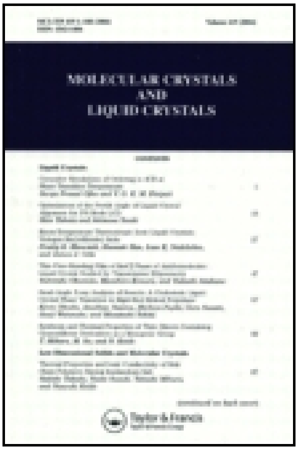

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Hydroxyapatite: An Environmentally Friendly Filler for Elastomers

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Natural hydroxyapatite HAP, extracted from the animal bones was used as filler for carboxylated acrylonitrile-butadiene rubber XNBR. Physicochemical properties of the HAP were investigated. It demonstrated the tendency to create the structure in paraffin oil. When added to rubber, HAP formed a molecular filler network, which was observed from the dynamical mechanical analysis. Hydroxyapatite appeared to be active filler, since mechanical properties of the vulcanizates were improved upon filling. However, the dispersive component of the hydroxyapatite surface energy was slightly higher in comparison to the value which corresponds to the rubber.

Keywords: carboxylated acrylonitrile-butadiene rubber; filler; hydroxyapatite

INTRODUCTION

There are legal requirements, and environmental pressures, to resolve the problem of the waste disposal by finding new applications for the products, or byproducts, obtained from waste streams. Increasing attention has been paid towards utilization of natural products or their analogues. The meat industry makes a significant contribution to the volume of organic wastes produced per year. Previously, byproducts of the industry were used internally as fodder additives but since this practice has been forbidden, identification of new applications for components of these waste streams is an open issue of increasing importance.

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Elastomers have numerous practical applications, particularly when mixed with fillers to enhance their physical properties [1]. Carbon black has been primly used as an active filler of elastomers. However, it can be mutagenic due to aromatic compounds adsorbed on its surface [2]. That is why the other materials, especially minerals are considered as good alternative fillers for certain applications. They are environmentally friendly, which in accordance to the philosophy of green chemistry makes them very attractive materials. Many types of ceramics based on tricalcium phosphate, hydroxyapatite or glass ceramics, are widely used in dental or orthopedic surgery as a filling material [3].

In the present study hydroxyapatite was used as filler for carboxylated acrylonitrile-butadiene rubber. One of the most important factors, one that determines both the rheological and mechanical properties of a filled elastomeric system, is the strength of the interaction between the elastomer and filler [4,5]. However, many other factors can influence the efficiency of the filler in the application. The chemical nature of its surface, its surface energy, and filler-filler interactions are some of the more significant interactions that have to be considered. Moreover, the physicochemical properties of the filler cannot be neglected [6,7].

The studies described herein focus on the physicochemical properties of hydroxyapatite obtained from animal bones as well as the properties of the elastomer-hydroxyapatite composites.

EXPERIMENTAL

Nonstoichiometric hydroxyapatite (HAP) was extracted from the cortical part of the long pig bones according to the procedure described elsewhere [8]. The properties of pig bone HAP were determined by scanning electron microscopy (LEO 1530), light diffraction (Malvern Instruments, Nano S-90), nitrogen adsorption (Sorty 1750, Carlo Erba), thermogravimethry (Setaram Setsys TG-DTA 16/18), energy dispersive X-ray spectroscopy (Siemens D500), zeta potential (Malvern Instruments, Zetasizer 2000), inverse gas chromatography (chromatograph 5890 A, Hewlett Packard) and rheological measurements (Rheometric Scientific RM500).

Carboxylated acrylonitrile-butadiene rubber (XNBR, Krynac X 7.5, Bayer C.O.) and zinc oxide (100 nm, BTE 42.5 m^2/g, Quinetiq Nanomaterials Limitem) were used as received. The rubber mixtures (100 phr XNBR + 4 phr ZnO + HAP) were prepared on a laboratory two-roll mill at ambient temperature. Composites were prepared by vulcanization at 160°C for 30 min. Composites were characterized by dynamic

(DMTA V, Rheometric Scientific) and static (Universal Testing Machine–Zwick 1435) mechanical properties, and crosslinking density (on the basic of equilibrium swelling measurements).

