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**THE USE OF MASS SPECTROMETRY
AND NUCLEAR MAGNETIC RESO-
NANCE SPECTROSCOPY IN THE
STUDY OF POLYMER COMPOSITES**

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ABSTRACT

Miska Rissanen: The use of mass spectrometry and nuclear magnetic resonance spectroscopy in the study of polymer composites

literature review

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Polymer composites are widely used in the current world. The group of materials contains a wide variety of materials like fibre reinforced polymers, particle polymer composites, structural polymer composites, and wood-based materials. Both synthetic and natural materials are represented. With the variety of materials, the methods used to produce and recycle them varies, having many ways to affect their structures. Similarly, there is variations in the microstructures as well as macrostructures of the materials. For this purpose, powerful methods for the analysis of these materials are required.

Mass spectrometry and nuclear magnetic resonance spectroscopy are widely used analytical methods in the field of analytical chemistry used for analysing substances, and their intra- and intermolecular structures. The methods are capable of providing useful information about the microstructures of polymer composites and as such are worth taking a closer look at in practice.

While mass spectrometry and nuclear magnetic resonance spectroscopy are powerful methods even alone, they might not be enough. Using many different methods of study to gain data about the same and different properties provides more trustable data with the possibility to find correlations between phenomena. For this reason, mass spectrometry and nuclear magnetic resonance are often used together with each other and other methods.

To better understand the way the methods are used in the study of polymer composites, it is useful to review some examples relating to various materials of interest. With the variety in examples available and the possibilities of the methods, mass spectrometry and nuclear magnetic resonance spectroscopy prove highly valuable in the study of polymer composites.

Keywords: mass spectrometry, MS, nuclear magnetic resonance spectroscopy, NMR, solid-state NMR, polymers, polymer composites, polymer matrix composites

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TIIVISTELMÄ

Miska Rissanen: Massaspektrometrian ja ydinmagneettisen resonanssispektroskopian käyttäminen polymeerikomposiittien tutkimisessa

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Polymeerikomposiitit ovat laajalti käytössä oleva materiaalityttö. Ryhmään kuuluu paljon erilaisia materiaaleja, kuten kuituvahvisteisia polymeerikomposiitteja, polymeeripohjaisia partikkelikomposiitteja, rakenteellisia polymeerikomposiitteja ja puupohjaisia materiaaleja. Sekä synteettiset että luonnolliset materiaalit ovat osana tätä materiaalityttöä. Suuren määrän vaihtoehtoja myötä tulee myös paljon keinoja valmistaa ja kiertää näitä materiaaleja, johtaen moneen keinoon muokata näiden materiaalien rakennetta. Vastaavasti materiaalien mikro- ja makrorakenteissa on paljon vaihtelua. Tästä syystä on hyvä olla tehokkaita menetelmiä näiden materiaalien rakenteiden tutkimiseen.

Massaspektrometria ja ydinmagneettinen resonanssispektroskopia ovat laajalti käytettyjä analyttisen kemian menetelmiä aineiden ja näiden aineiden molekyylien sisäisten sekä ulkoisten rakenteiden tutkimiseen. Nämä menetelmät pystyvät antamaan hyödyllistä informaatiota polymeerien ja polymeerikomposiittien rakenteista ja näin ovat sen arvoisia, että niiden käyttöä kannattaa vilkaista tarkemmin.

Vaikka massaspektrometria ja ydinmagneettinen resonanssispektroskopia ovat yksinäänkin tehokkaita tutkimusmenetelmiä, eivät ne välttämättä riitä yksinään. Monen eri tutkimuskeinon käyttäminen yhdessä samojen ja muiden asioiden tutkimiseen voi tuoda tutkimukseen varmuutta ja mahdollisuuksia löytää korrelaatiota ilmiöiden välillä. Tästä syystä massaspektrometriaa ja ydinmagneettista resonanssispektroskopiaa yleensä käytetään yhdessä toistensa ja muiden tutkimusmenetelmien kanssa.

Paremmiin ymmärtääkseen näiden menetelmien käyttöä käytännössä, on hyödyllistä käydä läpi esimerkkejä niiden käytöstä valikoitujen materiaalien tutkimuksissa. Laajan esimerkkivalikoiman ja menetelmien mahdollisuuksien avulla voidaan massaspektrometrian ja ydinmagneettisen resonanssispektroskopian olevan hyvinkin arvokkaita polymeerikomposiittien tutkimuksessa.

Avainsanat: massaspektrometria, MS, ydinmagneettinen resonanssispektroskopia, NMR, kiinteän aineen NMR, polymeerit, polymeerikomposiitit, polymeerimatriisikomposiitit

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TERMS AND SYMBOLS

AC	Alternating Current
API	Atmospheric Pressure Ionisation
CFRP	Carbon Fibre Reinforced Polymer
CI	Chemical Ionisation
CP	Cross Polarization
CSA	Chemical Shift Anisotropy
CW	Continuous Wave
DART	Direct Analysis in Real Time
DC	Direct Current
DDM	4'4-diaminophenyl methane
DMHM	N-(4'4-diaminophenyl methane)-2-hydroxypropyl methacrylate
DSC	Differential Scanning Calorimetry
EI	Electron Impact ionisation
ESI	Electrospray Ionisation
FAB	Fast Atom Bombardment
FD	Field Desorption ionisation
FT	Fourier Transform
FTIR	Fourier Transform Infrared spectroscopy
GC	Gas Chromatography
GFRP	Glass Fibre Reinforced Polymer
GMA	Glycidyl Methacrylate
GPC	Gel Permeation Chromatography
HPPD	High Power Proton Decoupling
ICP	Inductively Coupled Plasma
IR	Infrared absorption spectrometry
LC	Liquid Chromatography
LCC	Lignin-Carbohydrate complex
LDI	Laser Desorption Ionisation
LF-NMR	Low Field Nuclear Magnetic Resonance spectroscopy
LSIMS	Liquid Secondary Ion Mass Spectrometry
MALDI	Matrix Assisted Laser Desorption Ionisation
MAS	Magic Angle Spinning
MS	Mass Spectrometry
NMR	Nuclear Magnetic Resonance spectroscopy
PABZ	5-amino-2-(4-aminophenyl) benzimidazole
PBIA	Poly-p-phenylene-benzimidazole terephthalamide
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate)
PET	Polyethylene terephthalate
PHEMA	Poly(2-hydroxyethyl methacrylate)
PMC	Polymer Matrix Composite
PMMA	Polymethyl methacrylate
PPTA	Poly-p-phenylene terephthalamide
PVA	Polyvinyl alcohol
RF	Radiofrequency
ROSMAS	Rotor Synchronised Magic Angle Spinning
SIMS	Secondary Ion Mass Spectrometry
TFAA-PHEMA	Trifluoroacetic anhydride-derivatised poly(2-hydroxyethyl methacrylate)
TMS	Tetramethylsilane

