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Mini-Review Article

Characterization of polymeric materials and their degradation products

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ABSTRACT

Everybody experienced the spatial smell of a new car, or when ride a car which was exposed for a long time to the sunshine. What causes it and is new-car smell bad for our health? Most of the interior of an automobile consists of polymers and plastics held together with a number of polymeric adhesives and sealers. As a result of degradation/oxidation, polymers release volatile organic compounds which cause the smell. In this article, we will describe how degradation of polymers happens, how it effects on their performance and how polymeric materials can be characterized before and after degradation.

Keywords: Polymeric materials; Characterization; Degradation; Aging

What types of degradation are known for polymers?

Polymers represent one of the largest single classes of materials in commercial production at the present time. Their degradation under external environments is a subject of both practical and theoretical importance and has been studied extensively during the past few decades. The relatively rapid deterioration of such materials when exposed to the outdoors seems to be related in nearly all cases to chain scission caused by photooxidation reactions induced by the UV light of the sun. Therefore, the inhibition of degradation or the control of the lifetime of these materials is a subject of considerable importance. The performance of polymeric materials and the science of polymer degradation and materials reliability are of ever increasing importance for sustainable global economic development. Many of the challenges we face, require better performing, cheaper and more specialized polymers ranging from composites and thermosets to thermoplastics and elastomers, and increasingly originating from biomass rather than fossil resources. Polymer degradation is a change in the properties — tensile strength, color, shape, etc. — of a polymer or polymer-based product under the influence of one or more environmental factors such as heat, light or chemicals such as acids, alkalis and some salts. These changes are usually undesirable, such as cracking and chemical disintegration of products, or, more rarely desirable as in biodegradation, or deliberately lowering the molecular weight of a polymer for recycling. While degradation of a macromolecule started to happen, what changes are happen in its performance? What volatile products are released from them?

In the coating technology, polymeric coatings are of very widespread use as coatings or paint made with polymers that provide superior adherence and protection from corrosion. Polymeric coatings are used for a variety of purposes, e.g., decorative, protective, and functional (as dielectrics or insulators). A special application of polymeric coatings is their use as lithographic materials for making integrated circuit elements. Examples of polymeric coatings include: natural and synthetic rubber, urethane, polyvinyl chloride, acrylic, epoxy, silicone, phenolic resins and nitrocellulose. Irrespective of the intended purpose of the coating, it must adequately be resistant to photooxidation and thermooxidation which are two major degradation processes of them in the atmosphere. So the need to understand the change in structure and characterization of these materials is quite obvious. In the last 20 years, there have been new theoretical developments and advancements in instrumentation which have helped greatly in the arena of polymeric coatings' characterization. Some recently developed microextraction techniques are

also of great help to extract and determine trace concentration of released molecules during polymers' aging. This article provides an overview of polymer characterization test methods. The methods and instrumentation described here are classified in these categories: microscopy, chromatography, spectroscopy, thermal analysis and rheometry. We will also talk about the volatiles which are released during polymer degradation, using new microextraction techniques, especially solid phase microextraction.

Polymers for coating

Today, there are primarily seven commodity polymers in use: polyethylene, polypropylene, polyvinyl chloride, polyethylene terephthalate, polystyrene, polycarbonate, and poly(methyl methacrylate) (Plexiglas®). These make up nearly 98% of all polymers and plastics encountered in daily life [1]. Polymers are vital part of coatings and paints, as well as adhesives and foams. Paints are applied not just for aesthetic reasons but also to protect the surface under them from rusting and against microorganism. They are normally filled with pigment, which lowers their strength, even with absorbing more sunlight. Adhesives are also a kind of polymers made for binding surfaces. Foams are polymers with a lot of pores inside normally used as insulators and for packaging. Polymers can also be classified as thermoplastic and thermoset, terms which describe their behavior on heating. Thermoplastics (such as nylon and polyethylene terephthalate, PET) can be heated repeatedly with little change in properties, while thermosets will cross-link on heating. Cross-linking binds all the chain molecules together by covalent bonds, so that the shape of the material is permanent when the reaction has occurred. Thermoplastic polymers comprise the majority of synthetic polymers. Although number of thermosets are small, but they are an important class of polymers for adhesives (such as epoxies) and composite materials, where they are used as the matrix to bind reinforcing fibers together (epoxies and polyesters for example). Each of these polymers has its own characteristic modes of degradation and resistivity to heat, light and chemicals. The properties of all materials, including synthetic polymers, are dominated by the type of bonding between the atoms and molecules. These properties are determined not by their strongest bonds (the covalent bonds in the chains), but by their weakest van der Waals bonds between the chains. This is basically why they generally exhibit low melting and other thermal transitions compared with ceramics and glasses. Mechanism of degradation of polymers is dependent on their structure and chemical bonds as

well. For example, polyethylene usually degrades by random scission of its chemical bonds and degrades to molecules of different molecular weight and sizes, while polymethylstyrene bands are breaking from specific positions. Even in case of some polymers such as PVC, benzene rings can be formed during thermal degradation [2].

