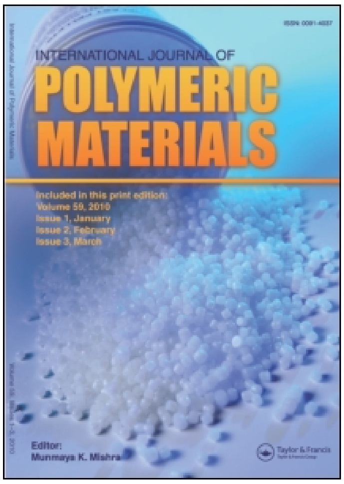

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Definition of Terms and Classification of Processes Relating to Aging Polymers

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Definition of Terms and Classification of Processes Relating to Aging Polymers

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The research team of the Institute of Chemical Physics at the Russian Academy of Sciences that has been involved in the investigation of aging of polymers for many years developed a list of terms and definitions associated with the aging process.

Keywords: Aging of polymers; property changes; physical and chemical transformations; characterizations and predictions; definitions

0. INTRODUCTION

During treatment, processing, storage and use, the polymeric materials are exposed to numerous factors causing or promoting various chemical and physical changes that affect their properties. Since such changes develop in time and usually result in deterioration of properties, the term "aging" appears to be appropriate to characterize the processes involved.

The term aging is applied broadly to processes that are spontaneous and result in deterioration of the properties of material.

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It should be noted that there are certain physical and chemical conversions that improve the properties of polymeric materials. However, such processes are normally carried out with a deliberate purpose and should not be included under the term "aging". In biology aging is understood as a sequence of irreversible transformations. With polymers, however, such a definition may not always be valid. Consider for example the conditions under which the transformations may be reversed and some of the properties restored, as is the case with the removal of chemisorbed moisture at high temperature. [1 – 11].

Aging of a polymeric material is a series of physical and chemical processes in a polymer material bring about a spontaneous variation of its composition and structure. The following definitions are used to describe the processes and changes in polymeric materials aging.

1. AGING OBJECTS

Aging object refers to polymers, polymer materials and items manufactured from them as well as to high- and low-molecular compounds used in the manufacture of polymeric materials and items.

• Polymers are high-molecular compounds whose molecules consist of a large number of identical units held together by chemical bonds.

Polymers consisting of molecules having a high molecular mass retain their individuality in various phase transitions and dissolution. This distinguishes polymers from molecular and ionic crystals which also consist of recurrent atomic groups.

• Oligomers are the members of the homological series occupying the place between monomers and polymers as regards the size of molecules.

Prepolymers are oligomers or polymers containing reactive groups and used for the production of polymeric materials.

Polymeric materials are compositions containing a polymer as one of its basic components and prepared by a specified process.

The process for preparing a polymeric material must be specified with sufficient information to enable its unambiguous reproduction. Apart from the polymer as one of the basic components, a polymer composition may include various other ingredients, e.g.:

special-purpose additives to impart desired properties to the material: fillers, pigments, plasticizers, stabilizers, etc.

- Material may also contain undesirable impurities, e.g.:
- residues of catalyst, monomer, etc.

Polymer materials may be classified according to composition, morphology and use.

Secondary polymeric material a material produced by processing of used materials or items or industrial waste.

Polymer items are polymer materials given the desired shape and capable of performing the desired function.

It must be noted that polymer items are not always produced directly from polymeric materials; many polymer items are made first from monomers, oligomers or prepolymers, with the polymer being formed directly in the manufacturing process.

2. POLYMER MATERIAL PROPERTIES

Aging affects the properties of polymeric materials.

Properties are qualitative and quantitative characteristics of the material.

Properties of materials are assessed in terms of property indices, and the aging process may be controlled by monitoring the variation of some property index.

Property index is a parameter characterizing qualitatively or quantitatively the polymer material property in question.

Characteristic index is a parameter which most adequately characterizes the applicability of the aging object for some particular use.

