



Artificial aging

Predicting material behavior

Summary

An airplane is made of a wide range of materials that are subject to various different stresses. For instance, the plane might take off in hot, tropical air and then cruise at an altitude of 33,000 feet at temperatures well below freezing. In addition to extreme climatic differences, there are other stresses, such as vibrations, that strain the materials during flight. These stresses may age the materials and cause their properties to change.

For this reason, artificial aging tests are carried out early in the development stage in order to prevent material failures during flight. However, to save costs and time, accelerated tests that increase the stress levels are often carried out. The final assessment and evaluation provide an indication about whether a particular material is suitable for its intended use, information which can significantly reduce subsequent costs otherwise caused by the continual replacement of the component.

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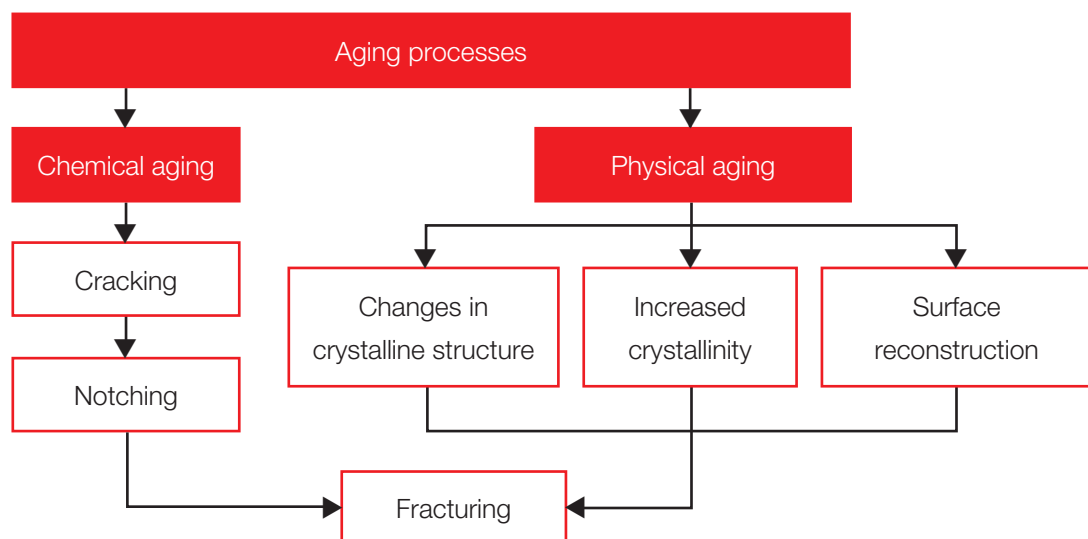
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What is aging?

People use materials of all types for a wide range of applications. Throughout their use, the materials are subject a wide range of forces and stresses that may considerably affect their service life. One example is an airplane, which might take off in hot, tropical air and then cruise for extended periods at an altitude of 33,000 feet at temperatures well below freezing. In addition to extreme climatic differences, there are other stresses, such as vibrations, that strain the materials during flight. The various stresses may affect the materials to such an extent that their properties are irreversibly changed. This is what is referred to as the aging of the material, which is defined in DIN 50035 Part 1 as

“All irreversible chemical and physical processes that occur over time in a material.”¹

In general, however, it is not possible to use the effects of the processes to distinguish between chemical and physical processes that occur. Normally, these processes occur simultaneously and therefore lead to a complex effect. The diagram below shows a simplified version of how an aging process occurs.



¹ DIN 50035 Part 1, Section 1 Aging, 03-1989

What is aging?

Aging always implies a negative change in, or even the loss of, the properties of the material. In this context, materials science and quality assurance refer to the former effect as material fatigue and the latter as material failure. However, changes in the material are not considered to be an aging process if the original characteristics of the material can be re-established by treating a component with heat.