Ageing of polymers

Polymers were originally introduced into commercial use as bulk structural materials primarily because they were inexpensive and easy to form compared with existing alternatives such as metal and wood. They were, however, subject to deterioration due to a variety of environmental factors, including light, mechanical stress, temperature, pollutants, and others. Mechanical tensions are major reason for degradation: a typical car tire comprises of natural rubber blended together with several other polymeric materials. The tread has to grip the road, so energy absorption is important in maintaining a high coefficient of friction. Here we only focus on chemical degradation of the polymers coated on the surfaces, i.e. during degradation, a chemical change happens in the polymer. Because most of the polymers are made up of carbon and hydrogen in a reduced state, and because oxygen is abundant, polymers are highly susceptible to degrading oxidation reactions.

Generally chemical degradation of the macromolecules is due to:

1) Chemical reactions: as soon as a polymeric layer is coated on any surface it is exposed to the chemical attacks. From the lower part by the binder or the surface and from the upper surface by the atmosphere gases mainly oxygen, ozone and moisture (oxidation reaction and hydrolysis).

Oxygen (O_2) in the air is the most active ingredient which degrade polymers (and metals as well) by oxidation. Oxidation in general must always be an expected agent of attack, because oxidizing agents are universally present always. There are two routes of start of oxidation: by the addition of radicals to double bonds (only in unsaturated substrates) and by the abstraction of hydrogen, in any polymer. There are two main types of oxidation here: photooxidation and thermal oxidation which about them we will give more details soon. We should not forget that several other gases in the atmosphere can also makes changes on polymers. Ozone (O_3) makes up only 0.6 ppm of the atmosphere, but it is more powerful oxidant than O_2 and it is toxic. It degrades rubbers very quickly. Acid and alkali work against step-growth polymers by hydrolysis. The

chain is broken down by cleavage at the functional group linking the chains together. For example, whenever in nylon is the amide (-CO-NH-) groups became attacked, the molecular weight of it drops rapidly, and once the entanglement threshold is reached, the material breakdown to pieces. Chlorine (Cl₂) and bleaches (sodium hypochlorite) are two common cleaning agents which are also quite corrosive to many polymers.

2) Radiation: A common cause of failure of polymeric materials happens when they are exposed to the UV light of the sun. In fact, the most important mechanisms causing weathering of polymers are photolysis and photo-oxidation that are two names for UV-degradation. Photo-oxidation is the effect when oxidation is facilitated by radiant energy such as UV or artificial light, while photolysis happens when a polymer is attacked directly by radiation which breaks its bonds. If a polymer (such as all other materials) wants to absorb any part of electromagnetic radiation, it should have chromophores which are "light" absorbing functional group in the molecule. Since most of the polymers are clear in the visible region of electromagnetic radiation, how sunlight can degrade them? That's mainly due to the fact that despite the absorption of majority of UV light by ozone layer, still there are enough UV light which can be absorbed by them and initiate a radical chain reaction. Even some polymers (such as polyolefins) which has no chromophore in the UV and visible region of electromagnetic waves, can be photolysed due to some double bands (mainly C=O) which are created during their processing [3].

3) Thermal degradation: thermal degradation of polymers is molecular deterioration as a result of overheating. If this heating brings atmospheric molecules to react with the atoms of the polymer, the degradation process is called thermooxidation.

Polymer characterization

One of the first steps in characterization of any polymer is measurement of its molecular weight, since polymers are chain molecules; their mechanical strength is directly related to their molecular weight. Size exclusion chromatography is the method of choice for this purpose. Especially gel permeation chromatography (GPC) is unique to polymers, since it can give precisely the complete molecular weight distribution (MWD) of them. GPC separates molecules in solution by their "effective size in solution". To be ready for GPC analysis, first a polymer dissolved in a suitable organic solvent, then it is injected into a high performance liquid

chromatography (HPLC) column containing a cross-linked gel which acts like a molecular sieve, therefore molecules are separated according to their size, and since size has a direct relation to the MWD, one can see easily and quickly get the MWD profiles of the sample. Since all compounds refract light, the detector that is universally used to monitor fractions of MWD is a differential refractometer (RI).