Polymer material properties and the corresponding property indices are listed in Appendix I.

3. AGING FACTORS AND CONDITIONS

Aging of polymeric materials takes place under conditions determined by various factors which may roughly be divided into internal and external ones.

External aging factors are the environmental factors causing aging of polymeric material.

APPENDIX I Properties an property indeces of polymeric materials

No. *1*	*Property* *2*	*Property Index* *3*
	Molecular mass, molecular mass distribution	number average molecular mass $\overline{M}_n$ weight average molecular mass, $\overline{M}_w$ average molecular mass, $\overline{M}_z$ visocosity average molecular mass, $\overline{M}_\eta$
I.	Thermophysical Properties	
1.	Dimensional characteristics:	
	a) volume and density	V [M^3] and ρ (kg/m^3)
	b) thermal expansion	Volumetric coefficient of thermal expansion, α [K^{-1}] Linear coefficient of thermal expansion, β [K^{-1}]
	c) expansion in fusion	Increase of molar volume in fusion, ΔV_m
2.	Calorimetric Characteristics	
	a) heat capacity	Specific heat capacity at constant volume c_v(J/kg K) Specific heat capacity at constant pressure, c_p(J/kg K) Molar heat capacity at constant volume, C_v(J/kg K) Molar heat capacity at constant pressure, C_p(J/kg K)
	b) heat of fusion (crystallization)	ΔH_m (J/mol)
	c) enthalpy and entropy	ΔH (J/mol), ΔS (J/mol K)
	d) heat resistance	T (K)
	e) thermal stability	T (K)
3.	Cohesion and Adhesion Characteristics	
	a) molar energy of cohesion	E_{coh} (J/mol)
	b) internal pressure	π (Pa)
	c) surface energy	E_s (J/mol)
	d) Adhesion between polymers	Reversible work of adhesion, W_{adh} (N/m^2)
4.	Transition Temperatures	
	a) glass transition temperature	T_g(K)
	b) melting point	T_m(K)
5.	(Thermodynamical and Kinetic) Flexibility of Macromolecules	
6.	Solubility	
	a) solubility parameter	δ ($J^{1/2}$/m$^{3/2}$)
	b) solubility limit critical mixing temperature	Flory point T (K)
II.	Polymer Properties in Force Fields	
1.	Mechanical (viscoelastic) Properties	
	a) elastic properties	Bulk modulus K (N/m^2) Shear modulus (stiffness) G (N/m^2) Young's modulus E (N/m^2) Poisson's ratio (ν)

APPENDIX I (Continued)

No. *1*	*Property* *2*	*Property Index* *3*
	b) viscoelasticity of resins	Young's modulus E (N/m^2)
	c) viscoelasticity	Elasticity and viscosity modulus
	d) dynamic mechanical parameters	Mechanical loss tangent, tgδ
	e) stress relaxation and creep	Complex modulus of elasticity E^*. Relaxation time spectra.
2.	Ultimate Mechanical Characteristics	
	a) stress-strain curves of solid polymers	Elasticity modulus E (N/m^2) Yield strength σ_y(Pa) Breaking stress, σ_b(Pa) Ultimate elongation ε, %
	b) fatigue strength (breaking stress)	f.s. (Pa)
	c) durability	Number of loading cycles to rupture under given mechanical stress, N
	d) impact strength (resistance to instantaneous impacts) Izod, Charpy, Distant tests, under tension	I(J/m^2)
3.	Long-Term Mechanical Characteristics	
	a) durability	τ (sec)
	b) deformation at rupture	ε, %
4.	Other Fracture Characteristics	
	a) hardness (Brinell, Vickers, Rockwell, Shore)	H_B(kg/mm)
	b) resistance to scratching (wear)	Wear resistance (mg/1000 cm^3)
	c) friction (internal, surface)	Friction coefficient μ
5.	Optical Properties	
	a) light absorption	Absorption coefficient ε (lm/mol cm) Light, transmittance T, %
	b) light refraction	Refractive index n; Molar refraction R
	c) dissipation	Haze, turbidity
	d) reflection	Refractive index, n
6.	Electric Properties	
	a) dielectric polarization	Dielectric constant ε Molar polarization of dielectric ε_n Dipole moment μ; loss tangent of dielectric, tg δ
	b) static charge accumulation and electric conductivity	Bulk conductivity γ (1/Ohm m^{-1}) Bulk resistivity Ω (Ohm/m)
	c) ultimate electric characteristics	Dielectric strength (kV/mm) (break-down voltage) Electric arc resistance
7.	Magnetic Properties	
	a) magnetic susceptibility	æ
	b) magnetic resonance (ESR, NMR)	
III.	Transfer phenomena in Polymers	
1.	Heat energy transfer	Heat conductivity (J/cm m K)