ToF	Time-of-Flight
UHMWPE	Ultra-High-Molecular-Weight-Polyethylene
XRD	X-Ray Diffraction
a	Acceleration (scalar)
B	Magnetic flux density (scalar)
\vec{B}	Magnetic flux density (vector)
E	Energy
F	Force (scalar)
\vec{F}	Force (vector)
I	Spin number
L	Length (distance)
m	Mass
m/z	Mass-to-charge ratio
r	Radius (distance)
t	Time
v	Speed (scalar quantity)
\vec{v}	Velocity (vector quantity)
V	Voltage
z	Charge
δ	Chemical shift
$^{\circ}$	Degree (angle)
$'$	Minute (angle)

1. INTRODUCTION

Polymer composites are a large group of materials encompassing composite structures where at least one component is a polymer. The use of polymer composites is widespread as the benefits of the materials make them suitable for many uses. Polymer composites can, for example, offer high strength-to-weight ratio, be cheap to produce, be mouldable to wanted forms, and be highly adjustable to do whatever is needed. One reason for this is that the term polymer composite is so vast. Polymer composites can be constructed by placing or dispersing fibres or particulates into a polymer matrix, layering polymer layers on top of each other or with other materials among other methods. These materials can also occur naturally as wood is also a polymer composite.

While polymer composites provide various benefits as materials, they, like all materials, have some issues relating to them that should be addressed. The issues with polymeric composites become more relevant as their use becomes more commonplace and widespread. Possible points of issue are the environmental considerations of the production and recycling of the composites, and reliability in their intended uses. For recycling the different phases should be removed, as contaminants decrease the recycled material's quality. Preferably, the dispersed phase of the composite could be used again too. Reliability of the material goes hand in hand with recycling as mechanical recycling of polymers can have an effect on the polymers' molecular weight [1]. Some recycling techniques can also worsen the performance of the filler. Mechanical recycling of polymer matrix composites chops the fibres shorter, and the resulting material is usually of lower quality than the initial material [1]. As such, methods that keep the dispersed phase intact have more potential for efficient recycling. Nevertheless, recycling processes affect the properties of the different parts of polymer composites and thus it is necessary to quantify the effects on the resulting material. This also holds true to production methods in general, as it is important that the produced material is what it is meant to be on both micro- and macroscale.

Mass spectrometry and nuclear magnetic resonance spectroscopy are tools of analytical chemistry, where they are used to identify chemicals and their structures. The use

of these methods has expanded to a wider range of materials with time. Due to their value in analytical chemistry these methods are widely in use and well researched.

In this text materials of interest, methods, and practical examples will be discussed. First the materials will be discussed by going through polymers, composites, and specifically the materials of interest. The discussion includes their structure and relevant properties. Next, mass spectrometry and nuclear magnetic resonance spectroscopy are introduced with their underlying physical phenomena. After that their use in practice is briefly discussed. As the third main point, examples of the methods in various research are discussed and their implications are considered. Lastly, all the discussed parts are summarized.

This text aims to discuss why polymer composites need to be analysed through analytical chemistry as well as why and how to use mass spectrometry and nuclear magnetic resonance spectroscopy in researching polymer composites. It is relevant to understand the underlying problems with the materials to know what to look for when studying them. Likewise, understanding the methods used is crucial as that makes it possible to understand and better interpret the data received from measurements and how these measurements should be done in the first place.

2. POLYMER COMPOSITE MATERIALS

Polymer composite is a general term for materials composed of a polymer matrix and a dispersed phase providing a desired property to the composite. Polymer composites have a separate subclass called polymer matrix composites, or PMCs for short. PMCs encompass polymer composites containing a fibrous dispersed phase which often gives the material high strength. Other polymer composites are particle and structural polymer composites. Particles mixed into a polymer matrix can offer various new properties and structural composites can use a polymer phase in a macroscopic structure in various ways.

Polymer in the matrix phase acts as a typical polymer would on its own, but its interaction with the dispersed phase provides different attributes to the composite. Thermoplastic polymers can deform more easily in moderately high temperatures but also offer some advantages such as reprocessability and cost-effective manufacturing [2]. Thermosetting polymers on the other hand can be rigid and offer solvent resistance among other properties [2]. Sometimes the interaction of the different phases is not that important as polymer matrixes can naturally provide a ductile and light matrix to the dispersed phase.

Different types of additives give the composite structure different properties and in different ways. Fibres tend to bear load strengthening the material [3] whereas particles can provide thermal, electrical, and mechanical properties among others [2]. Mixes of different polymers can also be used to further adjust the material properties.

2.1 Microstructure and mechanical transformation

For materials mixtures usually, the rule of mixtures applies: the properties of the whole are the volume percentage weighted sums of the properties of the base materials. Thus, it is important to understand the individual constituents as well as their combinations.

