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Development of Reinforced Composites Containing Tea Tree Oil and Propolis for the Treatment of Horse Hoof Cracks

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Abstract: The aim of the study was the evaluation of properties of variously composed composite materials based on polyurethane filled with tea tree oil (TTO) and addition of other ingredients. The tea tree oil/cyclodextrin inclusion complex was prepared by using the 'Paste method' described in Shrestha, M and others. (2017) (Shrestha et al. 2017). To analyse the properties of composite materials following testing methods were conducted: density, tensile strength, compression test, impact resistance. In the study, pursued in the Lodz University of Technology in Poland, thirteen materials with different percentile content of additives: TTO/β-CD, propolis, TTO/β-CD/Propolis, TTO were prepared and tested to establish the most favourable characteristics. Properties of sample containing Tea tree oil/ β-cyclodextrin/Propolis were the most satisfying and were assumed to be accurate in fulfilling the role of the hoof crack filler the best in the first study. With the higher amount of the additive the mechanical properties weakened preventing the use of the product in the hoof cracks.

Keywords: Polyurethane, Tea Tree Oil, Cyclodextrin, Propolis, Encapsulation, Hoof Cracks

1. Introduction

Hoof crack is a damage in the wall of the hoof. There are various types of cracks such as grass, sand, heel, bar, toe and quarter cracks. These defects might appear in every hoof of hoofed animal, whereas this study is focused on horses. Hoof-wall defects, especially quarter cracks, are a prevalent cause of decreased athletic performance in competition horses and frequently lead to foot lameness. (O'Grady, 2001).

Unluckily, quarter cracks might be painful. Generally, the reasons are infection or instability, caused by movement of the hoof wall posterior to the crack. This frustrating cause of lameness originating in the foot usually represent a significant therapeutic challenge for both veterinarian and farrier. It is especially problematic for equine practitioners according to the fact that in general horses that develop quarter cracks must continue to perform. To let that happen, it is crucial for the reconstruction to arrange both stability and strength to the hoof wall injury. As the result, the horse will be allowed to perform while the healing will take place so that the crack will grow out.

In most cases, it is unlikely that hale regular horn will split. However, if a line of weakness exists in the hoof wall, resultant domestic stress concentration might result in the formation of a fissure in the hoof wall. (O'Grady, 2001).

Mechanical stabilization is required for the treatment of hoof cracks. Both in this study and in the previous one composite materials were used. In the first study, in the Suleyman Demirel University, the composite consisted of: solid polyurethane, β-cyclodextrin and tea tree oil, whereas in discussed study, executed in the Lodz University of Technology, the same ingredients with the addition of propolis were used. The addition of propolis was intended to make the fragile samples from the previous study more flexible.

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Polyurethane is a copolymer formed by conjugation of diol and diisocyanate groups has high strength; extremely good abrasion resistance; good resistance to gas, greases, oils, and hydrocarbons; and excellent resistance to oxygen and ozone. (Ebewele, 2000) Moreover, it is biocompatible. The tea tree oil was used according to its properties: antifungal, antibacterial, antiseptic, anti-inflammatory, anti-cancer, insect repellent and insecticide. (Callander, 2012) However, this essential oil cannot be used without a sufficient and appropriate barrier to increased solubility in water and volatilization. In order to attain the barrier, the TTO is being encapsulated in β-cyclodextrin particles. (Bhandari, 1998).

The propolis is a new ingredient used in this research. It is a natural resinous mixture produced by honeybees from substances collected from parts of plants, buds, and exudates, is a lipophilic in nature, brittle and hard material and it becomes soft, gummy, pliable and very sticky when heated. (Hausen et al. 1987) Generally, raw propolis is composed of about 50% resins, 30% waxes, 10% essential oils, 5% pollen, and 5% of various organic compounds. (Wagh, 2013) The temperature mainly affects the consistency of propolis. It is much harder and more resistant to temperature than wax. At 15 ° C, propolis is hard and brittle, at 34.5-36 ° C (nest temperature) it becomes soft and plastic, and at temperatures above 45 ° C - sticky and sticky. It is liquid at 70-80 ° C, although for some propolis samples the melting point is above 100 ° C. (Kujumgiev et al. 1999) Propolis has various pharmacological activities. It is the most biologically active among bee products. The most important and known properties of propolis are antimicrobial and antiinflammatory, antioxidant, antitumor and immunostimulatory activity (Wagh, 2013). Propolis presence should strengthen the composite and improve its properties. (Wolska et al. 2016)

2. Material and Method

Ingredients: Izopianol 40/30 W/PIR, Purinova Sp. z.o.o being a mixture of polyols and selected auxiliary agents. Purocyn B, Purinowa Sp. z.o.o being a polymeric diisocyanate of diphenylmethane. Propolis: Gospodarstwo Pasieczne Łukasiewicz (Poland). B-cyclodextrin from Pol-Aura (Poland). Tea tree oil from Vivio (Poland). All solvents used in the studies were analytical grade.

