the EPDM rubber batch, the processing additives and starch as a filler were mixed togeth-

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er. In the second step, the curing system was added.

The curing process of rubber compounds was performed in hydraulic press at 150 °C under a pressure of 15 – 17 MPa for the optimum curing time.

The tensile properties of cured rubber compounds were measured by using ZWICK ROELL/Z 2.5 appliance at cross-head speed of 500 mm/min at laboratory temperature in accordance with the valid technical standards. The hardness of vulcanizates was measured using durometer Shore A.

In order to determine cross-link density of vulcanized samples was used equilibrium swelling in xylene (νch - chemical cross-link density), that is based on Kraus modified Flory-Rehner equation (1) for filled vulcanizates: [5]

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\nu_{ch} = \frac{V_r \ln(1 - \nu_r) + \nu_r + \chi V_r^2}{V_r^{1/3} V_{ss}^{2/3} - 0.5 V_r}

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νch - cross-link density (mol/cm³)
νr - volume fraction of rubber in equilibrium swelling sample of vulcanizate in absence of fillers
νs - volume fraction of rubber in equilibrium swelling sample of filled vulcanizate
Vr - molar volume of solvent (for xylene = 123.45 cm³/mol)
χ - Flory - Huggins interaction parameter (for measuring conditions χ = 0.5316

Physical - mechanical properties and cross-link density of EPDM vulcanizates were evaluated after exposure of samples in air at 70°C during 168 clock too.

3. Results and Discussion
At application of native corn starch was observed increasing optimal curing time tc(90) with increasing filler content (Fig. 1). In comparison with reference compound 100-123% increase of optimal curing time of EPDM compounds was detected.

From dependence optimum cure time on content of starch in rubber blends (Fig. 1) is clear, that the application of thermoplastic starch (TPS) in EPDM compounds has opposite effect decrease of optimal curing time tc(90) with increasing filler content.

The Fig. 2 shows decrease of scorch time at application of all three filler types. With increasing content of native starch in EPDM compounds, is obvious almost linear decrease of scorch time. Similar trend were observed also in case of compounds, which contains TPS, but
with more significant decrease value of scorch time.

The tensile strength at break of EPDM vulcanizates showed the decreasing tendency with increasing amount of starch filler applied for all three types starch as shown in Fig. 3. As seen vulcanizates contain of TPS 1 value achieved with the least small decline of tensile strength at break in comparison with the reference sample. The deterioration of tensile strength at break can be caused by over-filling of test vulcanizates.

Native starch caused by linear decline of elongation at break of vulcanizates based on EPDM in comparison with reference sample without starch (Fig. 4). This was caused by worse interfacial interaction between matrix and starch particles. Application of both types of thermoplastic starch led to an increase of values elongation at break of test samples. By incorporation of modified thermoplastic starch TPS 1, the elongation at break increased with increasing of filler content to 20 phr. But next increase amount of filler between 20 to 40 phr has caused fluctuation on the value ± 520%. Increasing content of thermoplastic starch (TPS) was caused of small increasing of values elongation at break in comparison with reference sample without starch which content only carbon blacks N550 and kaoline as a filler.

From Fig. 5 is evident that the increasing of native starch content in blends leads to increase in the hardness of EPDM vulcanizates up to 4 ShA in comparison with the reference sample because the starch particles have higher hardness. On the other hand independently to content of thermoplastic starch TPS were obtained values of hardness comparable or less smaller than reference sample nearly regardless of filler content. In blends containing of modified thermoplastic starch TPS 1 were recorded significant decline of hardness in comparison with reference sample. Plasticizer in applied thermoplastic starch causes softening of the particles and thus decreasing the hardness of the tested samples themselves.

Modulus M300 of EPDM compounds, which contains native starch, shows only 6% decrease of values, in comparison with reference compound (Fig. 6). Application of thermoplastic starch (TPS) caused linear decreased of modulus M100, M200 and M300. At application of modified thermoplastic starch (TPS 1) in EPDM compounds is seen similar effect as at application of TPS, but there was
observed stabilization of modulus value already at 20 phr.

