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THE USE OF VEGETABLE FILLERS AS REINFORCEMENT MATERIAL IN SBR BASED BIO-COMPOSITES

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Abstract: *The use of natural fillers as reinforcement material in the production of composite materials has gained extra attention in recent years from the environmental point of view. For this purpose, the use of vegetable fillers as a potential reinforcement material in elastomeric composites was investigated for the production of footwear sole material. In this study the acorn cups and the waste of acorn obtained after the tannin extraction was used as the reinforcement materials for styrene-butadiene rubber based composites. Acorn cups and pulps (acorn wastes) with different ratio (2, 4 and 6 wt%) were compounded with SBR by Banbury and the preparation of the composites with different filler loadings was performed via compression molding. The thermal characteristics of the bio-composites produced for the footwear sole were investigated in terms of Differential Scanning Calorimeter (DSC), and Thermogravimetric (TGA) analyses. The results revealed that different concentrations of vegetable fillers had no significant effect on DSC results and the highest TGA results were obtained by the use of 2% acorn cups as a reinforcement material. Besides, the homogenous dispersion of vegetable fillers within the elastomer matrix was achieved successfully and the obtained bio-composite materials were found to be a good candidate to be a bio based sole material in footwear production.*

Key words: *Bio-composite, acorn cup, acorn waste, DSC, TGA*

1. INTRODUCTION

In footwear production, various materials with different properties are used for providing foot comfort, wear hygiene in addition to ensure firmness and aesthetic properties. Footwear consists of two main parts as upper and sole, while upper leather covers the top and sides of the foot, sole makes the contact with the surface and is produced from polymer, rubber, neolit and leather. Sole is known as one of the important component of footwear and should be durable and flexible [1].

Sole leather provides different characteristics to footwear and is considered as a healthy and lightweight material with high air permeability properties. However, low abrasion resistance, low slip resistance, high water absorption and high prices are the drawbacks [2, 3]. Natural rubber soles costs high but it has high abrasion, slip and chemical resistance properties [3]. Polymeric materials used in sole production, such as poly vinil chloride (PVC), ethylene vinyl acetate (EVA), styrene-butadiene rubber (SBR) and polyurethane (PU), have different softness, flexibility, abrasion and chemical resistance as well as slip resistance properties and all of these features still couldn't be catch on a single sole material [4-8].

The use of natural fillers as reinforcement material in the production of composite sole materials has gained attention due to the decrease in the production costs and to provide higher mechanical and strength properties. Although various studies have been carried out on the utilization of natural fillers such as rice husk, jute, cotton and cellulose fibers [9] as a reinforcement material, up to date according to our knowledge this will be the first study about acorn cups and waste of acorns used as reinforcement materials for the production of footwear sole. Considering the rubber sole materials, some studies have been found regarding composite sole production such as bambu fibers reinforcement for the rubber sole production [10] and wastes of shoe production utilized in rubber sole [11].

For this purpose, the use of vegetable fillers as a potential reinforcement material in elastomeric composites for the production of footwear sole material was investigated. Acorn cups and the waste of acorn obtained after the tannin extraction was used as the reinforcement materials for styrene-butadiene rubber (SBR) based composites. Acorn cups and pulps (acorn wastes) with different ratio (2, 4 and 6 wt%) were compounded with SBR by Banbury and the preparation of the composites with different filler loadings was performed via compression molding. The effect of different filler ratios on the thermal characteristics of the bio-composites produced for the footwear sole were investigated in terms of Differential Scanning Calorimeter (DSC), and Thermogravimetric (TGA) analyses.

2. MATERIAL AND METHOD

2.1 Material

In this study, acorn cups and the waste of acorn were used as the reinforcement materials for the styrene-butadiene rubber (SBR) based composites. The acorn cups and acorn wastes were supplied from AR-TU Chemical Company in Salihli, Izmir.

The commercial styrene-butadiene rubber (SBR 1502) was used as a matrix component of bio-composites.

2.2 Method

The acorn cups and acorn wastes were milled to particle size of 200 µm using laboratory grinder [12, 13].

The preparation of bio-composites with different filler loadings (2, 4 and 6 wt%) was performed via compression molding.

Thermo gravimetric analysis (TGA) was performed on raw materials and composites using Perkin Elmer Diomand TG/DTA apparatus applying a heat range of 10 ^oC/min up to 600 ^oC.

Differential Scanning Calorimetry (DSC) analyses were carried out using Shimadzu-DSC 60 Plus apparatus. The samples were kept in aluminum vessels and scanned between 20 ^oC and 200 ^oC with 10 ml/min flow rate of N_2 and heating rate of 10 ^oC/min.

3. RESULTS AND DISCUSSION

3.1. DSC Results

The data of differential scanning calorimetry analysis of SBR, vegetable additives and composites are given in Table 1. The DSC curves of acorn cups and waste of acorns showed only one large endothermic peak between 40-150°C with peak temperatures at 65-91°C, possibly due to the removal of free and bounded water.

