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HYDROPHOBIZED LIMESTONE AS FILLER IN POLYMER MATERIALS

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Abstract: The article shows changes in certain mechanical properties of polyvinyl chloride (PVC) depending on the quality of added limestone as a filler. Natural limestone and limestone hydrophobicized with stearic acid were added. Modification experiments were carried out with “wet” and “dry” processes in order to find out the required amount of stearic acid for a complete surface coating of limestone - degree of coating 99.90%. Coating of the limestone surface was achieved in the “wet” process with 1.5% stearic acid, while in the “dry” process the same degree of coating was achieved with 3% stearic acid. A significant amount of both “wet” and “dry” modified limestone was prepared. Such a product was added to PVC mixture in order to investigate mechanical properties of the obtained PVC product. Research into the mechanical properties of PVC has shown that PVC containing limestone modified by the “wet” process exhibits better mechanical properties than that containing limestone modified by the “dry” process. For example, PVC obtained from a mixture containing limestone modified by the “wet” process with 1.5% stearic acid shows a better tensile strength of 54.20 MPa, while limestone modified by the “dry” process with 3% stearic acid shows a tensile strength 53.20 MPa.

Keywords: PVC; limestone; calcite; hydrophobization; mechanical properties

1 INTRODUCTION

Considering the structure of polymer materials, it is expected that in polymer without fillers, fracture occurs where its texture is weakest, i.e. at the highest strain spot, as a result of the deformation process. Local fracture further spreads out through the entire material, Figure 1. demonstrates breaking of Van der Waals connection between two chains of PVC under the influence of tension force on the example of polyvinyl chloride as polymer without filler.

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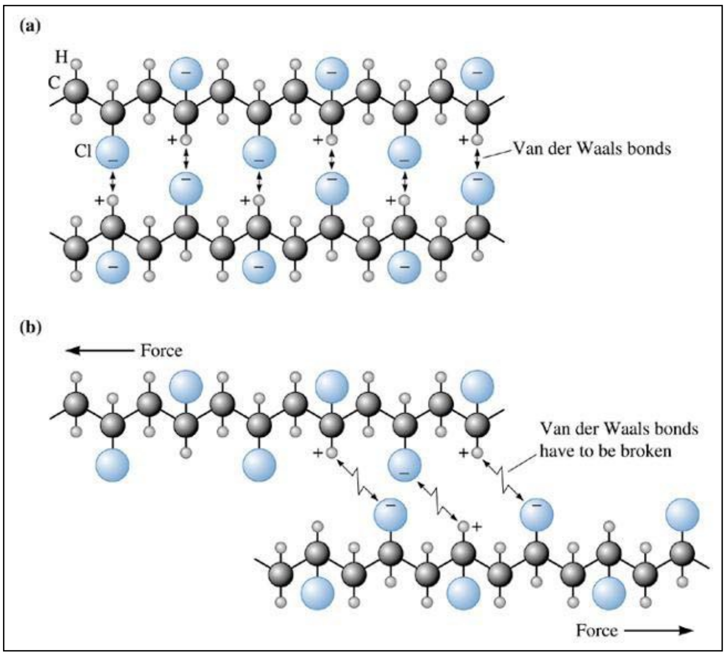

Figure 1 Scheme of molecular connections in polyvinyl chloride (PVC) a) Van der Waals connections between two PVC chains, b) breaking of Van der Waals connections between two PVC chains under the influence of tension force

In polymer with filler, fracture can occur in the matrix itself, in the interspace polymer/filler or within agglomerates for some reason formed in filler. Elongation limits greatly depend on the quantity of the filler, but not on the quantity of the additive for filler modification too. On the other hand, tensile strength and elongation at fracture are properties observed at large deformations in product, since they show its structural properties better there, (Kovačević, Lučić and Cerovečki, 1997; Kovačević et.al., 1996; Kovačević et.al., 1994). Phenomena and mechanisms occurring at calcite surface during limestone surface modification authors of this paper clarified in the paper, (Mihajlović et. al., 2009a; Mihajlović et. al., 2009b). This paper provides findings obtained by further observation of the limestone surface modification