APPENDIX I (Continued)

No. 1	*Property* 2	*Property Index* 3
2.	Polymer solution viscosity	Ultimate viscosity number (intrinsic viscosity, Staudinger index) (cm^3/g)
3.	Polymer melt viscosity	
4.	Melt elasticity	
5.	Polymer dissolution and melting	
6.	Permeability of polymers. Gas, vapor and liquid transfer by diffusion in polymers	Solubility of gases and vapors in polymers, $S(cm^3/cm^3 Pa)$ Permeability for gases and vapors, $P(m^3 m^2/m^3 \, Pa \, sec)$.
	Diffusion of simple gases, vapors and liquids	Diffusion coefficient, $D(m^2/sec)$.

External factors include heat, light, ionizing radiation, physically or chemically active media, living organisms and their metabolism products, various mechanical loads, electric, electromagnetic, ultrasonic fields, etc.

In the course of aging, a material is often subject to the combined effect of many external factors, e.g., heat and light, radiation and oxygen attack.

Internal aging factors are factors related to the structure, composition, manufacturing process and other internal conditions promoting and/or otherwise influencing the aging of polymeric material.

Internal factors may include the presence of residues of catalyst and initiating agent, internal stresses in the material, cracks, weak bonds in macromolecules, reactive groups in macromolecules, etc.

Internal factors, reflect, to a certain extent, the properties of polymer material determined by its pre-history. Besides, such internal factors as cracks, local stresses, etc., may arise in material during the aging process itself through actions of external factors.

Depending on the processes involved, aging factors may be divided into physical, chemical and biological ones.

Aging conditions are the factors acting on the material during processing, working, storage and use.

Service is the sum of the preparation and use of polymeric material for an intended function.

There has been an earlier definition of the term "service of item": according to GOST 21964–76, "the service of an item is the sum of the production and use of the item for an intended purpose, maintenance, storage, transportation as well as all forms of repair carried out by the user". Here, the term signifies the lifetime of an item from the moment of manufacture to the end of service. According to this Standard, storage and transportation of items are just special cases of their use. What distinguishes the use of a material from the use of an item is that after the item as a whole can no longer perform its function (fails), its parts may still be usable and may be re-processed for re-utilization.

Processing means a series of steps needed to convert a polymeric material into an item or one item into another.

Storage is the keeping of a polymeric material under conditions known to prevent deterioration of its properties.

4. PROCESSES INVOLVED IN AGING

The processes occurring during aging are of chemical, physical and physico-chemical nature.

Chemical transformations involve alteration of the chemical structure of polymer or other non-polymeric components of a polymer composition.

The chemical processes which accompany aging of a polymeric material usually comprise three major stages:

- initiation (formation of active sites);
- development stage;
- decay of active sites.

Active sites are chemically active particles such as free radicals, excited particles, active atoms and molecules.

At the development stage the dominant processes are degradation, cross-linking, polymer-analog reactions of macro-molecules.