A large number of various factors may cause aging, and these can be divided into two categories. First, there are what are called internal factors, which can include stress relief, phase transition, microstructural transformation or changes in chemical composition. These internal factors will not be addressed in any greater detail in this white paper. The second category of factors comprises the external causes of aging, such as temperature changes, humidity, oxygen concentration, visible, ultraviolet or ionizing radiation, and chemical factors.



Aged material

Material aging can manifest itself in many different ways. The particular form in which this occurs depends not only on the properties and composition of the material, but also on the kind of stress. External factors can be divided into six different primary types of aging, which may also appear in combination. In the example of the airplane thermal, climatic and mechanical stresses play a role alongside corrosive or electric stresses. Another type of aging that should be mentioned is material changes caused by UV radiation, which can be visibly observed, particularly in polymers, in the form of a yellowing. Additional details on the various types of stresses that cause aging are discussed in Section 4.

What is aging?

Because of the wide range of factors, a material may age in several different ways. This is described in terms of the change in properties with respect to the material. Here, the material's resistance to a particular stress plays a decisive role. Generally, the change in a property can be expressed by the following simplified formula:

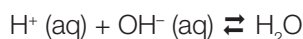
$$\text{Change in property} = \text{Resistance} \times \text{Stress}$$

However, sensitivity may change as the material ages, which can then accelerate or slow the change in the property. This can be influenced, e.g. in polymers, by adding special stabilizers, which change the sensitivity of the polymer. In general, any organic material is unstable in air and will show signs of change over a period of time. Not even stabilizers can prevent this from happening. At most, they can slow down the processes.

In addition, the composition of the material is not the only factor in aging: The material's prior history as well as its processing must also be taken into consideration. This is an important criterion, especially in artificial aging (which will be discussed in Section 5), since this technique involves the use of accelerated aging. Other important criteria are storage and the changes in properties that arise during storage, as aging reactions caused by thermal stress, for example, can be initiated under these conditions.

A brief excursion into history: Svante Arrhenius

Svante August Arrhenius was born in 1859 in Sweden. His father was a land surveyor for the Uppsala University, where the son would later study mathematics, chemistry and physics. After studying in Uppsala, Arrhenius moved to the Physical Institute of the Swedish Academy of Sciences in Stockholm, where his research focused mainly on the conductivity of electrolytes. In 1887 he published his „Chemical Theory of Electrolytes“ on the topic. This theory demonstrates that electrolytes dissociate in water or aqueous solutions. It produced the definitions of acids and bases that are still used today. These definitions state that acids are substances that produce H^+ (aq) ions in aqueous solution, while bases are substances that produce OH^- (aq) ions in aqueous solution. These ions can, however, recombine to neutralize as water.



As a result of his work in this area, Arrhenius received the Nobel Prize in Chemistry in 1903.

However, Arrhenius did not dedicate himself solely to the dissociation of electrolytes, he was also interested in the dependency of reaction rates on temperature. To express this relation, he developed an equation which defines the reaction rate constant as a function of activation energy and temperature.

$$k = A \times e^{-E_a / (R \times T)}$$

- k reaction rate constant
- A constant characteristic to the reaction
- E_a activation energy
- R ideal gas constant
- T temperature

The equation shows the relationship between temperature and activation energy. The multiplier $e^{-E_a / (R \times T)}$ is the factor that indicates when the activation barrier is exceeded. The reaction rate constant increases exponentially as the temperature increases. This means that even a small increase in temperature can lead to a significant change, i.e. increase, in the reaction rate.

A brief excursion into history: Svante Arrhenius

The connection to aging in materials then also becomes clear. The Arrhenius equation thus explains both why thermal aging occurs and how it can be artificially accelerated. Yet there are other aging mechanisms that cannot be represented by the Arrhenius equation.

With his equation for calculating reaction constants, Arrhenius established an approximation that can be applied in many areas. It forms the foundation of various aging models used today for predicting aging.

Types of aging

Thermal stresses

A material is affected by thermal stresses when it is exposed to different temperatures. Here, the temperature may be constant or change continuously over an extended period. Depending on the properties and composition of the material, temperature can have completely different effects. For this reason, different materials that are used in combination may age at differing rates. In any case, higher temperatures are the most frequently occurring cause of aging in a material. This is due to the fact that increased temperatures generally result in accelerated chemical reactions. Chemical reactions between a material and the oxygen or hydrogen atoms in the air are always present and cannot be prevented.