RESULTS AND DISCUSSION

The hydroxyapatite used in the present studies contained a fraction of water (4.8%) and carbonate groups (3.5%) incorporated into HAP structure, (Table 1). The percent crystallinity calculated from the X-ray diffraction measurements was about 72%, with the crystals size 353 Å. The surface charge on the HAP particle was characterized by the zeta potential. The pH of the dispersion was adjusted by addition of 0.1 M HNO_3, 0.1 M H_2SO_4, or 0.1 M H_3PO_4 and 0.1 M NaOH. The isoelectric point for pig bone HAP was found to occur at pH ~ 12, which is higher than the reported value [9]. This can be attributed to a number of factors, including difficulties in measuring pH accurately and dissolution of HAP. Small differences in zeta potential when different acids were used could occur because of the different solubility of HAP particles in each acid. When the pH was lower than 7, complete solubility of HAP was observed, (Fig. 1).

Specific surface area, as measured by the nitrogen adsorption, was 71 m^2/g. Particle size determined from the light scattering measurements, was in the micrometer range, (2,600 nm). SEM images showed the individual particles had agglomerated so that we assume this measurement provided the size of the agglomerates rather than single particles, (Fig. 2).

Rheological measurements can provide useful information about the ability of the filler to create and maintain its own structure when dispersed in a matrix material. Based on Mooney's equation, the volume content of filler aggregates, ϕ, in paraffin oil was calculated [10] to be 2.7% when the 1.9 vol% of HAP was added. Figure 3 shows that significant viscosity changes occurred for small changes in shear rates which demonstrates destruction of the initial formed structure of the filler.

TABLE 1 Physicochemical Properties of Hydroxyapatite

Agglomerates size	2600 nm
Surface area	71 m^2/g
Thermal stability	– 4.8% (200°C) – 3.5% (800°C)
Crystallinity	72%
Crystals size	353 Å

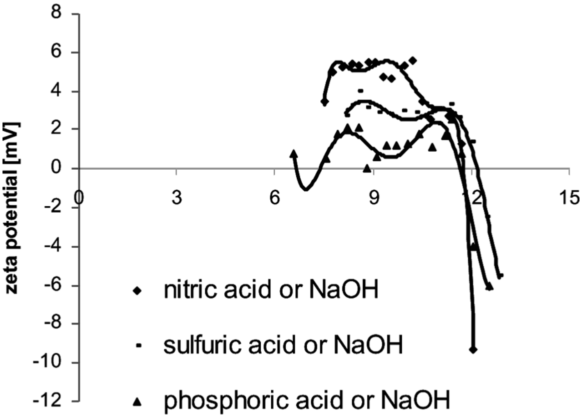

FIGURE 1 Zeta potential of hydroxyapatite dispersion as a function of pH.

The surface energy of the filler particles plays the important part in the process of reinforcing elastomers. The dispersive component of hydroxyapatite surface energy was calculated from the inverse gas chromatography measurements [11] by extrapolation the values to 25°C, $\gamma_S{}^D = 58.2\,\mathrm{mJ/m^2}$ (Fig. 4). The dispersive component of the rubber is within the range of 30–50 mJ/m^2 [12]. The more similar those values are for the filler and for the rubber, the better the interaction between them, which results in improved mechanical properties.

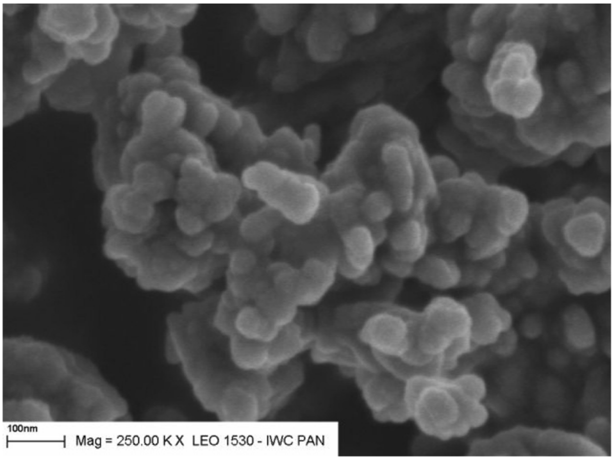

FIGURE 2 SEM image of hydroxyapatite particles.