In determining polymer properties, atoms consisting the chain and other functional groups are of most importance, because they determine many of the characteristic physico-chemical properties of a polymer. Fourier transform infra-red (FTIR) spectroscopy is the main technique for qualitative identification of various functionalities. Figure 1 shows the FTIR spectrum of a butyl sample. This sample contains butylated hydroxytoluene (BHT, an anti-oxidant), epoxidized soya bean oil (ESBO), stearic acid, and calcium stearate. The contents of all these components can be determined from this single spectrum.

Helpful information on chemical composition of a polymer also can be discovered by elemental analysis. While there are reports of using ion chromatography and ion selective electrodes for this purpose, still the most common form of elemental analysis is either inductively coupled plasma (ICP) or atomic absorption spectroscopy (AAS) which can determine metallic (or organometallic) elements and compounds of a sample. ICP excels at the rapid analysis of multi-elements in the samples. Both ICP and AAS have the ability to become fully automated. As an example, PVC polymer becomes unstable under the influence of heat and light, resulting in discoloration and embitterment. It has been established that by adding certain organotin derivatives this kind of degradation process can be prevented. These compounds cause serious environmental or toxicity problems. Trace of butyltin stabilizers could be determined in PVC using electrothermal atomic absorption spectrometry [7]. However, AAS and ICP are not suitable for halogens and light elements such as H, C, N, and O (Sulfur requires a vacuum monochromator) which are the main constituents of a polymer. They are also limited to the analysis of liquids only. For elemental analysis of these elements, a CHNS analyzer should be used that is accomplished by combustion analysis. CHNS stands for carbon/hydrogen/nitrogen/sulfur elements.

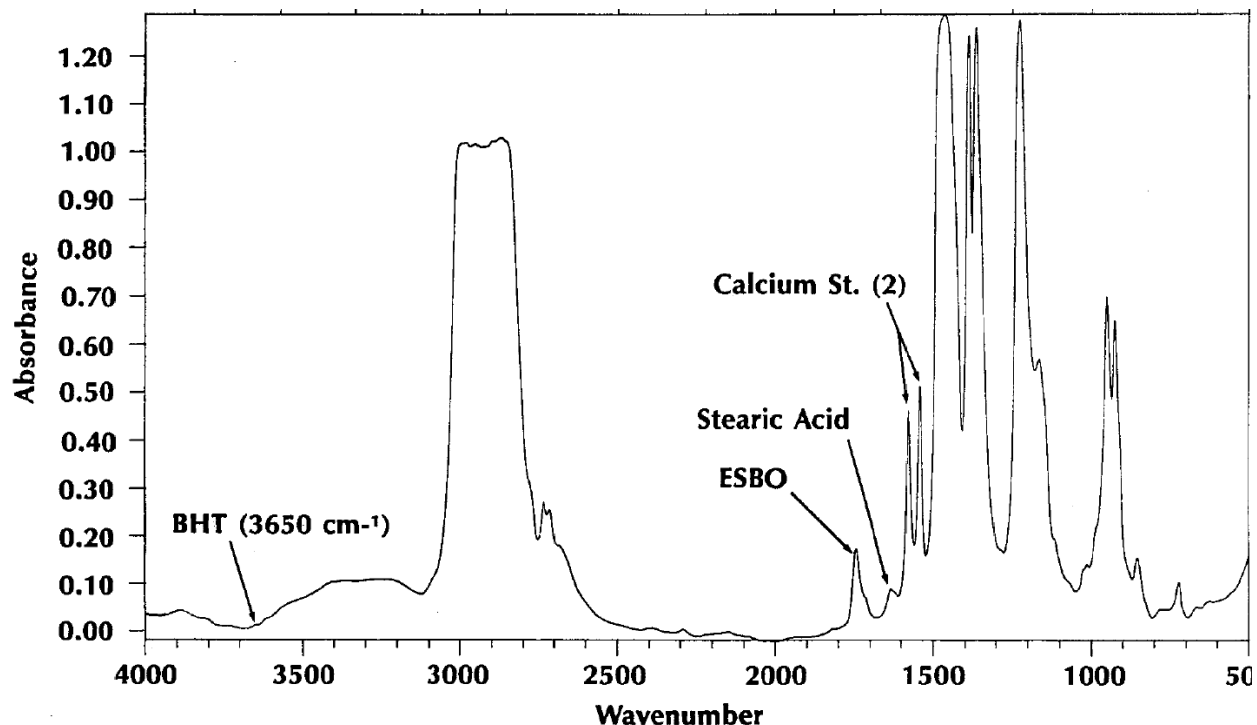


Figure 1. Example of an FTIR Spectrum for butyl rubber (from ref 6).