Degradation is the process leading to breaking of chemical bonds in the main macromolecular chain which results in reduction of the degree of polymerization of the plastic.

The composite process of degradation may include the following sub-processes.

- decomposition the breaking of chemical bonds of the main macromolecular chain.

- depolymerization separation of the terminal monomer molecules from the macromolecule.
- cross-linking formation of chemical bonds between neighbor macromolecules.
- polymer-analogous reactions the transformation of a group of atoms in a macromolecule with the degree of polymerization remaining the same.

The physico-chemical processes include such processes that cause a change of the composition of polymeric material.

- Sorption is any process of absorption of a substance by a polymeric material
- Adsorption is surface sorption.
- Absorption is sorption in the bulk of material.
- Desorption is the process of liberation of the sorbed substance by polymeric material.

Diffusion is directional transfer of matter under the effect of a gradient of chemical potential due to the thermal motion of particles.

Diffusion processes play a very important role in the interaction of polymeric material with aggressive media, gaseous (O_2, O_3, SO_2, NO_2, etc.) and liquid (acids, bases, etc.). Diffusion is responsible for the migration of additives or impurities in a polymeric material; the examples are the sweating and washout of additives.

- Plasticization is an increase of elasticity or plasticity of a polymeric material during the processing stage achieved by addition of special agents (plasticizers).

Low-molecular aging products may also have a plasticizing effect.

Physical transformations involve changes in the physical structure of polymer materials. The most important of them are phase transitions, change of the physical state and submolecular structure.

Crystallization is the first-order phase transition resulting in spatial ordering of macromolecules in material.

Amorphization is the first-order phase transition resulting in spatial disordering of macromolecules in material.

Polymorphic transformation is the first-order phase transition of one crystalline form to another.

Glass transition is the transition of polymer to a glassy state (i.e. the state in which segmental motion of macromolecules is frozen).

Orientation is rearrangement of the structural elements of a polymeric material under effect of a directed internal or external stress causing the macromolecular axes to assume predominantly the directions along the reference axes.

Relaxation processes are also a class of physical transformations.

Relaxation processes are the changes of properties of polymeric material in the course of physical transition from a nonequilibrium to equilibrium state.

Submolecular structural changes are variations of the physical structure of polymeric material characterized by various forms of mutual ordering of its macromolecules.

The basic submolecular structural elements are globules, fibrils, spherolites and crystallites.

Physical and chemical transformations bring about changes in the physical and chemical structure of polymeric material which manifest themselves macroscopically in:

Crazing the violation of material continuity either on the surface or in the bulk.

•Fatigue a change of polymeric material properties under effect of multiple cyclic loading.

•Creep is the time-dependent increase of a strain of a polymeric material under effect of a constant mechanical stress.

•Fracture is the loss of integrity of material under the effect of mechanical stresses.

5. BASIC TYPES OF AGING

Aging processes may be classified according to the major aging factor.

Thermal aging is the aging of a polymeric material under the effect of heat and in the absence of effects from other factors.

Light (photo) -aging the aging of polymeric materials under the effect of UV or visible light.

Chemical aging the aging of polymeric material under the attack of chemically active agents.

Since aging in oxygen and ozone are very common types of aging, they are defined as independent entries.

• Oxidative aging (or thermooxidative aging) the aging of polymeric material under oxygen attack.

• Ozone aging the aging of polymeric material under ozone attack.

Radiation aging the aging of polymeric material under the attack of an ionizing radiation.

Biological aging is aging of polymeric material under the effect of living organisms and products of their metabolism.

• Electric aging is aging of polymeric material in an electric field.

• Ultrasonic aging is aging of polymeric material in an ultrasonic field.

Ablation is aging of polymeric material in a hot stream of gas and solid particles.

Aging under mechanical loading is aging of polymeric material under effect of static and/or dynamic mechanical loads.

In practice, aging is normally stimulated by a set of factors, e.g., light plus heat, heat plus oxygen, etc.

