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Investigation of the Influence of Alkaline(outer) Hydrolysis on
the Long Term Resistance
of
Highly Oriented Polyester(PET)-Yarns for Geotextiles

English Summary

The behaviour of five typical polyester(PET)fiber products: three highly oriented yarns, one mechanically bound filament nonwoven and a woven geogrid was studied during exposure to inner and outer (alkaline) hydrolysis.

It is known that in the presence of humidity always inner hydrolysis is taking place, while outer hydrolysis depends on special conditions. If outer hydrolysis is to be studied it is therefore necessary to take into account the overlapping of both kinds of hydrolysis.

Therefore it was initially necessary to study inner hydrolysis in order to be able to separate the effects of outer hydrolysis. While mechanical strength of the materials studied is a summarizing material property, the special tool to quantify inner hydrolysis is the determination of carboxylendgroups (CEG).

Looking at the behaviour of the PET-materials in nearly neutral deluted salt and acid ($< 0,01$ M) solutions it was found that hydrolysis runs nearly with the same velocity as in pure water, hence we are dealing with inner hydrolysis. The acids used were acetic acid, p-hydroxybenzoic acid and sulfuric acid. These acids are known as metabolites of microorganisms or degradation products of humic acids or oxidative products of microorganisms or air pollutants. Usually they are met at lower concentrations. The results made it obvious that inner hydrolysis is hardly influenced by these deluted media. This is presumably always true if the substances are not able to permeate the fibers. The kinetics of inner hydrolysis can be characterized by Arrheniusdiagrams. By this means it is possible to assess the behaviour at lower temperatures.

For the determination of the Arrheniusenergy E_A the tensile behaviour at at least three temperatures has to be studied. Preferably the temperatures of 90°C , 70°C and 60°C are used. Due to the exponential dependence on E_A precise measurements are urgent. For the tested materials E_A was in the range of 96 to 112 kJ/mol.

Further problems arise from the following circumstances: the temperature region of practical interest is lying below 50°C i.e. clearly below the glass transition temperature T_G of PET in the wet state of about 60°C . Due to the very low reaction velocity of inner hydrolysis this range is very difficult to explore. It will therefore as a rule be necessary to extrapolate into the region below T_G . The resulting uncertainties have to be covered by coefficients of partial security. Further complications arise from the tendency of PET-materials to crystallize under wet conditions, especially above T_G . Below T_G physical aging might be relevant. Both processes have impacts on the tensile behaviour and lead to a more brittle conduct. These processes still might overlap with relaxation processes leading to a more ductile behaviour. These uncertainties also should be covered by suited coefficients of partial security, since they influence kind of evaluation of the plots.

A general connection between CEG and resistance to inner hydrolysis could not be found. In any case for each material the increase of CEG is ruled to be an exponential law, as postulated by Zimmermanns equation. Therefore the measurement of CEG is well suited to follow the kinetics of inner hydrolysis. A detailed study of the connection to molecular weight and morphology was not possible in this study.

An influence of outer hydrolysis on inner hydrolysis could not be observed. Therefore their independence is supposed. Outer hydrolysis in contrast to inner hydrolysis is rather sensitive to the composition of the surrounding fluid medium. In comparison to other cations like Na^+ , K^+ , Mg^{2+} , Fe^{2+} , Mn^{2+} or Ba^{2+} a clear acceleration of outer hydrolysis is observed cet. par. in the presence of Ca^{2+} .

A saturated suspension of gypsum was therefore used as a conservative reference system for the study of outer hydrolysis. This substance is ubiquitous and its solubility is only slightly depending on temperature. -The velocity constant of outer hydrolysis is found to be proportional to hydroxyl ion concen-

tration $[OH^-]$. It has to be determined for each material, since it depends on morphology and geometry of the materials. Highly oriented fibers are less sensitive to outer hydrolysis than less oriented fibers. The E_A of outer hydrolysis was found to be clearly lower than that of inner hydrolysis and in the range of 46 to 80 kJ/mol. This means that *et par.* outer hydrolysis is less accelerated by temperature. But it is convenient for testing that the process can be easily accelerated by higher $[OH^-]$.

Therefore in this case T_G is no problem. Above T_G it has to be supposed that crystallisation might additionally stabilize the materials. This is a not conservative action concerning security aspects. The same holds for physical aging. Therefore coefficients of partial security have to be considered. Those aspects could not be covered by the studies.

Finally the morphology of alkaline hydrolysis has been studied by REM. It is clear that this reaction results in notches which are dangerous for reinforced structures. In outer hydrolysis therefore clear influence of tensile tension was found in contrast to inner hydrolysis. But these studies could not be extended.

The extrapolated life time at 20 °C at pH 10 of PET-materials for a reduction of tensile strength by 10% by outer hydrolysis was clearly found to be much shorter than that by inner hydrolysis. Therefore it is recommended not to use PET-materials in reinforced long term structures if $[OH^-]$ is greater than $10^{-5}M$. This would be about pH 9 at 20 °C.

Thus by studies of this kind the stability of PET-materials can be investigated in a straight way to answer special questions of special surroundings.