Polymer molecules are composed of repeating units varying from simple to complex ones. In a polymer mix these repeat units might be randomly ordered within an individual chain or comprise completely separate chains. Polymer chains tend to be separate long chains of the repeat units, but with some polymers the chains can have varying levels of

branching. In some cases, often after specific treatments, the chains can form cross linkages with neighbouring chains essentially forming a massive macromolecule in the form of a polymer network. Polymers tend to have varying levels of crystallinity, often dependent on their thermal history. Branching and cross linkages lower the crystallinity of a polymer or can even force the material to be completely amorphous. Free polymer chains form crystals by packing tightly together or by folding in on themselves and having the repeat units position themselves in an orderly fashion. As a completely systematic structure is practically impossible to form, polymers rarely have high crystallinity.

The strength of intermolecular bonding in polymers depend on the length of the chains. Long chains have more sites capable of forming intermolecular bonds and can also be physically more tangled with other chains. Branching chains can more easily be tangled with other chains, but the lower crystallinity can make it more difficult for them to form intermolecular bonds as sites suited for bonds can be forced away from each other. Many typical repeat units have a side group to them, which can act similarly to short branches. Having large side groups decreases crystallinity as chains cannot be packed as closely to each other. Polymer chains can be oriented in different ways in bulk material. Especially in amorphous polymers, the chains can be randomly oriented and curl around each other. More commonly the chains are at least somewhat parallel to each other, forming crystals more easily and having anisotropic properties.

Polymers tend to be relatively soft and have low moduli of elasticity, though depending on the specific polymer, the properties may vary largely. Low stiffness usually means that the material is very ductile, and polymers can often be stretched elastically relatively much with extensive plastic deformation being common, too. Polymer chains can, due to the covalent intramolecular bonds, bear load well in the longitudinal direction, whereas in the transverse direction, as only intermolecular bonds and the potential cross linkages hold the chains together, the strength is noticeably lower. When placed under stress, polymer chains start to orient themselves along the stress axis. Often polymers are strengthened via stretching them in order to orient the chains with the direction of the usual load as in for example, a fishing line. As the parallel chains experience stress, they can also slip in relation to each other. Polymer crystals tend to stretch out this way so that the crystal layers on the opposite side of the crystal are pulled away from each other in the plane of the layers.

Compared to the polymer chains, the particles and fibres are much larger, as they are typically macroscopic objects and even visible to the human eye. The particulates are

usually mixed evenly into the polymer matrix, or the matrix is formed around a fibre mesh. With fibres, depending on the used methods, it is possible to affect the fibre orientation. This is important because aligned fibres have anisotropic properties. The fibres adhere to the matrix polymer and a load is distributed to the fibres, mostly in the longitudinal direction of the fibres. The particulates are generally composed of a much stronger material, leading to molecular and structural movement in the composite to be impeded strengthening the material.

2.2 Dispersed phase properties' effect on bulk material properties

The dispersed phase can be made of any desired material with the wanted properties. Usually, the fibre or particle has a specific property that is wanted for the bulk material. The most common reason for creating a composite material is to strengthen the base material. Often the particulates are stronger than the matrix leading to a polymer composite strengthening with the addition of the dispersed phase. Metals are typically much stronger than the polymer matrix and can additionally provide electric effects. Ceramic particulates are very strong and hard, leading to strengthening and possibly to an abrasive surface. Even other polymers can be used, as some polymer fibres are common.

As previously mentioned, many material properties of composites follow the rule of mixtures, which allows for high tunability for the wanted properties. For example, in PMCs the strength and ductility of the composite can be tuned by the ratio of the fibres in the material.

2.3 Materials of interest

Polymer composites are ubiquitous in the modern world. As a material type is used vastly in various situations, it is important to gain good understanding of the behaviour of the materials. Understanding why a specific material works in some way can lead to easier or cheaper ways for replicating the wanted behaviour or avoiding failures in some materials to improve safety. Going through a few materials of interest will bring a better understanding of why knowing more about them is important.

Wood is a polymer composite, as its main structural constituents, cellulose, hemicellulose, and lignin, are all polymers. The primary cell wall in wood is generally made of

cellulose microfibrils embedded in hemi-cellulose, pectin, and proteins [4]. The secondary cell wall forms after the cell has ceased growing and additionally contains lignin, that forms a three-dimensional structure stiffening the wood structure [4].

Cellulose consists of a chain of β -(1-4)-linked D-glucose units [4]. Note that here β refers to a certain type of geometry in the molecule, but it can also refer to a specific carbon in lignin units. Figure 1 shows the chemical structure of a D-glucose molecule with the carbon atoms named and the cellulose repeat unit.