Aging processes may, besides, be classified according to the environmental conditions.

Artificial weathering is aging of polymeric material under conditions created artificially to imitate the natural conditions or accelerate the aging process.

Natural weathering is aging of polymeric material under the effect of the complex of natural environmental factors.

Natural weathering is divided into several distinct types, viz. aging on an open platform, shalf aging, aging in a heated or unheated room, etc.

Aging in the cosmos is aging of polymeric material in the outer space.

Aging in the living body is aging of polymeric material incorporated in the tissues (organs) of the living body.

Such terms as "aging in the ground" and "aging in an aqueous medium" are also used at times.

6. METHODOLOGY OF AGING CONTROL

Some of the properties of polymeric materials are fundamental. This includes the chemical composition, molecular mass distribution of each component, the physical structure of material, etc. Other properties are secondary.

In scientific and industrial research certain particular properties of polymeric materials may attract special interest depending on the object of research. The investigators use the time histories of these parameters as indicators of the aging process.

To distinguish aging from eventual alterations of a property due to changed external conditions (temperature, humidity, etc.), the variations of a relevant property index are measured under fixed conditions as function of time.

7. CRITERIA OF RESISTANCE OF AGING

Aging resistance (stability) is the ability of a polymeric material to retain its properties within specified ranges under specified aging conditions.

The polymer may be resistant to some particular aging factor. For instance, the light resistance (stability) of a polymer material is determined by its ability to retain properties under the effect of light; chemical resistance (stability) is the resistance of a polymer material to the attack of chemically active agents, etc.

Keeping quality is the property of a polymeric material (item) to remain serviceable during and after storage.

Shelf life is the time for which a material (item) may be stored under specified conditions until its serviceability is impaired.

Serviceability is the state of a polymeric item in which it is usable for a given function and its performance characteristics are within the specified ranges.

Service life or life-time is the time during which a polymeric item is able to perform its function until it becomes unserviceable.

The lifetime of a material of which an item is made may be longer than that of the item itself, since item may fail because some other component may have failed. Therefore, the lifetime of a material used in an item is usually calculated theoretically rather than experimentally determined.

Guaranteed life-time is the time over which item performance within the specified limits is guaranteed by the manufacturer.

As a rule the guaranteed life differs from the service lifetime.

Reliability is the property of a polymer item to remain serviceable throughout a specified service lifetime.

Such characteristics as keeping quality, guaranteed life and reliability may be used as special criteria of material resistance to aging.

Quantitatively the material resistance to aging is represented by the aging factor or service lifetime.

Aging factor is the relative variation of a property index at a given moment of time during the aging process.

Aging factor is usually defined either as y/y_0 or as $(y - y)/(y_0 - y)$, where y_0, y and y are the initial, current and final values of the property index.

Aging function is a mathematical representation of the aging kinetics of a polymeric material (item) based on some aging model or experimental data.

The aging function of a material is obtained through generalization of the available data about the material. With its help one may predict variation of the properties of material under any conditions. The question of reliability of such predictions may be answered by carrying out the statistical analysis of the experimental data from which the aging function was derived.

Aging kinetics the time-dependent variations of material property under specified conditions.

Aging model is a hypothetical mechanism or a procedure for an empirical description of the kinetics of aging of a polymeric material (item).

8. PREDICTIONS

The properties of a polymeric material (item) in storage or service may be forecast and predicted.

Forecast is a scientifically-substantiated conclusion about the expected polymer material (item) properties after a specified period of use or storage.

Prediction is a description of the possible changes of the polymer material (item) properties on the basis of the expertise.

The expected service lifetime and property variations are the characteristics which have to be forecast more often than other characteristics.

The service lifetime forecast-is the determination of the service lifetime of a polymeric item from the results of preliminary tests.

The property variation forecast is the determination of the variation in time of a property index under specified service conditions from the results of preliminary tests.