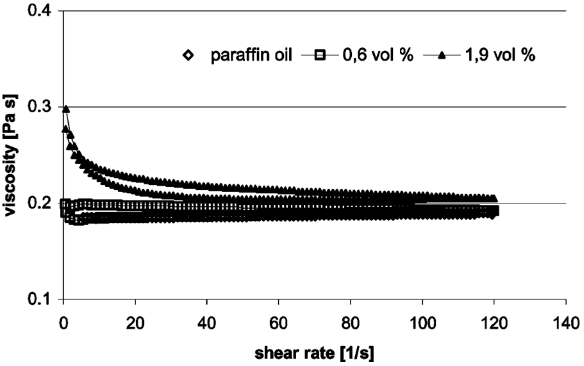

FIGURE 3 Viscosity of the hydroxyapatite dispersions in paraffin oil, volume% of HAP 0.6% and 1.9%.

The reinforcing activity of fillers is associated with the strength properties of the filled vulcanizates. It appears that hydroxyapatite can be an active filler for carboxylated butadiene-acrylonitrile rubber, (Table 2). The stiffness of the XNBR vulcanizates containing HAP increased with the amount of filler added to the composite. The tensile strength of the system filled with the 40 phr of HAP was significantly higher than the value for the unfilled one.

The reinforcing effect of added filler may result from several factors, including the possibility of the filler to create its own network inside the elastomer network. The presence of so-called secondary structure can be easily confirmed by dynamic measurements on the composite,

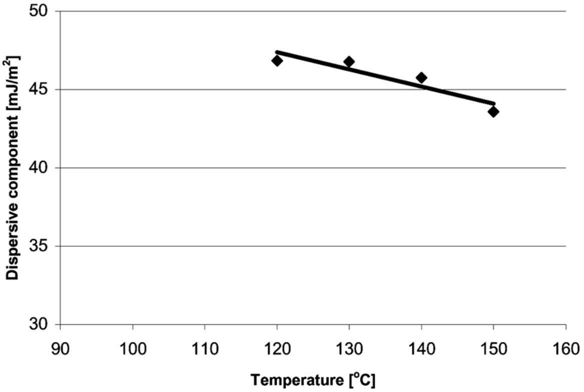

FIGURE 4 Dispersive component of hydroxyapatite surface energy (γ_{D}s, mJ/m^2) as a function of the temperature.

TABLE 2 Mechanical Properties of Vulcanizates of Carboxylated Acrylonitrile-Butadiene Filled with Hydroxyapatite

Vulcanizate	δ_{100} [MPa]	δ_{200} [MPa]	δ_{300} [MPa]	TS [Mpa]	ε_b[%]
100XNBR + 4ZnO	1,56	1,98	2,45	20,97	659
100XNBR + 4ZnO + 10HAP_H	1,92	2,64	3,30	15,38	624
100XNBR + 4ZnO + 20HAP_H	2,69	4,14	5,96	21,24	598
100XNBR + 4ZnO + 40HAP_H	5,98	10,32	14,81	28,04	495

σ_{100}, σ_{200}, σ_{300}–stress at elongation 100; 200; 300%; TS–tensile strength; ε_r–elongation at break.

especially as a function of strain amplitude, (the Payne effect, whose measure is the change in the modulus of elasticity due to the increasing amplitude of shearing deformations). The highest Payne's effect was observed in the case of the vulcanizate filled with 40 phr of HAP. We assume that filler particle interactions could be the reason for the reinforcing properties of hydroxyapatite, (Fig. 5).

It appeared that hydroxyapatite increased the cross-linking density of the vulcanizates, as calculated from the swelling in toluene. [10] Table 3 shows the changes in the cross-linking density of vulcanizates filled with HAP. The number of ionic crosslinking points, $\Delta\nu/\nu_{e(T)}$, whose formation could take place with the participation of Ca^{2+}, was particularly high when the 40 phr of HAP was added to the composite.