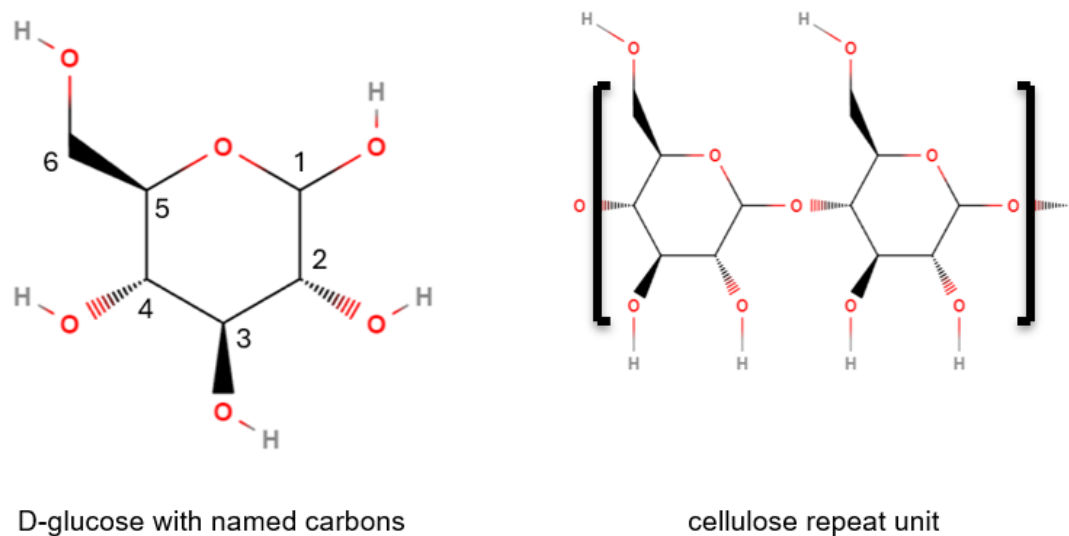


Figure 1. The chemical structure of D-glucose [5] with the carbon atoms numbered and the repeat unit of cellulose.

Hemi-cellulose contains a large variety of different monomers. The exact ratios of the monomers depend on the species of plant. Some of the most common monomers include D-glucose, D-xylose, L-arabinose, D-mannose, and D-galactose [6]. The chemical structures of the monomers are shown in figure 2.

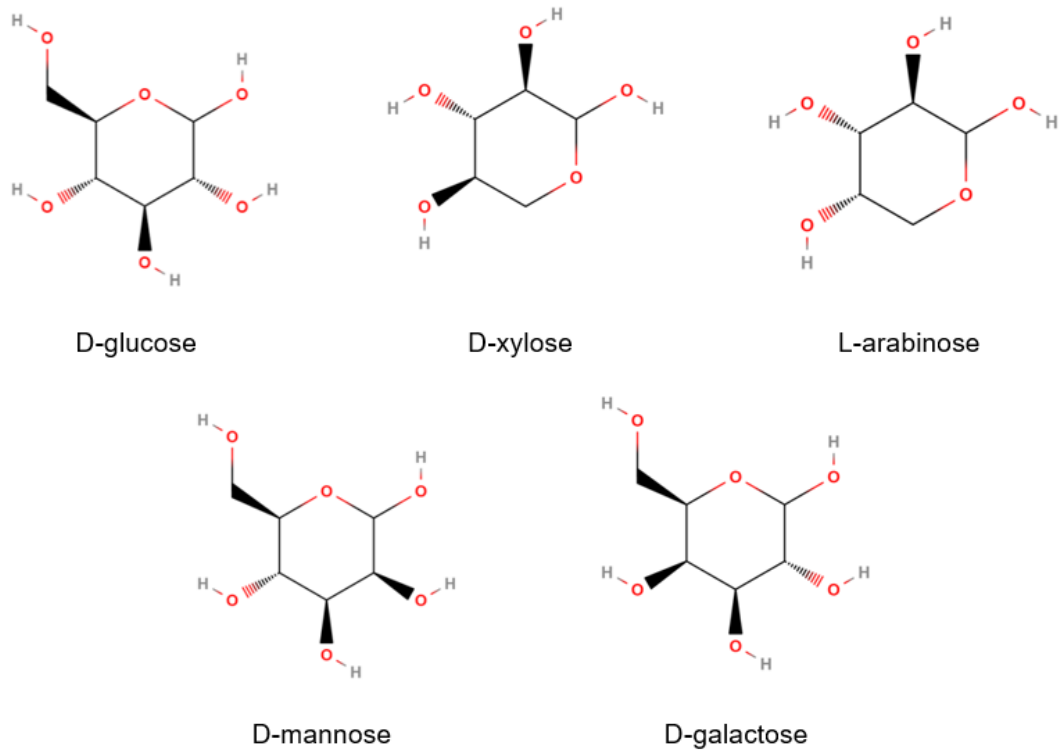


Figure 2. The chemical structures [5] of the most common hemi-cellulose monomers [6].

Lignin also consists of multiple different repeat units. The main monomers of lignin are sinapyl alcohol (S-unit), coniferyl alcohol (G-unit), and paracoumaryl alcohol (H-unit). The chemical structures are shown in figure 3.

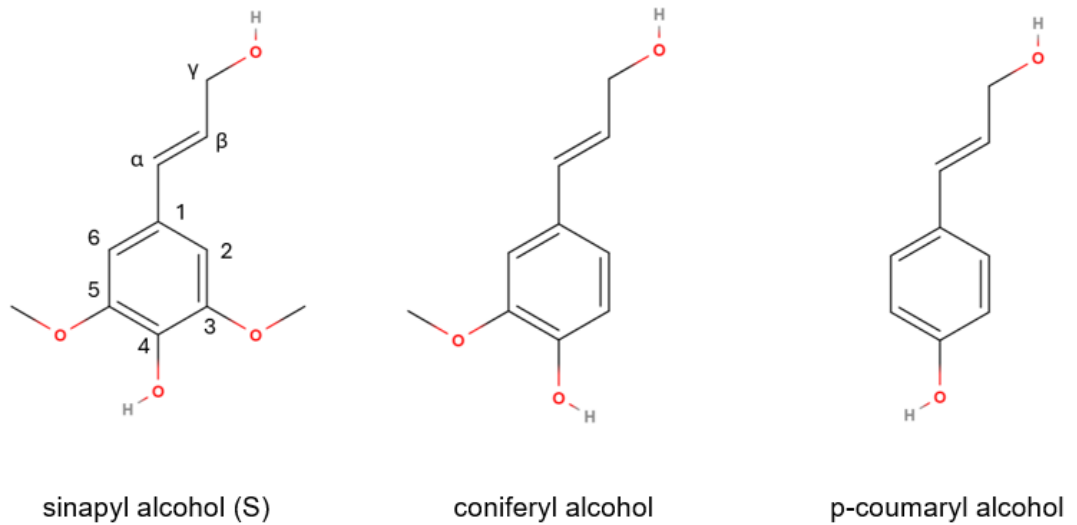


Figure 3. The chemical structures of lignin S-, G-, and H-units [5]. The carbon atoms of the structure are named on sinapyl alcohol.