2 EXPERIMENTAL

For experimental research of this paper limestone 95% -10 μm and of the following chemical composition: 53.77% CaO; 0.084% Fe_2O_3; 0.035% Al_2O_3; 1.79% MgO; 0.24% SiO_2; 0.027% Na_2O; 0.036% K_2O; 44.05% was used. Properties of stearic acid used for limestone surface modification in experiments were the following: Molecular formula $CH_3(CH_2)_{16}COOH$; molecular weight, g/mol 284.47; density, g/ml 0.847; dissociation constant, pKa 5.7; solubility in water, g/100 ml 0.034 (25ºC), 0.1 (37ºC); solubility in alcohol, g/100 ml 2.5 (cold); solubility in ether, $CHCl_3$, CCl_4, CS_2 very soluble.

3 RESULTS AND DISCUSSION

Since previous experiment showed that complete limestone surface coating with stearic acid is achieved with 1.5% of stearic acid by the “wet” process and 3% by the “dry” process, 5 kg of limestone modified this way were prepared, (Mihajlović, Sekulić and Petrov, 2005; Mihajlović et. al., 2009a; Mihajlović et. al., 2009b; Mihajlović et. al., 2012). This product was mixed with PVC in order to make panels, the mechanical properties of which were to be tested. This was done in order to investigate which modification process provides better ultimate effects in PVC final products, even though both were completely coated with stearic acid on the surface “TIRA-test 2300“ universal testing machine with 10 kN load cell, 0-10 kN testing range, accuracy class 1, was used for assessment of mechanical properties of PVC mixture. Testing material was prepared by milling process in the shape of type A test tube. Prepared samples were tested for tensile strength, tensile yield strength, tensile elongation and elongation at break according to ISO 527-2 standard. The obtained results are presented in Table 1.

Table 1 Mechanical properties of PVC mixtures

Mechanical properties	Method	Unit	Samples				
			PVC+C	PVC+CD-1.5	PVC+CW-1.5	PVC+CD-3	PVC+CW-3
Tensile strength	ISO 527-2	MPa	52.70	52.70	54.20	53.20	53.60
Tensile yield strength	ISO 527-2	MPa	36.50	36.20	38.20	37.90	39.10
Tensile elongation	ISO 527-2	%	4.30	4.40	4.35	4.46	4.30
Elongation at break	ISO 527-2	%	35.90	35.40	29.30	22.50	24.60

The samples are presented in Table 1 as follows: C- calcite; PVC+CD-1.5- mixture containing calcite modified with 1.5% stearic acid by “dry” process; PVC+CW-1.5- mixture containing calcite modified with 1.5% stearic acid by “wet” process; PVC+CD-3- mixture containing calcite modified with 3% stearic acid by “dry” process; PVC+CW-3- mixture containing calcite modified with 3% stearic acid by “wet” process.

3.1 Tensile strength and elongation

Limestone modification with stearic acid makes its surface hydrophobic and thus compatible with PVC basis, which decreases the degree of friction between polymer and filler, (Kovačević et.al., 1994; Mihajlović et. al., 2009a; Mihajlović, Sekulić and Petrov, 2005). This conclusion was confirmed by the results obtained from testing of PVC mixture mechanical properties in this paper. The "wet" process of calcite modification with stearic acid (Table 1) increases tensile strength from 52.70 MPa (sample of uncoated limestone) to 54.20 MPa (sample with 1.5% stearic acid). Further increase in the amount of stearic acid to 3% decreases tensile strength to 53.60 MPa. This can be explained by the fact that excess stearic acid in modification process causes bonding between filler particles and agglomerate. Large particles in material structure weaken the material and decrease its fluidity, thus leading to the decrease in tensile strength, (Mihajlović, Sekulić and Petrov, 2005).