X-ray fluorescence spectrometry (XRF) is another simple to use method of elemental analysis which is non-destructive and rapid which requires minimal sample preparation. XRF is based on the principle that each element emits its own characteristic X-ray line spectrum. When an X-ray beam impinges on a target element, inner-shell electrons are ejected. The resulting vacancies are then filled by outer electrons which release energy in the form of X-ray radiation that is called X-ray fluorescence. Since every element has its own electronic configuration, its XRF is also unique which its intensity depends on the concentration of that element in the sample. In an energy dispersive spectrometer, the emitted XRF from the sample focuses directly on a solid state detector which is capable to assign X-ray energies to the elements inside of the sample, so multi-element analysis will be possible in a single run. Elements from atomic number 12 (magnesium) can be measured over a wide dynamic range by XRF.

Nuclear magnetic resonance (NMR) is another spectrometric technique which can be used for determining chemical structures of organic molecules, including polymers. The most common nuclei examined by NMR are ¹H and ¹³C, as these are the NMR sensitive nuclei of the most abundant elements in polymers. *cis:trans* isomer ratio of the polymeric chain and its double-bond

contents can be determined by ^1H NMR (Figure 2). This method avoids the calibration problems that is presented in the other techniques, thus, it should be highly reliable [8].

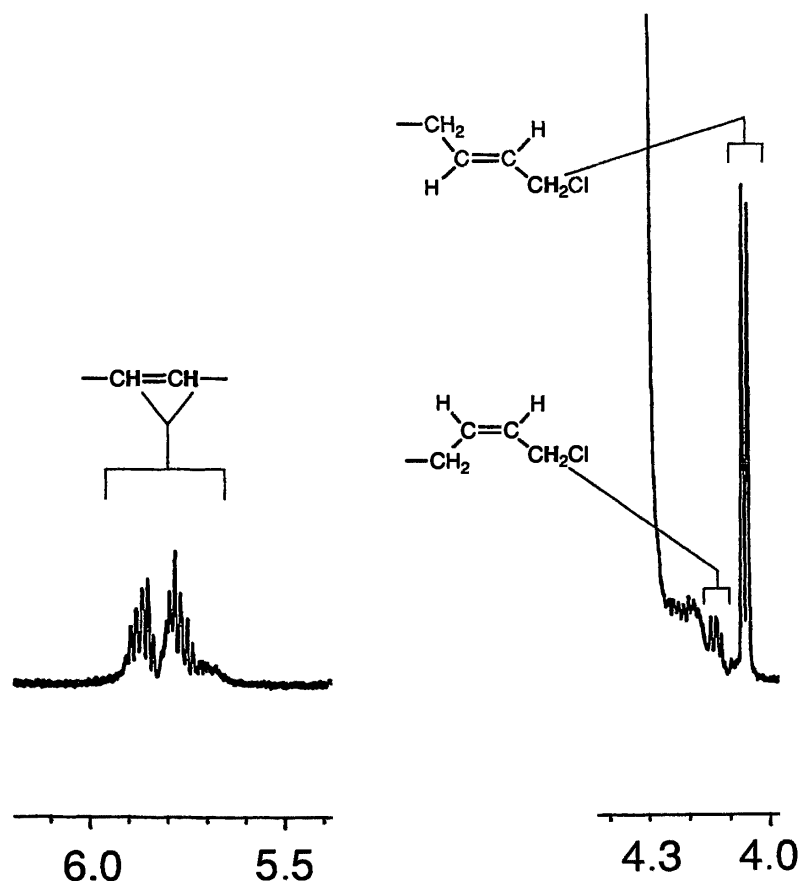


Figure 2. 500-MHz ^1H NMR spectra of a suspension PVC (from ref 8).

There are also other techniques of elemental analysis which are of less important such as neutron activation analysis, potentiometric titrations, ultra-violet/visible spectrophotometry and as mentioned, use of ion selective electrodes and ion chromatography.

Simple visual examination of a degraded polymer is obviously fast and cheap, but naked eye resolution is limited and subjective; therefore, higher magnification is needed using microscopy. Methods include stereo microscopy, reflected light microscopy and scanning electron microscopy (SEM). Light microscopy with a magnification power of up to $\times 1000$ is used to study the microstructure of opaque materials. For polymeric materials, thin sections can also be examined using polarized microscopy to get information on the structure, such as if it contains filler materials such as gypsum. Nowadays, digital microscopy (consists of a small CCD camera with an in-built light source) became more and more common, owing to its ease of use compared

with light microscopes. It does not need some optical elements such as eye-pieces, and can be directly connected to a computer to observe and save the images. Also, magnification of $\times 200$, is achievable.