Carbon fibre and glass fibre reinforced polymers (CFRP and GFRP respectively) are common examples of high strength polymer composites. They are used in many different applications requiring high strength and light weight. Carbon fibres are prepared from usually polymer precursors via carbonising creating graphitic structure [7]. The fibres are bundled together and can further be woven or wound into useful shapes such as sheets or tubes to name a few [7]. Glass fibres are made by drawing molten glass through a bushing with a large number of holes leading to numerous thin and parallel fibres that are then rapidly cooled to maintain an amorphous structure [7].

Aramids are polymers often used as fibres. Aramids are generally divided into para-aramids and meta-aramids, depending on the placement of linkages in the benzene rings of the structure. The most known para-aramid is poly-p-phenylene terephthalate, known widely by its trade name Kevlar. Kevlar tends to be highly crystalline and with little surface interaction, so it often needs to be treated for better fibre-matrix adhesion [7]. Other polymers commonly used as fibres are ultra-high-molecular-weight polyethylene (UHMWPE) and nylon (a family of various polyamides).

Fibre reinforced polymers contain either continuous or short fibres. Continuous are often mats of fibre that can be placed on top of each other in various orientations to tune the mechanical properties in different directions due to the anisotropic nature of the mats.

Short fibres can be aligned or randomly oriented providing various levels of anisotropic properties.

Polymer films are often used in various packaging solutions. These films are often structural polymer composites that can be formed from many layers of different polymers, giving the film desired properties such as strength, or barrier properties. Reasons for combining multiple layers of polymers is that rarely a single polymer has all the wanted properties, or a simpler answer might be too expensive and partial use of a cheaper material could prove more cost effective.

As films are very thin, some of their material properties are not comparable to base material properties. For example, the sample for tensile tests made from a polymer film is a rectangular piece of the film compared to the usual thinner-in-the-middle sample. Some new relevant properties also emerge such as puncture resistance, which refers to the material's ability to resist deformation when under a load perpendicular to the film analogous to tensile properties, and tear strength, or how much energy goes into tearing the material. [8]

3. FUNDAMENTALS OF MS AND NMR

When investigating the properties of an unknown material, it is essential to know what the compound is and what it does. Thus, ways to analyse sample composition and structure are needed. Analytical chemistry is the study of matter such that these questions could be answered. Various methods ranging from simple physical phenomena to complex ways utilising advanced mathematics and modern understanding of physics have been created to attain the desired information.

3.1 Mass spectrometry

A modern method for analysing samples is mass spectrometry (MS). When thinking about ways to discern particles from each other the concept of 'size' quickly comes to mind. A simple measure for size is mass, so being able to create a spectrum of the concentration of particles for a range of different masses could provide useful information about the sample. Unfortunately, just measuring mass is not an easy task, but by taking advantage of the interactions of charged particles with electromagnetic fields, it is possible to measure the mass to charge ratio, m/z , of particles as a spectrum.

A mass spectrometer is a complex system but can be divided into three main sections [9]. The first step is an ioniser, where a given sample is dispersed and ionised. Second, in the analyser, the sample ions are sorted according to their m/z , and finally, the ions that pass through must be detected by a detector. The exact ways to perform each step can vary largely depending on the type of sample, the other steps of the process, or what is needed from the process from accuracy to test time or cost.

With a modern high resolution mass spectrometer, it is possible to distinguish signals a fraction of the mass of an electron apart [9]. This means that it is possible in most cases to tell apart different isotopes within a substance or to tell the chemical composition of the substance from a single measurement. Although, this kind of accuracy is much more difficult with higher mass particles the spectra can provide useful information about the relative concentrations of different substances or with polymers measure the chain length distribution. MS has many different variations that are discussed in the following sections.

Different methods can be used for different data, as some methods are better suited for specific tests than others.

3.1.1 Sample preparation and ionisation methods

The first step in a measuring process is preparing the sample to be analysed. This is largely dictated by the sample type and intended method of ionisation. Volatile compounds are often ionised in gaseous form so having them evaporate into the ionisation chamber is a simple and effective way of getting the sample in its desired place. Various chromatographic methods, such as liquid and gas chromatography (LC and GC) can also be used with various samples to enhance the achievable results by separating individual substances prior to ionisation [9]. With solid samples especially, the use of a solvent is often necessary. This can mean simply dissolving the sample to separate the various substances to measurable sizes or preparing the substances for chromatography. Additionally, non-volatile samples with poor solubility can be mixed with a matrix to disperse them more easily with specialised methods, such as MALDI [9].

The ionisation methods themselves can be separated into two groups: hard and soft ionisation [9]. Hard ionisation refers to methods where the integrity of the original sample molecule cannot be guaranteed as the excess energy from ionisation can fracture intramolecular bonds or the ions are specifically created by targeting these bonds. It is important to understand that molecules have characteristic ways of forming ions. For hard ionisation methods, the different parts a larger molecule breaks down into can tell about the structure and bonds of the sample molecule as specific bonds tend to break more easily. On the contrary, soft ionisation methods strive to keep the molecules intact with as little alterations as possible. Additionally, soft ionisation methods can be combined post-ionisation fragmentation methods to acquire fragments from an intact ion. Considering both ways of ionisation the ways the ions form are predictable with slight changes in mass as electrons, protons, or even larger ions are added or deducted from the sample molecule.