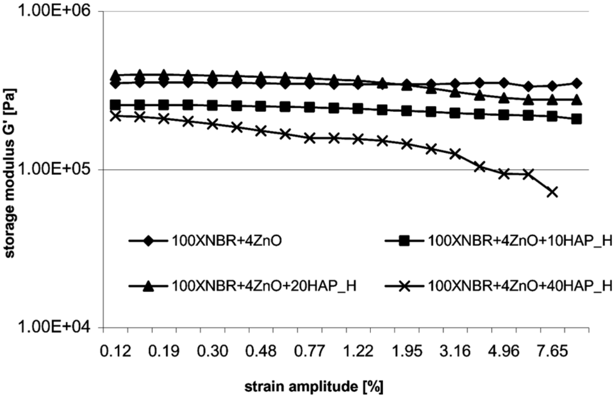

FIGURE 5 Storage modulus of vulcanizates during shearing as a function of strain amplitude.

TABLE 3 Cross-Linking Density of Vulcanizates of Carboxylated Acrylonitrile-Butadiene Filled with Hydroxyapatite

Vulcanizate	$\nu_e^* 10^5$ (T)	$\nu_e^* 10^5$ (A)	$\Delta\nu/\nu_T$ [%]
100XNBR + 4ZnO	2,46	2,83	15
100XNBR + 4ZnO + 10HAP_H	4,54	2,95	35
100XNBR + 4ZnO + 20HAP_H	4,81	4,21	12
100XNBR + 4ZnO + 40HAP_H	8,15	3,23	60

ν_e – crosslinking density calculated from the equilibrium swelling in (T) toluene or (A) toluene under the ammonia atmosphere; $\Delta\nu$ – concentration of ionic cross-links $(\Delta\nu = \nu_{e(T)} - \nu_e(A))$; $\Delta\nu/\nu_{e(T)}$ the relative changes of cross-links under the ammonia treatement

CONCLUSIONS

The rheological properties of HAP in paraffin oil demonstrate that hydroxyapatite extracted from pig bones shows a tendency towards agglomeration when dispersed in blends. The surface of hydroxyapatite was basic within the range of pH 7:11 and the dispersive component of the hydroxyapatite surface energy was slightly higher then the value measured for rubber. Nevertheless, hydroxyapatite could be used as active filler for the rubber and the mechanical properties of the vulcanizates were improved by addition of filler. This can be attributed the observation, demonstrated by dynamical mechanical analysis, that hydroxyapatite formed a molecular filler network throughout the rubber matrix.

REFERENCES

[1] Dannenberg, E. M. (1975). *Rubber Chem. Technol.*, *48*, 410.

[2] Donnet, J. B. (1993). *Carbon Black, Science and Technology*, Marcel Dekker: New York.

[3] Damien, C. J. & Parson, J. R. (1991). *J. Appl. Biomat.*, *2*, 187.

[4] Wang, M., Wolff, S., & Tan, E. (1993). *Rubber Chem. Technol.*, *66*, 178.

[5] Wolff, S., Wang, M., & Tan, E. (1994). *Kautstuck Gummi Kunstoffe*, *47*, 102.

[6] Wang, M. (1998). *Rubber Chem. Technol.*, *71*, 521.

[7] Wang, M. & Wolff, S. (1991). *Rubber Chem. Technol.*, *64*, 714.

[8] Haberko, K., Bucko, M. M., Brzezinska-Miecznik, J., Haberko, M., Mozgawa, W., Panz, T., Pyda, A., & Zarebski, J. (2006). *J. Europ. Ceramic Soc.*, *26*, 537.

[9] Harding, I. S., Rashid, N., & Hing, K. A. (2005). *Biomaterials*, *26*, 6818.

[10] Zaborski, M., Kunert, A., Pietrasik, J., Szynkowska, M. I., & Lesniewska, E. (2007). *Rubber Chem. Technol.*, *80*, in press.

[11] Zaborski, M., Slusarski, L., Donnet, J. B., & Papirer E. (1994). *Kautstuck Gummi Kunstoffe*, *47*, 1730.

[12] Zaborski, M., Rucinski, J., & Bielinski, D. (1991). *Polimery*, *36*, 109.