In the "dry" process of calcite modification with stearic acid (Table1) the highest value of tensile strength of 53.20 MPa is achieved in sample with 3% stearic acid. This confirms the fact that tensile strength increases as the filler's hydrophobicity rises, and it is highest when complete coating of calcite with stearic acid is achieved. This explains why higher amount of stearic acid (3%) is needed for coating of calcite of 99.90% in the "dry" modification process in comparison to the "wet" process (1.5%), as already shown, (Mihajlović et. al., 2009a; Mihajlović et. al., 2009b). Analysis of the obtained results leads to conclusion that for the same amount of stearic acid in calcite modification process tensile strength is higher in PVC mixture containing calcite modified by the "wet" process related to the PVC mixture containing calcite modified by the "dry" process. Namely, when the amount of stearic acid in modification process is 1.5%, tensile strength of PVC mixture containing calcite modified by the "wet" process is by 2.85% higher related to the tensile strength of PVC mixture containing calcite modified by the "dry" process. Also, when the amount of stearic acid in modification process is 3%, tensile strength of PVC mixture containing calcite modified by the "wet" process is by 0.75% higher related to the PVC mixture containing calcite modified by the "dry" process.

Since tensile strength and elongation are inversely proportional, samples of PVC mixture with higher tensile strength will demonstrate lower elongation. Namely, PVC mixture containing calcite modified with 1.5% stearic acid by the "wet" process shows by 0.5% less elongation related to the elongation of PVC mixture containing calcite modified by the "dry" process regardless of higher tensile strength. Also, PVC mixture containing calcite modified with 3% stearic acid by the "wet" process shows by 0.2% less elongation related to the elongation of PVC mixture containing calcite modified by the "dry" process, although its tensile strength is higher.

3.2 Tensile yield strength and elongation at break

Tensile yield strength of PVC mixture when calcite is modified by the “wet” process increases with the increase of the degree of sample coating (Table 1). Namely, tensile yield strength increases from 36.50 MPa in starting sample to 38.20 MPa in the sample with 1.5%. Further tensile yield strength increase to 39.10 MPa in sample with 3% stearic acid is observed, but that change is minor related to the sample with 1.5% stearic acid with tensile yield strength of 38.20 MPa, so it can be neglected. In the “dry” process of calcite modification with stearic acid, tensile yield strength of PVC mixture also rises with the degree of coating of the sample just like in the “wet” process (Table 1). Considering the fact that in the “dry” process calcite is modified with stearic acid in inhomogenous conditions, it is necessary to add more stearic acid than in the “wet” process (i.e. 3%) in order to achieve the degree of coating of 99.90%. In accordance with that, the highest value of tensile yield strength of 37.90 MPa is achieved in sample with 3%, while in the sample modified with 1.5% stearic acid tensile yield strength is lower- 36.20 MPa. Comparing tensile yield strength of PVC mixtures containing calcite modified by the “wet” process and tensile yield strength of PVC mixtures containing calcite modified by the “dry” process shows that higher tensile yield strength occurs in mixture containing calcite modified by the “wet” process (Table 1). Namely, when the amount of stearic acid in modification process is 1.5%, tensile yield strength of PVC mixture containing calcite modified by the “wet” process is by 5.5% higher related to tensile yield strength of PVC mixture containing calcite modified by the “dry” process. Also, when the amount of stearic acid in modification process is 3%, tensile yield strength of PVC mixture containing calcite modified by the “wet” process is by 3.2% higher related to PVC mixture containing calcite modified by the “dry” process. Tendency of a material to bend without breaking is decreased when calcite is modified both by the “wet” and the “dry” processes with increased degree of sample coating. This is expected considering the fact that strength and elongation of a material are inversely proportional. Namely, PVC mixtures with higher tensile yield strength will demonstrate lower tensile elongation. This is explained by the fact that modification of calcite mineral surface produces filler which increases system fluidity since its surface is hydrophobic, and as such compatible to PVC basis, (Mihajlović et. al., 2012). Elongation at break of PVC mixture decreases from 35.90% to 29.30% in sample with 1.5% stearic acid in the “wet” process of calcite modification. Increase in the amount of stearic acid to 3% in calcite modification process further decreases elongation at break to 24.60%. In the “dry” process of calcite modification elongation at break of PVC mixture also decreases with the increase of the degree of coating just like in the “wet” process. However, sudden drop in value of elongation at break with achieving maximum degree of coating is evident. Elongation at break decreases from 35.90% to 22.50% in sample with 3% stearic acid. Sudden drop in value of elongation at break from 35.40% to 22.50% is explained by the inhomogenous character of the “dry” process of calcite modification. The obtained results indicate that the investigated mechanical properties of PVC mixture depend on the strength of bond between calcite and the adsorbed organic component.