The simplest example for hard ionisation methods is *electron impact ionisation* (EI), in which a gaseous sample is ionised with a beam of high-energy electrons that can easily break covalent bonds. For vapour phase samples there is also the soft ionisation option of *chemical ionisation* (CI). In CI a reagent gas is introduced and ionised so that this reagent gas can cause the sample molecules to ionise. [9]

Sometimes it is not feasible to have the sample in a vapour phase but rather have it be ionised directly from a solid or liquid phase. This can be achieved in various ways, but the common idea is to give the solution just enough energy to emit a sample molecule. In *field desorption ionisation* (FD) a large voltage on a specialised carbon needle surface causes singular electrons to be removed from the sample molecules and then repelling those molecules away from the surface [9]. An alternative way to ionise the sample molecules directly from the solution is to bombard a liquid containing the sample with high energy atoms, usually noble gasses. This method is called *fast atom bombardment* (FAB), and it has a related method called *liquid secondary ionisation mass spectrometry* (LSIMS) in which high energy cesium ions are used [9]. Another important desorption ionisation method is *laser desorption ionisation* (LDI) where a pulsed laser beam ionises the samples. With the addition of a specialised matrix to hold the sample substance in a method known as *matrix assisted laser desorption ionisation* (MALDI) extremely large molecules can be ionised without breaking them. [9] This method is well suited for the analysis of polymers with the possibility for even long polymer chains to be measured while receiving information on the sample very close to its original state.

Sample molecules can be isolated by nebulising the sample solution and then evaporating the solvent away leaving only the sample ion. In *thermospray ionisation*, this is achieved using a heated capillary that nebulises the solution and evaporates part of the solvent [9]. This creates fine droplets of the solution from which the solvent soon evaporates leaving only the sample molecules behind. More recently *electrospray* (ESI) has been taking the place of thermospray [9]. ESI nebulises the sample solution with the use of nitrogen gas flowing in the direction of the mass spectrometer. Additionally, a high potential difference is kept between the capillary introducing the solution, and a target plate. This causes fine charged droplets to travel towards the ion intake of the spectrometer. As the solvent gradually evaporates away from the droplet, the size of the droplets goes down forcing the charged sample particles closer together. The sample ions ultimately push each other away due to coulombic forces completely disintegrating the droplets. Electrospray ionisation can be performed at or near atmospheric pressures leading to an additional name of atmospheric pressure ionisation (API) [9].

In more recent years a method for *direct analysis in real time* (DART) has been developed. DART is based on a reagent gas detaching and ionising sample molecules from a condensed phase sample and then pushing the ions towards the spectrometer's sample intake. First the reagent gas is subjected to a high electric field causing ionisation and the formation of excited-state atoms. Electric lenses then direct the altered gas out of

the gas source towards the spectrometer meanwhile filtering out the ions leaving only uncharged gas with regular and excited-state molecules. When a stream of gas with metastable molecules comes in contact with the sample, ions of the sample itself or of any compounds on its surface are desorbed. DART samples can be fed as solid macroscopic pieces directly into the gas flow for analysis making the whole process relatively quick. [10]

Sometimes information on complete or fragmented molecules is not very relevant, but information may be desired on elements and specific isotopes or on a combination of these. In such a case the sample would need to be completely ionised atom by atom. *Inductively coupled plasma* (ICP) ionisation is a method where the sample is ionised using a plasma torch. The usually liquid samples are nebulised with argon gas and this aerosol is then transported into a chamber, where a magnetic field and a high voltage spark ionise the sample and turn it into plasma [11]. The elemental ions in the plasma are then guided into the mass analyser by electrostatic lenses [11].

3.1.2 Sorting and detection of ions

After ionising a sample, the ions then need to be sorted according to their mass to charge ratio. This can be achieved via the use of interactions of ions with electric and magnetic fields as well as common physical relations. The ions can then be sorted so that only ions of a given m/z can get through or so that a group of ions is scanned in one go, effectively receiving data for all values of m/z simultaneously. Common methods for sorting are sector field, quadrupole, and time-of-flight mass analysers. Other used methods include ion trap and orbitrap mass analysers.

For mass analysers a common element is a pusher, which accelerates the ions with an electric field. When a charged particle is placed in an electric field, it will receive a kinetic energy according to the voltage between the end plates of the field or simply

$$E = zV = \frac{1}{2}mv^2. \quad (1)$$

A *sector field mass analyser* provides a simple solution for the filtering of ions. Charged particles also interact with magnetic fields. This interaction has the mathematical form of

$$\vec{F} = z(\vec{v} \times \vec{B}), \quad (2)$$

or in a scalar form,

$$F = Bzv \quad (3)$$

orthogonally to both the magnetic field and the velocity vector, granted that they are orthogonal to each other. With the use of Newton's second law and the formula for central acceleration,

$$a = \frac{v^2}{r}, \quad (4)$$

we can solve for m/z :

$$\frac{m}{z} = \frac{B^2 r^2}{2V}. \quad (5)$$

The ionised sample molecules are ejected into the magnetic field and then travel on a trajectory determined by their m/z . Ions with a specific m/z get through to the detector as other ions are deflected and collide with instrument walls or collection plates. This kind of analysers usually keep the radius of the turn and the acceleration voltage as constants so that varying the magnetic field strength can be used to let ions of different m/z through. The use of slits letting only ions on a specific trajectory through can be used to increase the accuracy of the instrument, but this comes with the trade-off of decreased sensitivity as less ions reach the detector. A simplified schematic of a sector field mass analyser is shown in figure 4.