Accelerated tests are most often used for such preliminary testing.

9. TESTS

Tests are operations carried out for the purpose of determining the property indices of a polymeric material (or item).

Tests may have to be used to determine the time-dependent variations (time histories) of the properties of material either under natural or artificial conditions. Tests may have the object of either determining the aging kinetics of a polymeric material or determining its stability under specified conditions.

Tests specimen (sample) is an object of given dimensions and shape made from a polymeric material specifically for testing purposes.

Accelerated test is the test carried out under conditions and by a method specifically designed to obtain the required data about the aging process.

Test program is the list or sequence of investigatory operations required to achieve the object of the test.

10. AGING PROTECTION

Polymer materials can be protected from the detrimental effects of aging in various ways. The one used most widely is by incorporation of agents which inhibit polymer aging processes. Less common forms of protection are chemical or structural modifications.

Stabilization of polymer materials – improvement of the resistance of a polymeric material to aging.

Stabilizers – are the agents incorporated in the polymer composition to improve its aging resistance.

Stabilizer effectiveness – a value characterizing the stabilizer's ability to improve the aging resistance of a polymeric material.

Stabilizing compositions – mixtures of compounds incorporated in polymer compositions to improve their aging resistance.

Synergism – the combined stabilizing effect of a mixture of compounds which is greater than or at least equal to the effectiveness of the most active component of the mixture taken in a concentration equal to the mixture concentration.

Antagonism – is the weakening or loss of the protective effect inherent in a given stabilizer or stabilizing composition as a result of addition of one or more compounds.

Inhibitors – agents incorporated in a polymer composition to retard the aging process.

Stabilizers are classified according to the basic aging factor.

Thermostabilizers – the stabilizing agents which improve polymer stability to heat.

Depending on the intended function, thermostabilizers are divided into free radical acceptors and aging product acceptor (acceptors of products catalyzing one of the aging process stages).

Free radical acceptor – stabilizer which combines with free radicals to form stable products, complexes or radicals.

Aging product acceptor – stabilizer deactivating the catalytically active aging products.

Light stabilizer – stabilizer which improves polymer resistance to.

There are two types of light stabilizers:

UV-absorber – uncolored light stabilizer having absorption in the UV region of the spectrum.

Quencher – light stabilizer protecting a polymeric material by physically or chemically quenching the excited electron states of the chromophor groups present in the polymer.

Antioxidants – stabilizers improving resistance of polymeric materials to attack of oxygen.

The broad class of antioxidants includes free radical acceptors, peroxide decomposers, metal deactivators.

Peroxide decomposer – antioxidant which decomposes peroxide without producing free radicals.

Metal deactivator – stabilizer suppressing the catalytic activity of metals and their compounds in processes of oxidation with molecular oxygen.

Antiozonant – stabilizer improving resistance of a polymeric material to ozone attack.

Fire retarding agent – stabilizer suppressing combustibility of polymeric materials.

Antirad – stabilizer improving polymer material resistance to an ionizing radiation.

Antifatigue agent – stabilizer improving resistance of polymeric material to repeated mechanical loading.

Structure forming agent – compounds capable of affecting the physical structure of a polymeric material.

Protective coatings – coats applied to polymer material surface to protect it from aging.

Sealant compositions – polymer-or oligomer-based compositions applied to surfaces of articles with the purpose of decreasing permeability with respect to different fluids.

Biocides – agents incorporated in a polymer material (article) to protect it from attack of living organisms.

Biocides include:

gicides – biocides protecting polymer materials (articles) from attack of microscopic fungi.

Lamicide – biocides protecting polymer materials (articles) from the attack of mollusca.

Algocides – biocides protecting polymer materials (articles) from the attack of seaweeds.

Bactericides – biocides protecting polymer materials (articles) from the attack of bacteria.

Properties and property indeces used in characterization of aging processes in polymeric materials are presented in Appendix I.

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