Probably you have seen cracks in tires which are due to ozonation [9] (Figure 3a). Better visualizing is feasible using microscopes (Figure 3b). Scanning electron microscopy is widely used for examining polymers because there are a wide range of signals that result from the interaction of the electron beam with such solid materials (Figure 3c). The spatial resolution is usually less than a micron and can go down to a few nm. For doing SEM, the sample needs to be electrically conducting. This is a problem with polymers which are generally insulating. One of the alternative strategies is to use an environmental scanning electron microscope (ESEM), by that, samples can be examined without the need for a conductive coating to stop charging of the surfaces. One big advantage of scanning electron microscopy is that it can be combined with energy dispersive X-ray analysis (EDX) to obtain information on elemental distribution as well. However, SEM/ESEM images are black and white and sample preparation is time consuming.

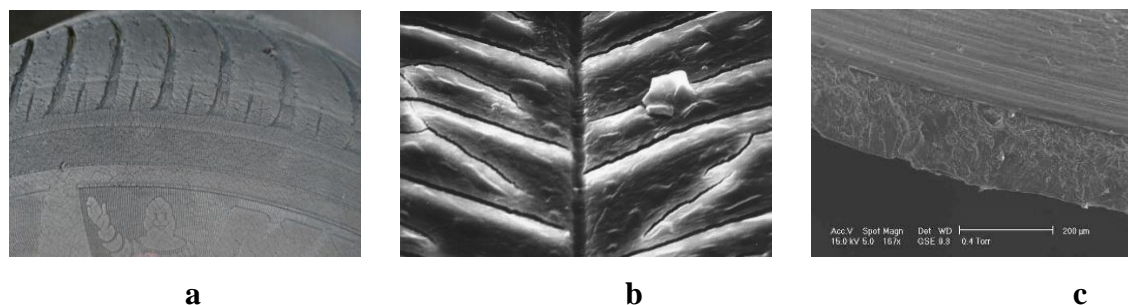


Figure 3. Cracks on tire (a), Polypropylene molded part (solvent induced stress cracking at seam.) $750\times$ (b), Close-up of ozone crack using ESEM (c)

Thermal analysis is one of the most important available devices for polymeric materials characterization. It is working on the basis of precision controlling applied temperature on the polymeric sample and measuring change in a material's property such as its mass or its enthalpy. The former technique is called thermo-gravimetric analysis (TGA) and the latter is differential scanning calorimetry (DSC). Only a few milligrams of polymer is needed. Thermal analysis curves are interpreted by relating the measured property versus temperature data to chemical and physical events occurring in the polymer. It is frequently a qualitative or comparative technique. In TGA, the mass loss can be due to such events as the volatilization of liquids and the

decomposition and evolution of gases from the polymer. In DSC the measured energy differential corresponds to the heat content (enthalpy) or the specific heat of the sample. TGA and DSC can give valuable information concerning a polymer composition and its response to temperature, including the glass transition temperature (T_g , the temperature when the plastic becomes elastomeric) and its decomposition temperature. While metals melt at a sharp temperature, polymers melt over a range of temperatures. A sample DSC thermogram can be seen in Figure 4 for various grades of polyethylene (PE) [10]. While it is possible to find the grade of PE by such curves, it will be possible to discover any impurities, even mixture of high density and low density PEs in the sample. For example, only a small amount of added ethylene units will lower the melting point.