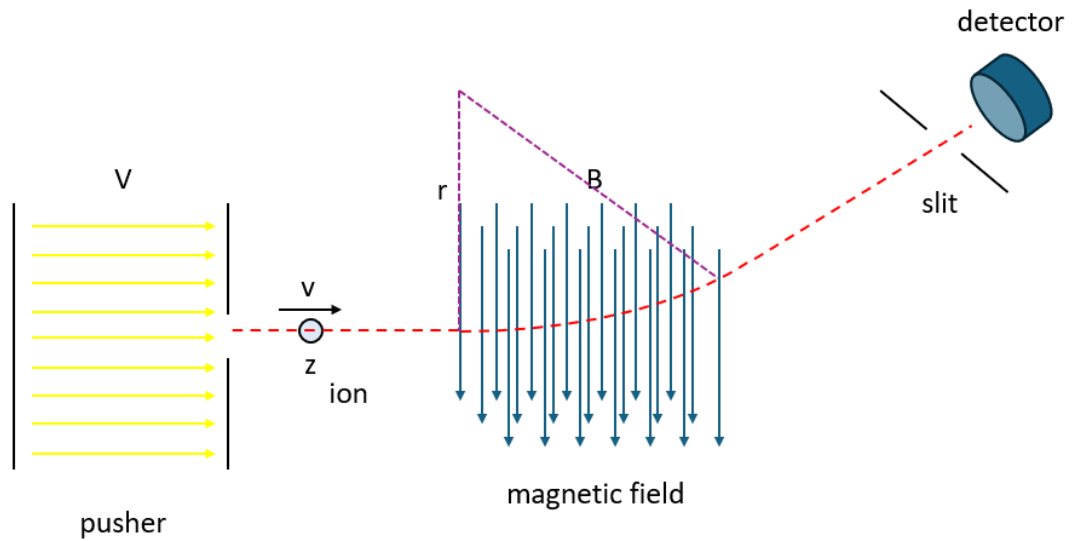


Figure 4. A schematic of a sector field mass analyser [9].

In some cases, having a large instrument with powerful electric and magnetic fields is not practical and a more compact solution is needed. *Quadrupole mass analysers* consist of four parallel rods usually 10-20 cm in length each having a cylindrical or hyperbolic shape to them. The poles are placed on the corners of a square forming a sort of tunnel in the middle. DC current is applied to the rods so that opposing rods have the same potential and poles next to each other have opposite potentials. Additionally, an AC current is applied to switch the potentials of the poles around. Ions introduced into this tunnel are affected by the periodic changes in the electromagnetic fields and for a given combination of DC and AC only ions with specific m/z can pass through. This compactness comes with a trade-off in accuracy, but covers for it with size, speed, and sensitivity. Similar data can be acquired via arrangements using more than four poles too. Figure 5 displays a simplified version of the quadrupole assembly. [9]

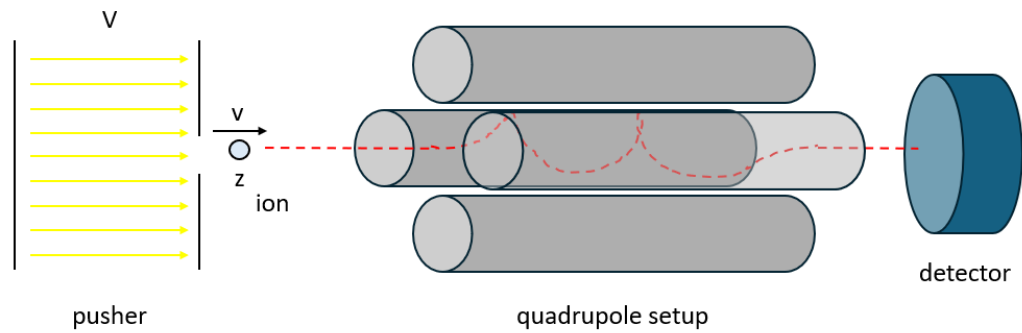


Figure 5. A schematic of a quadrupole mass analyser [9].

Similarly to quadrupole mass analysers, *ion trap mass analysers* use alternating electromagnetic fields to control the movement of ions, though instead of sorting them while in motion ion traps store ions of a given m/z range for a relatively long period of time. The trap is formed by three electrodes with hyperbolic surfaces. One electrode is in the middle of the trap with sinusoidal AC applied to it and both ends have an end cap electrode that can have ground potential, DC, or AC applied to it depending on the mode of analysis. A low pass filter for m/z or both low and a high pass filter can be achieved with this. Additionally, extra kinetic energy can be given to the trapped ions causing collisions and fragmenting. Ion traps are largely used in *tandem mass spectrometry*, where it is combined with other methods of analysis. [9]

Time-of-flight mass spectrometry (ToF) is based on, as the name suggests, the time of flight of given ions in specific circumstances. Using a voltage V , ions can be given kinetic energy according to equation (1) and when flying on a path with the length of L in a vacuum without external forces, the speed of the ion can be defined as

$$v = \frac{L}{t} . \quad (6)$$

From here we can solve for the time-of-flight t , and it resolves to the form of

$$t = \left(\frac{L^2 m}{2Vz} \right)^{\frac{1}{2}} , \quad (7)$$

meaning that the time-of-flight for a certain ion is directly proportional to the square root of m/z . This means that by accelerating sample ions with an electric field and then measuring the time it takes for the ions to reach the end of the measuring tube. A limiting factor with ToF instruments is the need for accurate measurements of time and length as the length of the measurement path needs to be known very accurately and the typical times of flight can be around 10^{-7} s [9]. The setup of a time-of-flight mass analyser is shown in figure 6.

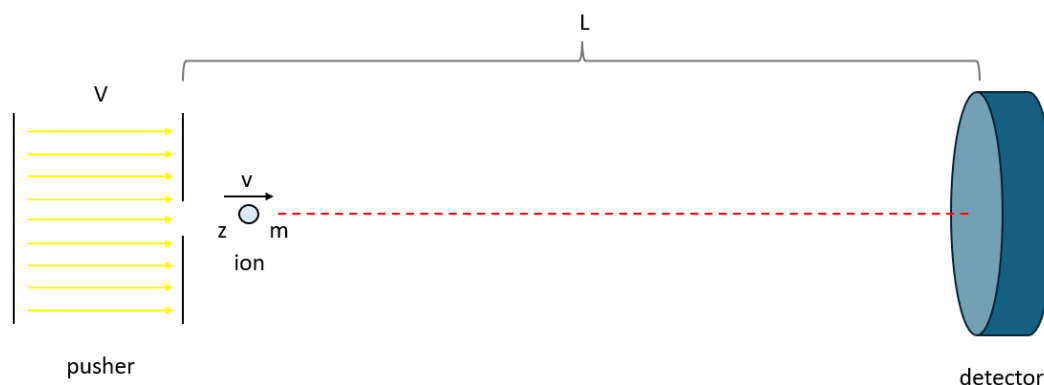


Figure 6. A schematic of a time-of-flight mass analyser [9].