The glass transition temperature of styrene-butadiene rubber was found to be at -66°C (Tg) and melting temperature at 85 °C (Tm). Besides, the reinforcements used by 2, 4, 6 % vegetable fillers effect was not found significantly on the thermal behavior of SBR. The similar Tg and Tm values were obtained from all bio-composite samples.

Table 1: *The results of DSC analysis of SBR, additives and composites*

Numune	T_g	Peak 1	Peak 2
Acorn waste	-	65.06	-
Acorn cup	-	82.05	-
SBR	-66.46	-	85.33
2% acorn waste	-67.72	-	78.62
4% acorn waste	-63.35	-	82.17
6% acorn waste	-61.12	9.86	88.31
2% acorn cup	-61.40	-	86.53
4% acorn cup	-67.10	-16.02	88.11
6% acorn cup	-70.46	-	83.51

3.2. TGA Results

The thermogravimetric curves of SBR matrix, vegetable additives (acorn cup and waste of acorn) and their composites are given in Figure 1-2.

And some data of thermal behavior of SBR, vegetable fillers and their composites are shown in Table 2.

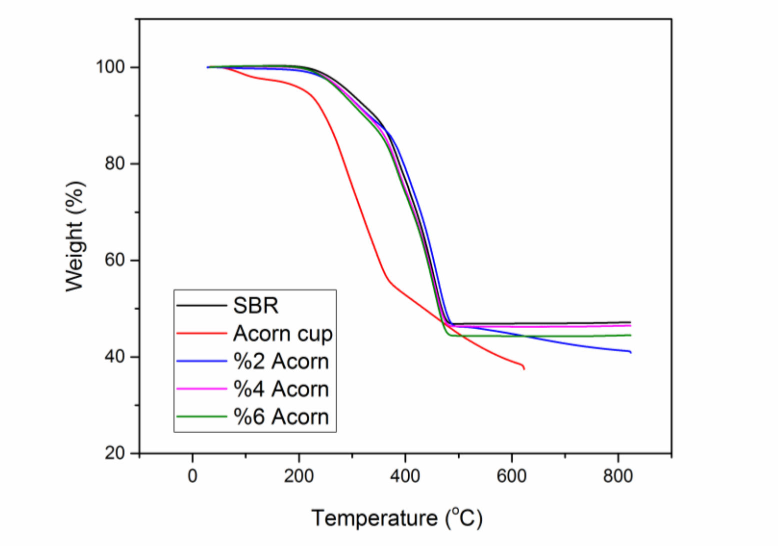

Fig.1: *TGA curves of SBR, Acorn cup and its composites*

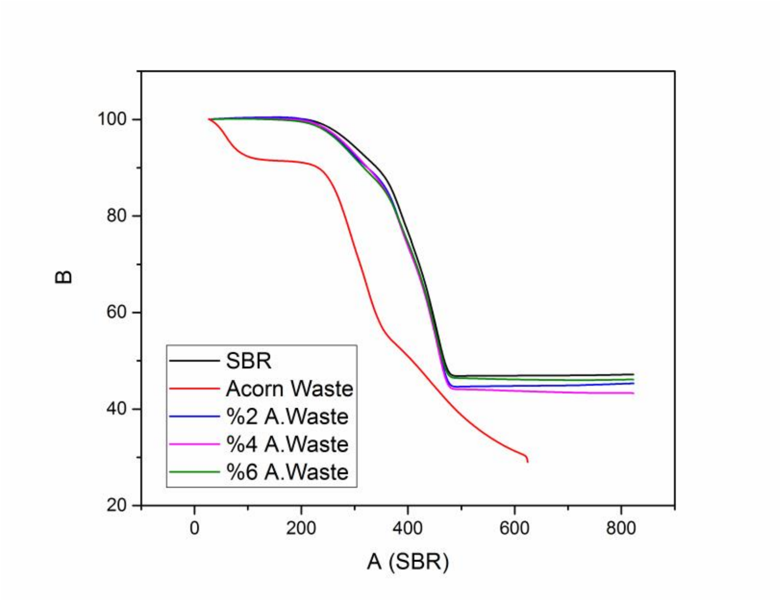

Fig. 2: *TGA curves of SBR, Acorn waste and its composites*

The results revealed that vegetable fillers start to decompose at lower temperatures than SBR. Considering the peak temperatures, the highest thermal values were obtained from the composites by the use of 2% vegetable fillers as reinforcement materials compared to SBR matrix. In general, the highest decomposition temperature and the lowest mass loss are provided by 2% acorn cups-SBR biocomposites. The thermal behavior of SBR matrix is affected by the addition of 2% acorn cups in a positive manner, although the other reinforcements caused a slight decrease in the thermal stability of the biocomposites. On the other hand, the results also showed the addition of bioparticles was not make significant changes in the thermal behavior of SBR so that it can be thermally processed with conventional procedures.