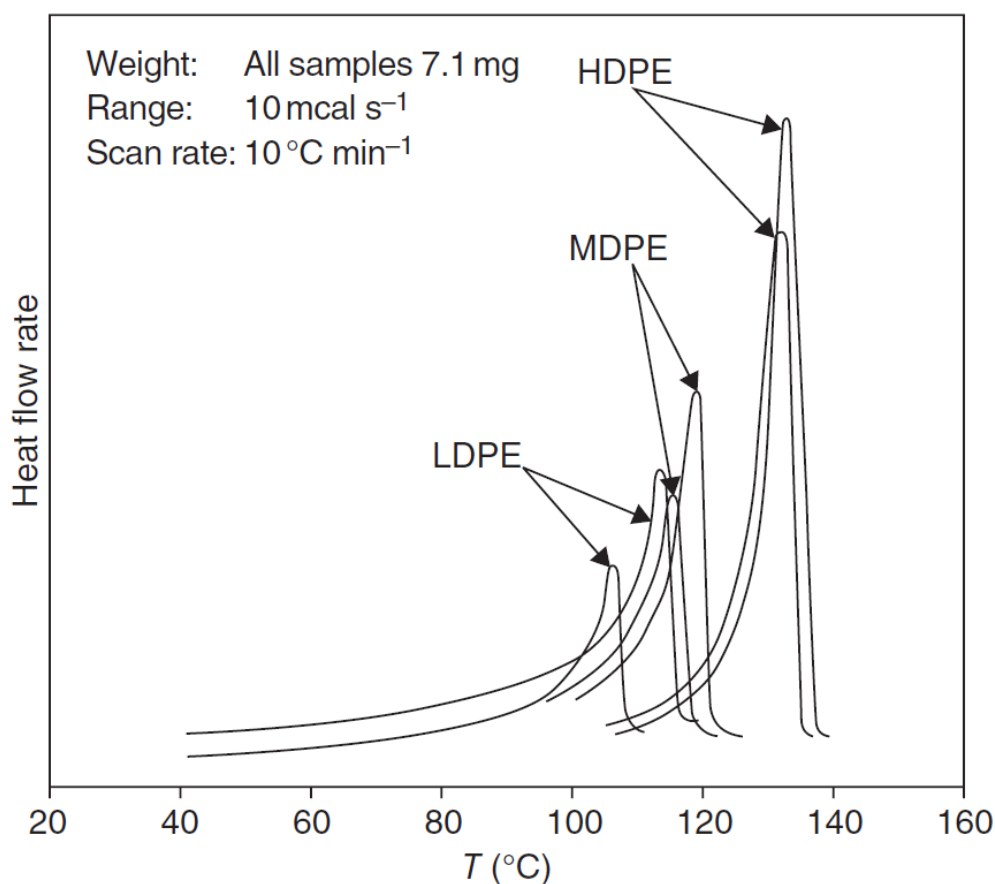


Figure 4. DSC of various polyethylenes (from ref 10)

Rheometry generically refers to the experimental techniques used to determine the rheological properties of materials that is the quantitative and qualitative relationships between deformations and stresses and their derivatives. A rheometer is a device used to measure rheological properties

in which a liquid, suspension or slurry flows in response to applied forces such as the viscosity, plasticizing rate, power and so on. For dynamic frequency sweeps (Figure 5), the polymer is strained sinusoidally and the stress is measured as a function of the frequency. From these measurements, one can determine fundamental properties such as zero shear viscosity (which is related to weight average molecular weight), Tan delta (which is related to the damping properties), plateau modulus (which can indicate the length and rigidity of crosslinks) and complex viscosity (which can be related to the steady shear viscosity).

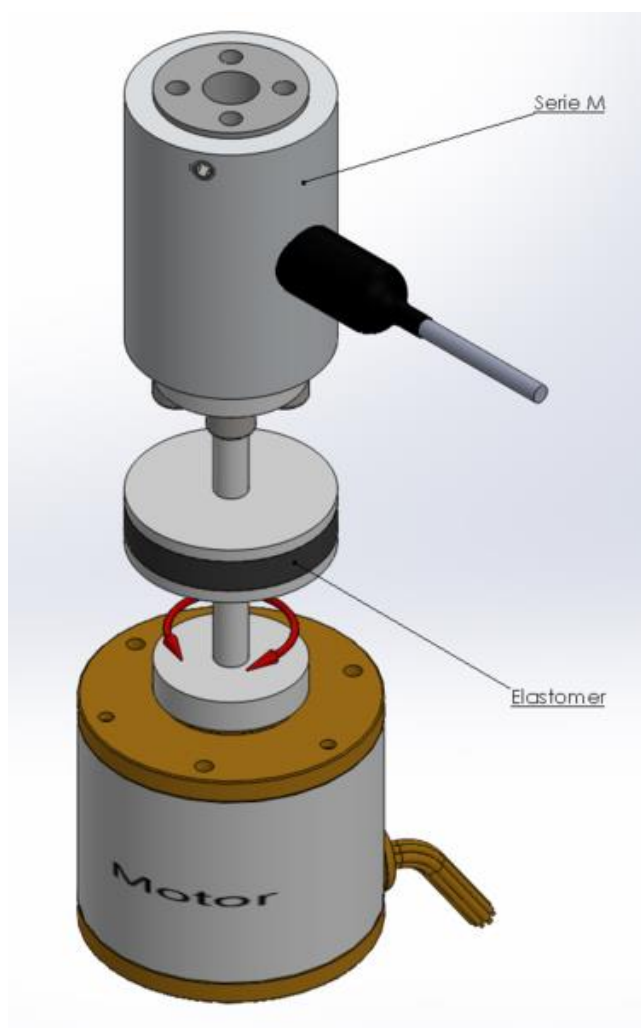


Figure 5. Schematic diagram of the dynamic rheometer (GTM-GmbH)

