Effect of Starch Fillers on the Dynamic Mechanical Properties of Rubber Biocomposite Materials

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SUMMARY

The results of the dynamic mechanical study of biocomposites filled with different amounts of potato starch and corn starch are discussed. The composites were obtained from rubber mixtures containing natural rubber (NR) as a main component. Plastification of NR and rubber mixture was achieved by using the rubber open mixing mill (friction ratio 1.08). The vulcanization process was realized with a hydraulic press under predetermined conditions (pressure ca. 5 MPa, temperature ca. 143 °C, and processing time of 7, 12, 17 min). Thermomechanical analysis (by DMTA) showed that the quantity of starch fillers had only a slight influence on the glass transition temperature of the produced vulcanizate materials.

Keywords: Biocomposites, Rubber materials, Starch, DMTA

1. INTRODUCTION

The current bioelastomer materials have practically changed every field of industry. Tyres, erasers, covers, swimming caps, balls and many other technical articles are usually made from rubber composites. The properties such as impermeability to water, good durability under harsh conditions and the ability to elongate make the rubber materials applicable in almost every sphere of life[1-6]. Elastomers are polymers which come back to their original form even after a considerable deformation. The ability of different elastomers, including produced from recovered or recycled semiproducts, to deform during tensile testing can reach even 1000%[7-9]. Natural rubber is a well-known elastomer. It is used as a matrix in the preparation of polymeric biocomposites, which can also include different synthetic or natural fillers. Compatible fillers should improve the mechanical and usable properties of products while, at the same time, cannot create problems during the manufacture of biocomposites[10]. In the case of engineering materials, the main aim is to replace non–renewable components by those originating from natural resources. It is quite common to use natural biopolymers as fillers in polymer composites with polymeric matrix. Starch, cellulose, chitin, DNA, lignin and natural rubber are all well-know biopolymers. Starch is a polysaccharide which contains 15-25 wt.% of the linear and helical amylose, and 75-78 wt.% of branched amylopectin. Wheat, rice, corn and potato tubers have particularly high content of starch. The starch grains are composed of crystalline aggregate layers. Starch is easily available, cheap and biodegradable. It has become widely used as a filler in biologically non-active polymers[11-14].

In the present work the results of the dynamic mechanical investigations of rubber biocomposite materials obtained from the mixtures of natural rubber filled with different amounts of potato starch or corn starch are described.

2. EXPERIMENTAL

2.1 Materials

- Natural rubber NR, density 0.93 g cm^{-3}, RSS
- Potato starch, density 1.65 g cm^{-3}; manufactured by “B.E.S.T.” ZPZ Sp.J.
- Corn starch, density 1,65 g cm^{-3}; manufactured by GLUTENEX
- Stearic acid, density 0.94 g cm^{-3} (20 °C); distributed by POCh S.A., Gliwice
- Zinc oxide, density 5.61 g cm^{-3} (20 °C); distributed by POCh S.A., Gliwice
- Accelerant T (TMTD, (disulphide tetramethylothiuramum), density 1.29 g cm^{-3} (20 °C); distributed by Standard Sp. z o.o., Lublin
- Sulfur, density 2.06 g cm^{-3} (20 °C), distributed by POCh S.A., Gliwice

- Machine oil; manufactured by Artefakt Oleje i smary Standard Sp. z o.o., Grudziądz.

2.2 Processing Methods

Rubber biocomposite materials were produced from rubber mixtures. The mixtures were filled with 10, 15 or 20% of potato starch or corn starch per 100 grams of natural rubber, and processed by using a Buzuluk mixing mill. Plastification of rubber mixture and NR was achieved by using the rubber open mixing mill (friction ratio 1.08). Vulcanization was performed by using the ZUP Nysa N512-40/1,8 hydraulic press under predetermined conditions (pressure 5 MPa, temperature 143 °C and processing time of 7, 12 and 17 min).

2.3 Test Methods

Glass transition temperature (Tg), storage modulus (E'), and loss modulus (E') of the produced rubber biocomposite materials were determined using a DMA Q 800 Analyzer. The measurements were conducted in the temperature range from -80 to 80 °C under nitrogen atmosphere. The operating frequency was 10 Hz, and the heating rate equaled 4 °C/min. Thin samples 18x10x2 mm in size were used during the analysis.