Alongside the study of vulcanization characteristics chemical cross-link density of prepared vulcanizates was analyzed. Physical interactions between constituents polymer-polymer, polymer-filler and also intramolecular and intermolecular bonds are creating of cross-link density. Changing of mechanical properties filled rubber are usually connected with changing of chemical cross-linking density. Fig. 7 shows substantial improvement of chemical cross-link density at application native starch, in comparison with reference compound. The increasing of native starch content leads to increasing of cross-link density of EPDM rubber blends. In the case of applications of both types of thermoplastic starch were observed the great decline of chemical cross-links density. This decline was caused by changing of character of phase structure of EPDM blends with application of thermoplastic starch. The reason can be reality that thermoplastic starch (TPS and TPS 1) does not function as filler but as polymer, which dilutes all components of vulcanizates. The thermoplastic starch (TPS and TPS 1) makes up besides of matrix second type of polymer, which does not contribute to production of chemical network.

The based on the results of mechanical properties is the most appropriate type of filler of thermoplastic starch TPS with contains plasticizer and modifier. This is the main reason why the aging tests carried out only on EPDM blends filled by modified thermoplastic starch (TPS 1).

Influence of thermoplastic starch and thermal-oxidative ageing on properties and cross-link density of rubber compounds

The thermal-oxidative ageing has not effect on the values tensile strength in break of test samples. As shown in Fig. 8 after aging the tensile strength of vulcanizates gently increases in whole concentration range in comparison with sample before exposure. But increasing of thermoplastic starch content was caused decrease of tensile strength at break of EPDM vulcanizates in both cases.

From Fig. 9 becomes is evident, the increasing of starch content in prepared EDPM compound was caused increase of elongation at break before exposure. The values of elongation at break decrease by influence of thermal-oxidative degrada-
tion. The smallest change of the original property occurred in reference sample without thermoplastic starch (TPS1) after 168 exposure. The values of elongation at break of prepared samples with application to 30 phr fluctuated in small range. The largest decline of after aging was measured with content of 40 phr TPS1.

The changes of hardness of EPDM vulcanizates as a consequence of aging it are possible to assess from Fig. 10. There is evident that application of thermoplastic starch has an influence on the hardness especially, which decrease with increasing of starch content in rubber compounds before aging. In case of EPDM blends after thermal-oxidative aging was recorded increase of values hardness at higher degrees of filler content in comparison with the reference sample. The increased of hardness is caused by better crosslinking of test vulcanizates after aging.

From equilibrium swelling in xylene ($\upsilon_{ch}$ – chemical cross-link density) was determined the cross-link density of prepared vulcanizates. The results of measurements shows (Fig. 11) decrease of chemical cross-link density $\upsilon_{ch}$ with using of thermoplastic starch TPS1 before aging in comparison with the reference sample. But the increasing amount of thermoplastic starch does not effect of the cross-link density EPDM vulcanizates. After thermo-oxidative aging was recorded improvement of degree chemical cross-link density, mainly at higher content of TPS1 up to 80%.

4. Conclusion

The application of corn starch and thermoplastic starch in EPDM rubber blends influences the curing process and also the physical-mechanical properties of rubber blends. With increasing content of starch in filled rubber blends, decrease of tensile strength at break at application in all three types of starches (native starch, thermoplastic starches TPS, TPS1) was detected. Same trend was detected at elongation at break of rubber blends, which were filled up by native corn starch. The reason, why corn starch is not acting like reinforcing filler, could be its tendency to create agglomerates and aggregates in rubber matrix. This behavior leads to weak interaction and adhesion between non polar rubber matrix and polar corn starch filler. On opposite side, on the rubber compounds, which contain both types of thermoplastic starches, an increase of elongation at break was detected. This effect was caused by polymeric character of thermoplastic starch and changing of phase structure of rubber blends. The significant effect of thermal-oxidative aging was observed in all tested properties. The presence of thermoplastic starch causes the increase of crosslink density vulcanizates during aging. This effect had resulted to increase of tensile strength at break of EPDM compounds. After thermal oxidative ageing the values of elongation at break decreased.

Current usage of these materials is primary seen in products, which will not be exposed to dynamical-mechanical strain. Composites, with native corn starch, could be applied in final products, which require higher hardness. On the other side, the compounds, which contain thermoplastic starches, could be used in products with significant elongation application.

Aknowledgements

This work was supported by the Slovak Research and Development Agency under the contract No. APVV-0694-12.

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