2.1. Preparation of tea tree oil/cyclodextrin inclusion complex

The inclusion complex was received by following the ‘Paste method’ recipe described in Shrestha, M., Ho, T. M., & Bhandari, B. R. (2017). (Shrestha et al. 2017). The preparation method was made in the exact way as the complex in the first study. (Sobkowiak et al. 2018)

2.2. Preparation of the composite material

Thirteen samples were prepared; they varied according to ingredients and its amounts:

- • Pure polyurethane – the reference sample (sample No. 1)
- • 1%, 3% and 5% TTO/β -CD and 99%, 97%, 95% polyurethane (sample No.2, No.3, No. 4)
- • 1%, 3% and 5% propolis and 99%, 97%, 95% polyurethane (sample No.5, No.6, No.7)
- • 1% TTO/β -CD + 1% propolis and 98% polyurethane (sample No.8)
- • 3% TTO/β -CD + 3% propolis and 94% polyurethane (sample No.9)
- • 5% TTO/β -CD + 5% propolis and 90% polyurethane (sample No.10)
- • 1%, 3% and 5% TTO and 99%, 97%, 95% polyurethane (sample No.11, No.12, No.13)

All samples were prepared by mixing an additive and polyol firstly and adding isocyanate afterwards: 65g ingredient A (polyol mixture) and 104g ingredient B (isocyanate). They were formed in plastics buckets.

3. Results

Four quantities were measured: density, tensile strength, compression test and impact resistance.

3.1. Density

Sample size: 25 mm x 25 mm x 25 mm. Five samples were tested. Samples were weighed on the laboratory balance. For the additive TTO/CD the density is decreasing with the increase in the amount of it. The same situation is for composite containing TTO/CD/Propolis. On the other hand, for samples with propolis and TTO tendency differs.

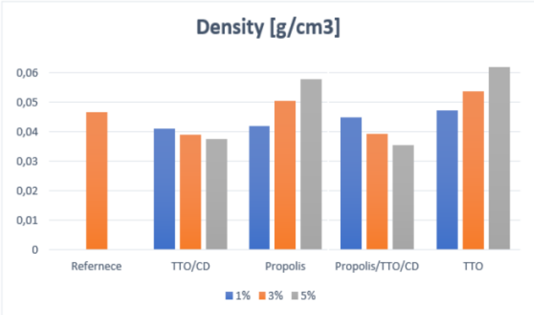

Figure 1. Density of the composites

3.2. Tensile strength

Tensile strength test was performed according to ASTM D3039 standard test method by means of Zwick Roell 1435. Sample size: 100 mm x 25 mm x 10 mm. Five samples were tested. Tensile strength for the reference is the highest. Results are the lowest for TTO/CD. Only for composite comprising propolis the tensile strength is growing with the percentage of a supplement.

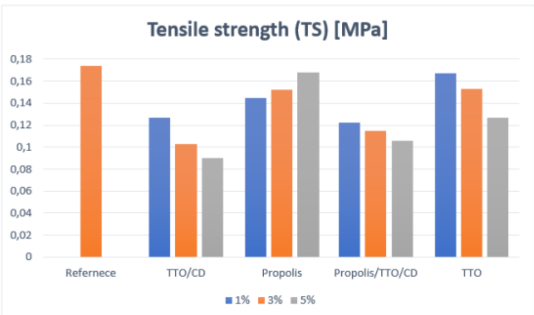

Figure 2. Tensile strength of the composites

3.3. Compression test

Compression test was performed according to ASTM D3574-C standard test method by means of Zwick Roell Retroline. Sample size: 25 mm x 25 mm x 25 mm. Five samples were tested. Addition of both TTO/CD and TTO/CD/Propolis resulted in gradual weakening of the composite. Results are the most satisfying for the sample with propolis. Composite containing TTO seems to be also successful, however, errors in the measurements are significant.

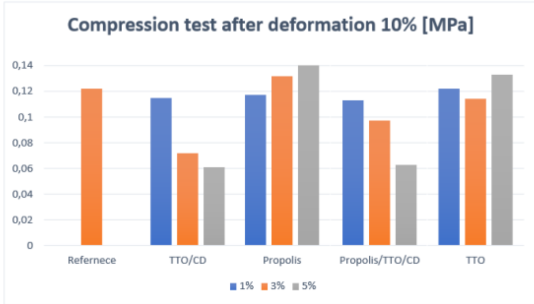

Figure 3. Compressive strength of the composites

3.4. Impact resistance

Impact resistance test was performed according to ASTM D 256 standard test method by means of Cometech QC-639P/Q with charpy's hammer of strength 2J. Tests were carried out on a cross-section not on the width. Sample size: 10 mm x 15 mm x 100 mm. Five samples were tested. Addition of TTO/CD resulted in significant weakening of the composite. Addition of TTO/CD/Propolis partly affected the lowering strength. 1% and 3% of propolis increased the strength while 5% decreased it. Here again the TTO seems to be also successful, however, errors in the measurements are significant.