3. RESULTS AND DISCUSSION

The addition of starch to the rubber mixture positively affected the storage modulus of the produced vulcanizate rubber biocomposite materials. Potato starch (coded SZ) used in the amount of 10 wt.% (**Figure 1**) caused a ca. 33% increase in the value of storage modulus compared to the reference sample (coded "0").

Corn starch (coded SK), added in the same amount, caused an increase in the value of storage modulus (E') by only a few percent.

Based on the analysis of loss modulus versus temperature curve, well-defined single peaks at ca. -48 °C (**Figure 2**) were observed, which mark the glass transition of amorphous phase.

The glass transition temperature (**Figure 3**) was read from the maximum of tan δ. The values of glass transition

Figure 1. Storage modulus (E') as a function of temperature for rubber vulcanizates containing 10 wt.% of starch

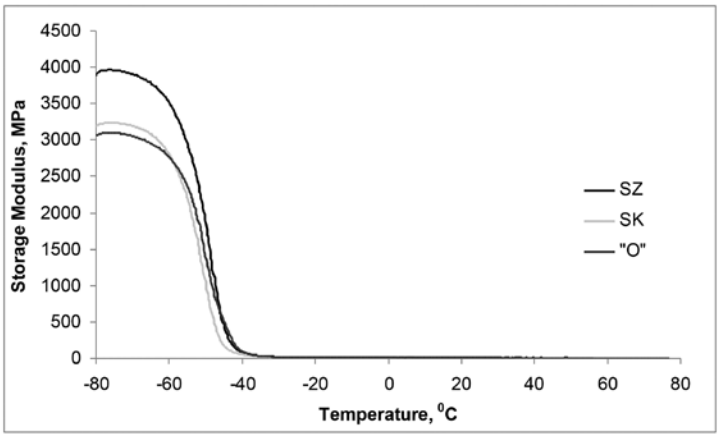


Figure 2. Loss modulus (E") as a function of temperature for rubber vulcanizates containing 10 wt.% of starch

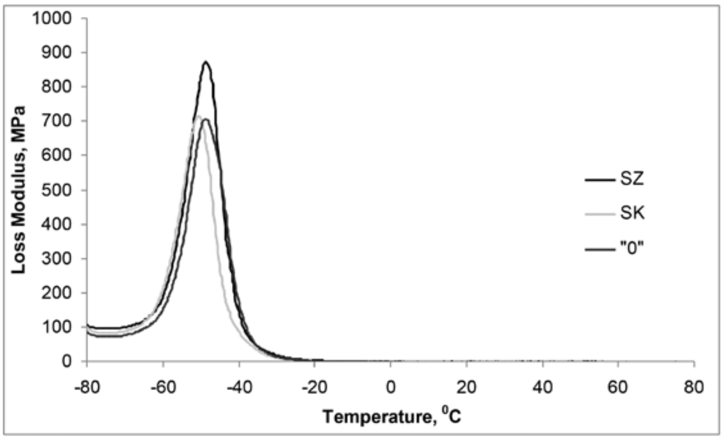
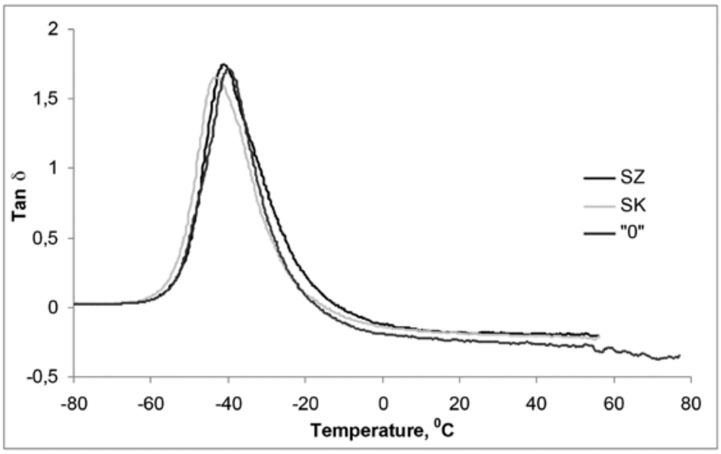


Figure 3. Tan δ as a function of temperature for rubber vulcanizates containing 10 wt.% of starch



temperature ranged from -39 to -43 °C. The results indicate that the addition of starch influenced the Tg of the produced rubber biocomposite materials.

The effects of potato starch on thermomechanical properties of the obtained rubber biocomposite materials are illustrated in **Figures 4** and **5**.