Climatic stresses

Climatic stresses refer to the interaction of temperature and humidity. Here, it is important to bear in mind that humidity is a function of temperature. At higher temperatures, more water can be absorbed into the mixture of gases that form the air.



Climatic stresses

Relative humidity is the ratio of the partial pressure of water vapor to the equilibrium vapor pressure of water at a given temperature. For example, if the temperature falls and no water condenses, the relative humidity increases.

This interaction between temperature and humidity must be taken into consideration for the aging of materials. Like temperature, humidity is an accelerating factor in chemical reactions. Humidity thus accelerates the aging of a material just as temperature does.

Types of aging

Corrosive stresses and chemical aging

Corrosion always takes place on the surface and can only occur in the presence of a chemical reactant. However, the chemical reaction that leads to corrosion cannot occur unless sufficient activation energy is present.

With corrosive stresses, as with all corrosion, more and more surface area is altered over the course of the reaction. If the process of corrosion were to be graphed as a function, the progression of corrosion would closely resemble that of a logarithmic function.

Mechanical stresses

Another type of stress that causes aging is mechanical stress, which describes the number of flexing cycles a material can tolerate. Depending on the bending radius or the tension a material is under, the number of flexing cycles may vary greatly.

One of the effects of mechanical stress is material creep, the “plastic deformation over time of a material under stress”². The effects of mechanical stress do not depend solely on the type of material, however; they also vary greatly depending on composition.

Electrical stresses

Electrical stresses only occur in electrically operated components. The aging of this type of components depends on the electric field, voltage and the duration of exposure.

UV aging

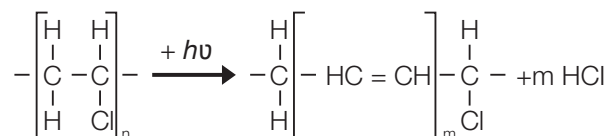
UV aging involves effects which are predominantly caused by solar radiation and, less frequently, by artificially produced UV light. In polymers the sun can cause surface discoloration, for example, or even induce aging at the molecular level.

Where aging is the result of solar radiation, any one of several reactions may occur. These are divided into three reaction types: photolysis, photooxidation and photocatalysis.

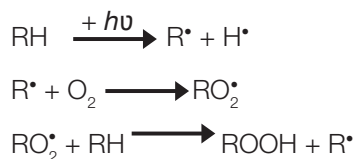
² Rösler, Joachim, Harald Harders, and Martin Bäker. *Mechanisches Verhalten von Werkstoffen [Mechanical Properties of Materials]*. Wiesbaden: B.G. Teubner Verlag, 2006

Types of aging

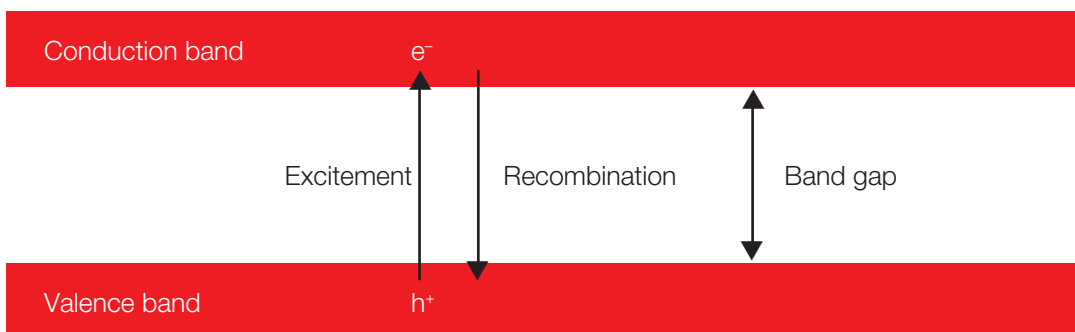
In photolysis, a photon is absorbed and this energy triggers a chemical reaction that is not dependent on oxygen.