Heating leads to degradation

Performance of a polymer is governed by its ability to resist chemical and physical degradation processes under thermal, photo, radiation, hydrolytic, and biological conditions. After

mechanical tension, heating is the major reason for polymers' degradation. Polymers are subject to heating for various reasons, mainly during processing by extrusion, thermo-formation, and injection molding. This is performed at elevated temperatures in the presence of ambient oxygen (thermal oxidation). Moreover, they can be heated while they are in use, such as in disposable food packages or while they are exposed to sunlight. Finally, during their combustion for obtaining energy or converting them to raw materials, or while they are in recycling process, they are subject to heating. Another major mechanism of polymer degradation is oxidation. It should be noted that the oxidation of polymers is not a surface phenomenon as is the oxidation of many inorganic solids, therefore, the presence of cracks, empty spaces at the interfaces in composites will favor propagation into the deeper layers of it. While a commercial polymer starts to degrade, low molecular weight compounds are formed in it which is the best indicator of its degradation. Detection and analysis of these compounds is important not only because of knowing the extent and mechanism of the polymer degradation, but also because these species can enter their surrounding environment, such as the smell of inside a new car. These released compounds can be monomers and oligomers, solvent residues, additives, products generated during heating (due to chemical reactions), and degradation. In this section, we review a few techniques that are employed for the measurement of these released low molecular weight compounds. FTIR is one of the most important techniques for the analysis of released gases. However, they can be better analyzed using a gas chromatography–mass spectrometry (GC-MS) instrument, since the degradation products of polymers have low molecular weights and therefore they are volatile. Moreover, the quantity of these compounds is very low, so their detection in gas phase is very difficult. This means that evolved gas analysis needs a preconcentration technique before their introduction into GC-MS.

Traditional preconcentration techniques which almost all of them are based on extraction, need large quantities of both sample and organic solvents, they are time consuming, of high cost and cannot normally be automated. In addition, in case of purge & trap, very light volatiles and gases will not be trapped on the adsorbent resins and therefore will be missed in the analysis. Nowadays, (almost) solventless microextraction techniques such as solid phase microextraction (SPME) and liquid phase microextraction have become some of the most important extraction techniques in sample preparation for analytical purposes. Due to the fact that for analysis of the degradation products of solid polymers, the samples are generally need to be heated or subjected

to long-term sampling, liquid phase microextraction technique never used for this purpose. SPME has been widely used in combination with GC-MS for many different compounds, especially for the extraction of volatile and semi-volatile organic molecules from biological, environmental, and food samples [11]. It is based on a fused silica fiber that is externally coated with a thin film of an appropriate polymeric stationary phase that acts as the extraction medium. The selectivity of the fiber is dependent on the coating used. Common commercially available fibers are Carboxen/polydimethylsiloxane, polydimethylsiloxane, polydimethylsiloxane/divinylbenzene, polyacrylate, and Carbowax. This fiber is attached to a stainless steel rod that is housed in a modified syringe (Figure 6).

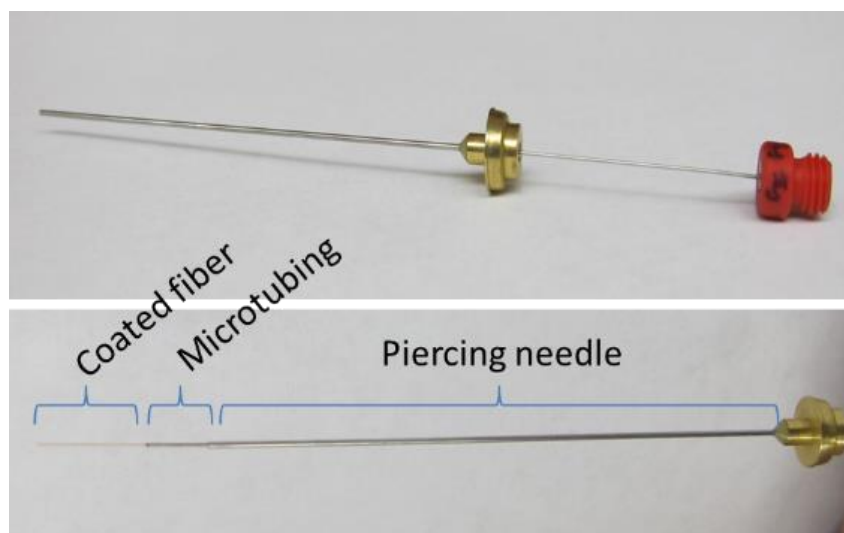


Figure 6. Schematic of a SPME

The fiber is exposed to the headspace over the (heated) solid polymers for a few minutes which extracts volatile degradation products of polymers from the headspace of the sample and at the same time preconcentrate them on its coating. Depends on the type of the polymeric coatings, molecules with different physico-chemical characteristics can be absorbed on the fiber. As an example, Figure 7 shows the GC-MS chromatograms obtained from extraction of degradation products of polyamide 6,6 by a PDMS/DVB SPME fiber [12].