An increased amount of potato starch in rubber biocomposite materials caused a decrease in both the storage and loss moduli, i.e. from 4000 to 2200 MPa, and from 900 to 500 MPa, respectively.

Increased amount of potato starch in rubber vulcanizate materials resulted in an increase in the Tg value from -41 to -37 °C (**Figure 6**).

4. CONCLUSIONS

Using the formulated recipes and selected conditions of the vulcanization process, rubber biocomposite materials were produced from natural rubber containing dispersed starch. The added starch influenced the glass transition temperature of vulcanized rubber biocomposite materials. Starch had a beneficial influence on the storage and loss moduli. The measured increase in storage modulus reached 33% compared to a reference sample.

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Figure 4. Storage modulus (E') as a function of temperature for rubber vulcanizates filled with different amounts of potato starch

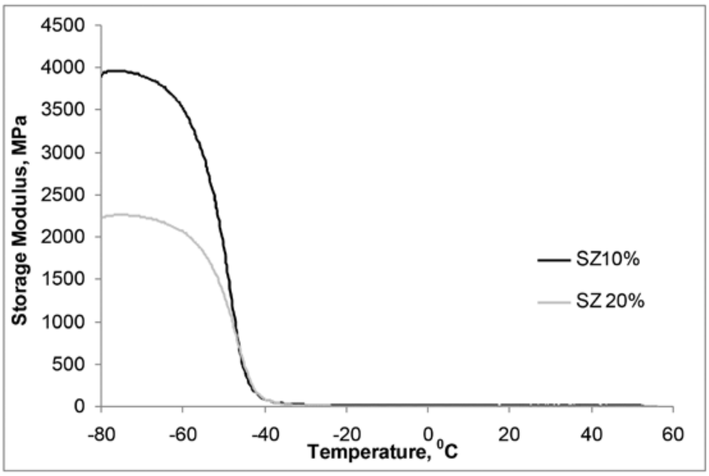


Figure 5. Loss modulus (E") as a function of temperature for rubber vulcanizates filled with different amounts of potato starch

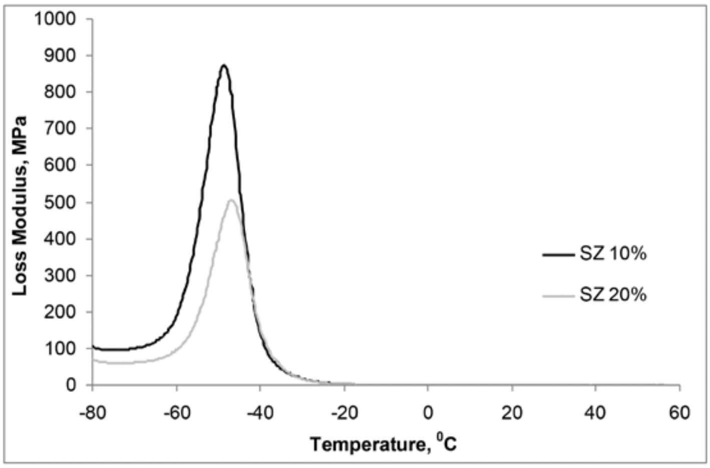
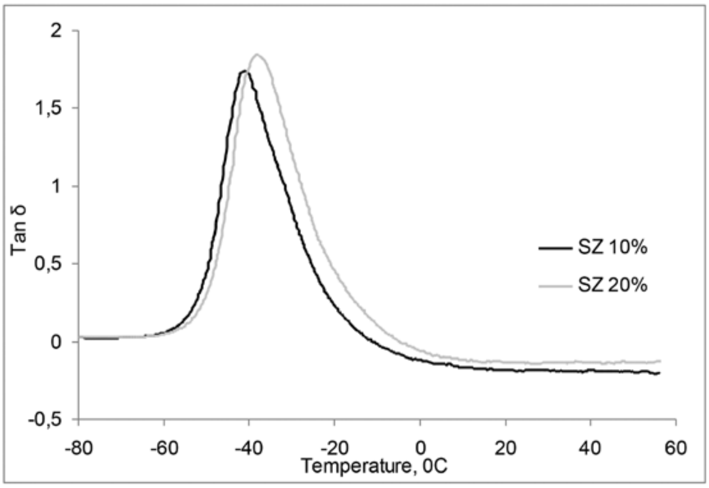


Figure 6. Tan δ as a function of temperature for rubber vulcanizates filled with different amounts of potato starch



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