The sample modified with 1.5% stearic acid concentration by wet process, as well as the sample modified with 3% stearic acid concentration by dry process, are totally hydrophobic, but PVC mixture with filler obtained by wet process shows better mechanical properties than mixture with filler obtained by dry process. This leads to conclusion that using filler in which surface active material is chemically adsorbed on calcite provides better mechanical properties of PVC mixture, as is the case with the sample modified by wet process with 1.5% concentration of stearic acid. In other words, the chemisorbed stearate on calcite allows stronger interaction in calcite-stearic acid-PVC system, i.e. better mechanical properties. Poorer mechanical properties were attained with filler obtained by dry process with 3% stearic acid concentration related to the PVC mixture with the sample obtained by wet process with 1.5% stearic acid concentration. In the sample modified by wet process with 3% stearic acid concentration, larger amount of the physically adsorbed surface active material was detected apart from the chemisorbed stearate, which evidently influences the intensity of interactions in PVC mixture. Poorer mechanical properties of PVC mixture with calcite modified by dry process with 3% stearic acid concentration are the result of physical adsorption of surface active material on the mineral.

4 CONCLUSION

Complete surface modification of limestone by stearic acid is achieved with 1.5% of stearic acid by the “wet” process and with 3% stearic acid by the “dry” process. Previous research has shown that with the “wet” modification process, a more uniform (homogeneous) distribution of stearic acid is achieved on the calcite surface compared to the “dry” process. This is why mechanical properties of a PVC product are better when limestone modified by the “wet” process is used for mixture. It was also observed even in case of limestone complete coating by the “dry” process with 3% stearic acid, limestone coated by the “wet” process grants better mechanical properties of PVC final product. Namely, tensile strength of PVC mixture containing limestone modified with 1.5% stearic acid by the “wet” process is by 2.84% higher related to tensile strength of PVC mixture containing limestone modified with the same amount of stearic acid but by the “dry” process. When limestone is modified with 3% stearic acid, PVC mixture containing limestone modified by the “wet” process shows by 0.74% higher tensile strength than PVC mixture containing limestone modified by the “dry” process. Breaking strength of PVC mixture containing limestone modified with 1.5% stearic acid by the “wet” process is by 5.23% higher related to the breaking strength of PVC mixture containing limestone modified with the same amount of stearic acid by the “dry” process. When the amount of stearic acid in the modification process is increased to 3%, PVC mixture containing limestone modified by the ‘’wet’’ process shows by 3.07% higer tensile strength than PVC mixture containing limestone modified by the “dry” process.

The results obtained imply that tensile strength, tensile elongation and elongation at break of PVC mixture depend on the strength of connection between calcite and the adsorbed organic component. The filler obtained by wet modification method and with concentrations of stearic acid which enable forming of chemisorbed stearate monolayer on calcite was found out to be the best. These mechanical properties are the best in PVC mixture with calcite obtained by wet process with 1.5% stearic acid concentration, which was totally hydrophobic, and in which chemically adsorbed surface material dominates, which means that the chemisorbed stearate on calcite enables stronger interaction in calcite-stearic acid-PVC system.

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