Polyvinyl chloride (PVC) is the main composition of the interior of cars. In a research published in 2003, [2] researchers detected of released compounds from PVC and found that huge number of volatile organic compounds (VOCs) are released from it even in not elevated temperatures. Some of these VOCs (such as benzene, toluene and formaldehyde) are deadly in sufficient

quantities and all of them are bad for health. While new car scent is pleasant to some car owner (you can buy a new car scent spray from here [13], major car companies started to eliminate PVC and other polymers by using different materials, coatings and adhesives in manufacturing. For example, Ford say they have switched to the use of more natural fibers and soy-based foam in seat cushions and Honda claims to have eliminated PVC entirely from interiors of most models. So, please avoid sitting in the car while it is parked in sunlight, and use a windshield solar shade to minimize heat buildup. Keep windows open for good ventilation before starting A/C.

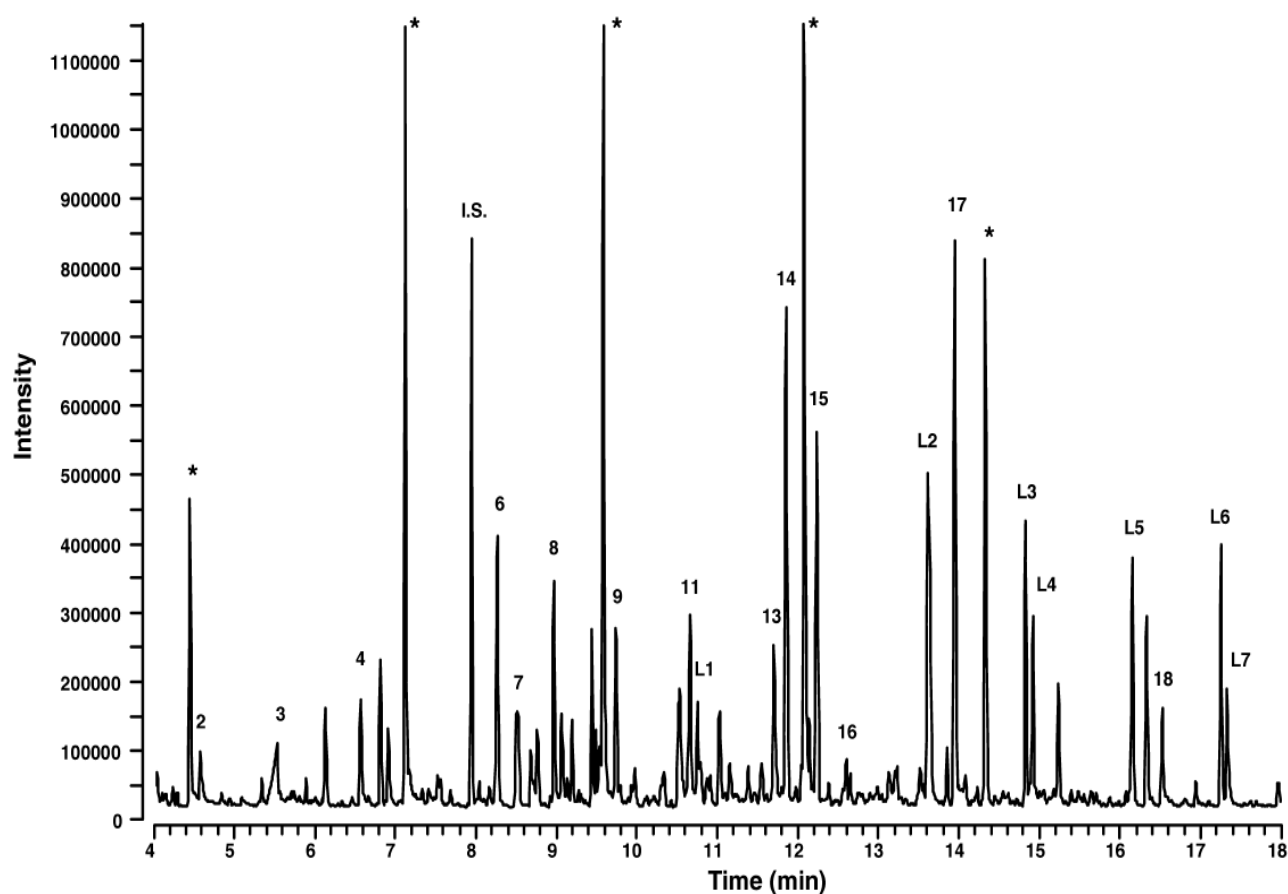


Figure 7. GC-MS chromatograms after 1,200 hours of aging of polyamide 6,6 at 100 oC. Peaks 1–18: low molecular weight degradation products evolved (including cyclic imides, pyridine derivatives, chain fragments, and cyclopentanones). L1–L7: alkanes and alkenes from a lubricant added to the polymer. S.I. D internal standard (from ref 12).

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