Table 2: *Some values about thermal behavior of SBR, and acorn based bio-composites*

MATERIAL	**Temp of 10% mass loss (°C)**	**Temp of 50% mass loss (°C)**	**T_{peak} (°C)**	**Final mass (%)**
SBR	342.11	468.43	454	47.16
Acorn waste	231,39	408,02	322,7	28,90
Acorn cup	248,54	435,20	287,3	37,41
2% acorn waste - 98% SBR composite	324.33	463.12	455	45.30
4% acorn waste - 96% SBR composite	324.73	461.69	455	43.26
6% acorn waste - 94% SBR composite	317.46	465.45	453	46.09
2% acorn cup - 98%SBR composite	331.89	474.66	459	40.82
4% acorn cup - 96% SBR composite	329.19	465.97	452	46.46
6% acorn cup - 94% SBR composite	321.87	462.57	455	44.48

4. CONCLUSION

In this study, the use of vegetable fillers as a potential reinforcement material in SBR based composites was investigated and following conclusions have been drawn;

The vegetable fillers were incorporated into the elastomer matrix successfully.

Different concentrations of vegetable fillers had no significant effect on DSC results and the highest TGA results were obtained by the use of 2% acorn cups.

Homogenous dispersion of vegetable fillers within the elastomer matrix was achieved successfully and the obtained bio-composite materials were found to be a good candidate to use as bio based footwear sole material.

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REFERENCES

[1] N. J Bonham, W.J.Burt, T. Hughes, C. Loader, E. J. Page and K. C. Dunthorn, "*Manual of Shoemaking",* (Eds. Miller, R. G. and Redwood, S. R.), 5th edition, Clarks Ltd. Printing Department, Bristol, England, 1980, pp 337.

[2] Y. Dikmelik, "*Deri Teknolojisi*", Sepici Kültür Yayınlar 4, ISBN 978-605-85630-0-1, İzmir, 1994.

[3] S. Çavunt, "*Lecturer Notes on Material Science*", İstanbul, 2005.

[4] K. Hanhi, M. Poikelispää, and H.M. Tirila, "*Elastomeric Materials*", Tampere University of Technology the Laboratory of Plastics and Elastomer Technology, Finland, 2007.

[5] Intertek, (2014, Jan.), "Footwear Materials: EVA", https://www.wewear.org/assets/1/7/2010January.pdf, 2010.

[6] Intertek, (2014, Jan.), "Footwear Materials: PVC", https://www.wewear.org/assets/1/7/2011January.pdf, 2011.

[7] G.R.E. Maries, G. Bandur, and G. Rusu, "*Influence of Processing Temperature on Some Mechanical-Physical Properties of Thermoplastic Polyurethane Desmopan KA 8377 Used for Injection Moulding of Performance Sport Products*", Chem. Bull. Politehnica Univ., vol. 53 (67), 2008, pp 1-2.

[8] O. Muehren, and S. Westerdale, "*Thermoplastic Polyurethane (TPU) for High Performance Cable Applications: Current Applications and Future Developments",* International Wire & Cable Symposium, 2012, pp 409-418.

[9] R. Santiagoo, H. Ismail and K. Hussin, "*Mechanical Properties, water absorption and swelling behavior of rice husk powder filled polypropylene/recycled acrylonitrile butadiene rubber (PP/NBRr) Biocomposites using silane as a coupling agent*", Bioresources, vol. 6(4), pp 3714-3726.

[10] T. Toda, K. Okubo, T. Fujıı, H. Hurutachı, Y.Yamanaka and H. Yamamura, "*Development of Rubber Shoe Sole Containing Bamboo Fibers for Frozen Roads",* 16^{th} International Conference on Composite Materials, 2007.

[11] M.J. Ferrerira, M.F. Almeida, and F. Freitas, "*New Leather and Rubber Waste Composites for Use in Footwear"*, Society of Plastics Engineers (SPE), 10.1002/spepro.002929, 2010.

[12] F. Erdoğan, A.C. Adıgüzel Zengin, O. Yilmaz, F. Akpolat, H.A. Karavana, "*Thermal Characterization of Vegetable Tannin Reinforced TPU based Biocomposites"*, International Conference on Sustainable Bioplastics, November 10-11 2016, Alicante, Spain.

[13] H.A. Karavana, F. Erdoğan, A.C. Adıgüzel Zengin, O. Yılmaz, F. Akpolat, "*Thermal and Antimicrobial Characterization of Olea Europaea Leaf Reınforced TPU-Based Bio-Composites*", XXXIV IULTCS Congress, Proceedings of the XXXIV IULTCS Congress, 05–08 February 2017, Chennai, India, 102.