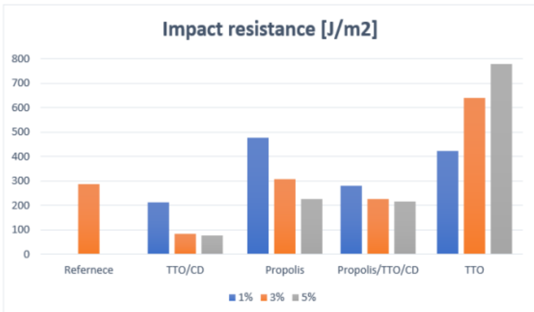

Figure 4. Impact resistance values of the composites

4. Discussion and Conclusions

First of all, in the composite material containing TTO/CD and TTO/CD/Propolis the density is decreasing, which means that pores inside the structure were increasing. According to this the tensile strength is decreasing. Over the compression test we can see lower shears, what is consistent with the theory. What is more, impact resistance test results are compatible. Unfortunately, the addition of the tea tree oil/b cyclodextrin inclusion complex in the composite influences the increase of porosity. The reason is probably the moisture residues. On the other hand, for samples containing TTO/CD/Propolis for the impact resistance test, there is no big drop in strength as it is for sample containing only TTO/CD. All test results are satisfying, especially for 1% of TTO/CD/Propolis, errors are not significant. In all likelihood, TTO/CD/Propolis is a promising sample and small changes in the system could be enough, such as changing the proportions of ingredients or finer grinding of propolis, heating it and dispersing to achieve better results. (samples No.2,3,4 and No.8,9,10).

The density of the composite material containing propolis, in comparison to the reference sample, is decreasing at the begging and increasing afterwards. Notwithstanding, during the tensile strength test the endurance does not show an upward trend with the increasing amount of propolis. Furthermore, it is not even higher the endurance for the reference sample. There is a possibility that addition of larger particles of propolis in the composite might cause the increase of an error (in the structure it appears as a dispersed wax in the form of slightly larger fragments). Whereas, these errors do not differ between each sample. The propolis affects the increase of compressive strength except for the sample containing 1%. The reason might be an insufficient amount of the ingredient. (samples No.5,6,7).

For samples containing tea tree oil the heterogeneous structure is visible after cutting the prepared composite. Moreover, it is visible in large measurement errors, which results from the dependence: the more homogeneous the structure, the more accurate the measurements. Therefore, despite the fact that the results in the impact resistance test are satisfying, they cannot be taken into account. Same of samples could not be tested according to its incorrect structure (Picture 1):

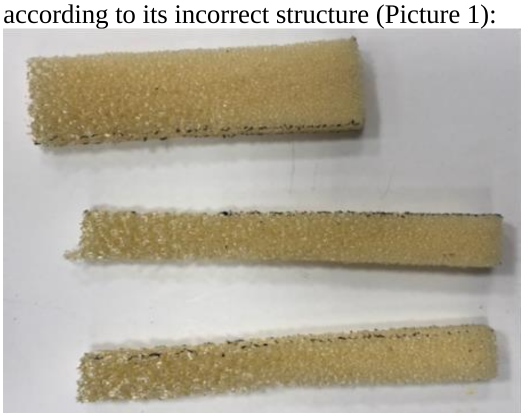

Figure 5. The incorrect structure of samples containing TTO

To summarise, both of studies conducted in Suleyman Demirel University, Isparta, Turkey and Lodz University of Technology, Lodz, Poland were very evolving and gave us the opportunity to get to know with the properties of composite materials with selected compositions. In both studies an addition of TTO/CD lowered the strength of the substance as its content increased. The reason is probably the moisture residues. It cannot be said that samples comprising tea tree oil/cyclodextrin inclusion complex or only propolis were unsuccessful, while they were worse than the another one. The sample containing mixture of propolis and tea tree oil/b-cyclodextrin was the most successful. Errors were not significant, and all results formed a coherent whole. The last composite, which included the tea tree oil could not be compared with the rest of samples according to big errors and heterogeneous structure, on the other hand, its reinforcement of the material is visible and might be inspected in future research.

Acknowledgements

This research is a continuation of the study conducted in the Suleyman Demirel University in Isparta, Turkey described in the article: Sobkowiak, K., Kocabıyık, A., & Karaboyacı, M. (2018). Development of Cyclodextrin Particle Reinforced Composites Containing Tea Tree Oil for The Treatment of Horse Nail Fractures. (Sobkowiak et al. 2018)

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