By contrast, both oxygen from the air and photon energy are required to induce the aging process in photooxidation.



Photocatalysis, on the other hand, can only take place if semiconductor properties are present in the surface of the material. Photon energy caused by solar radiation forms radicals, thereby enabling the oxidation of the material.



Artificial aging

What is artificial aging?

Artificial aging is the process of artificially producing stresses in the attempt to replicate the aging process of a material. This process can involve the use of environmental simulation chambers, weathering testing facilities or vibration testing systems.

Artificial aging is generally used in the development of new products or for research work. It is particularly important during development to observe and document changes in material properties. Of course, it is essential that all results be reproducible. This allows engineers to study the failure probability of a material. The term „failure“ includes the discoloration or yellowing of components, such as those found in the interior of a car, as a result of solar radiation.

Due to the wide range of different materials that need to be subjected to artificial aging, a number of different standards and guidelines have been created in recent years. These standards and guidelines regulate the parameters and testing equipment used in order to ensure reproducible results. In the field of electrical insulation materials, the IEC 60216, ASTM D5423 and ASTM D5374 standards represent the important testing norms for thermal stresses. In accordance with the specifications of the aforementioned standards, the tests to determine the long-term thermal properties of materials are carried out in special laboratory heating chambers such as the BINDER FP 115-S.

Artificial aging

Accelerated aging

Accelerated aging is becoming increasingly important thanks to the fact that it delivers test results faster, which saves both time and money. The basic concept behind accelerated aging is that material properties change more rapidly over time when several methods are applied, including eliminating rest periods, disregarding less stressed sections and raising the stress level. Adhesive bonds that are used on a daily basis, for instance, are subjected to accelerated aging. The chips in credit cards are a familiar example of this. These chips are attached with an adhesive that needs to be durable under a wide range of climatic and mechanical stresses. This includes not only storage at high temperatures but also climate change testing of the adhesive bonds. Environmental simulation chambers, such as those available in the BINDER product lines, are used for these tests.

The problem with artificial aging is that, during testing, it is possible for other components to fail which might not do so during actual use. The reason for this is the level of activation energy required for the chemical reaction. In thermally accelerated aging, the acceleration is achieved by increasing the temperature. This process introduces sufficient activation energy for reactions that are not relevant under actual use conditions. It is therefore critical that the testing process be verified, as is the case for weathering, for example. The testing process in a weathering testing facility is often checked against the results of natural weathering. A group of test specimens is simultaneously exposed to various outdoor stresses and then compared with the test specimens from the weathering testing facility. The areas chosen for exposure to the elements might be the roof of the laboratory or office building.

Despite these advances, the pressure to accelerate tests and procedures even further continues to mount in the face of the drive to obtain faster results. At the same time, stress levels are also being increased, primarily in order to save time when performing aging trials – and to thus save money in the development process.

Artificial aging

Assessment and evaluation

After the stress tests have been performed, they must be evaluated. Before the evaluation can be carried out, it must be possible to measure the aging of the material.

One possible option for this is to observe the failure probability based on multiple test samples. The decisive factor here is the time that elapses before a specified number of test samples fail. Another possibility is to observe changes in properties over a defined period of time. Here, it is important to keep in mind that the various properties of the material may be altered at different rates.

The subsequent assessment and evaluation provide an indication as to whether a component or material is at all suitable for its intended use. In some cases, it may be necessary to select a new material composition or a different component, and thus to run the tests again. This results in additional development time and costs. However, these costs are manageable when compared to the costs that could potentially be incurred if these added steps are not taken.

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| Company profile

BINDER is the world's largest specialist in simulation chambers for the scientific and industrial laboratory. With its technical solutions, the company contributes significantly to improving the health and safety of people. Our range of products is well-suited for routine applications, highly specialized work in research and development, production and quality assurance. With approx. 400 employees worldwide and an export quota of 80 %, BINDER 2014 sales were more than 60 million euros.

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