When holding ions trapped in a strong magnetic field their rate of revolution on a circular path is determined by their m/z . By applying a magnetic radiofrequency (RF) pulse to the trapped ions, their rotational frequencies can be brought to resonance and then an interferogram can be measured. This time domain interferogram can then be Fourier transformed to gain information on the distribution of different mass to charge ratios present in a process called *Fourier transform mass spectrometry* (FT MS). [9]

After the ions have been sorted, they need to be detected to form the spectrum. While the way the ions are separated can have an effect how the ions need to be detected, there are typical ways to do it. Commonly, a set of slits lets in only one set of sample molecules at a time to an electron multiplier that produces a signal [9].

3.2 Nuclear magnetic resonance spectroscopy

Nuclear magnetic resonance (NMR) spectrometry makes use of complex physical phenomena between non-zero spin nuclei and a combination of a static and an alternating magnetic field. After exciting nuclei with a combination of these magnetic fields, an electromagnetic signal can be observed emitting from the sample, which is known as nuclear magnetic resonance signal [9]. Together with mass-spectrometry, NMR is the

basis of modern chemical analysis. Concerning polymer composites, hydrogen and carbon atoms are universally present in most common materials and both have isotopes fit for NMR spectroscopy. Because of this, ^1H and ^{13}C NMR spectroscopies are powerful tools.

3.2.1 Physical foundation of NMR

The nuclei of atoms have spin numbers, that represent the effects of their charges' "revolution" around the axis of the nuclei analogous to macroscopic charges on circular paths. The spin number I can have values every half integer from zero upwards depending on the number of protons and neutrons in the nucleus. The nuclei with a spin number of $\frac{1}{2}$ are best suited for NMR. To receive useful data, nuclei largely present in the sample materials should be used for the method. Common polymers and organic compounds in general consist mostly of carbon frames substituted with hydrogen atoms with the occasional oxygen and nitrogen atoms. Most use would then be obtained from measurements with hydrogen and carbon atoms. It turns out that ^1H is well suited for NMR and that is why ^1H or proton NMR is the most commonly used NMR method. For carbon, the most common isotope, ^{12}C with 99% natural abundance, has a spin number of zero and is not suited for NMR. The isotope ^{13}C , however, has the spin number of $\frac{1}{2}$ leading to it being useful for sample analysis. While both elements have isotopes that can be analysed with NMR, it is important to notice the difference in their natural abundance. ^1H has a natural abundance of over 99%, meaning that most likely all hydrogen atoms in a single molecule are ^1H and the singular ones that are not, do not noticeably affect the results. ^{13}C , on the other hand has a natural abundance of about 1% meaning that most molecules will probably not have any ^{13}C atoms in them when common organic molecules are concerned. This difference in their presence in combination with other factors makes the methods using different nuclei vastly different. [9]

When subjected to an external magnetic field, spin $\frac{1}{2}$ nuclei are divided to two different energy levels for spins $+\frac{1}{2}$ and $-\frac{1}{2}$. Radiofrequency electromagnetic waves can be used to bring energy to the system and at a specific frequency, unique to the nuclei, the nuclei will absorb this energy and be elevated to the higher energy state leading to the system being in resonance. The interference caused by the absorption of energy can then be recorded as a spectrum. The radiofrequencies can be applied to the sample as either a continuous wave (CW), scanning over a desired range of frequencies, or all at once as a pulse with a method called pulsed Fourier transform NMR (pulsed FT NMR). In the absence of an external magnetic field, all the examined nuclei have a magnetic moment to themselves in a random direction, but the introduction of an external field

causes the spins to precess around the z-axis of the magnetic field resulting in a net magnetic moment in the z-direction. In both CW and pulse form introductions of the radiofrequencies the different nuclei are brought to the same phase in their precession resulting in the bulk magnetisation vector tipping away from the z-axis and towards the xy-plane. As the pulse dissipates or the Larmor frequency of a given sample nucleus is passed the bulk magnetisation vector tries to return back to the z-axis. In this precession the nuclei radiate their excess energy away as a measurable signal. [9]

3.2.2 Methods of acquiring information from NMR

When the excitation frequency is removed, the nuclei in the sample begin to return to a state of lower energy and their coherent precession radiates away the energy difference as a measurable signal. In continuous wave mode the signal is received while scanning through a range of frequencies and a spectrum can thus be formed. For a pulsed measurement, all nuclei within an excitation range excited at once, and after the pulse ends, relaxation starts to occur resulting in signal that is a superposition of all the different signals. This signal can then be interpreted via Fourier transform into a readable spectrum. Importantly, the signal is obtained during relaxation of the nuclei. Relaxation happens in two ways: excited nuclei can dissipate their energy to the surrounding nuclei leading to the bulk magnetisation vector returning to the z-axis and spin-spin relaxation in which the energy is spread among the precessing nuclei leading to individual magnetisation vectors fanning out. In the case of ^1H NMR both relaxations happen fast enough that the resulting peaks are proportional to the number of protons present leading to the possibility of integrating the spectrum to receive information about the number of specific types of protons. [9]

For a specific nucleus, how much the magnetic field affects it, depends on how shielded the nucleus is magnetically. The electron cloud surrounding a nucleus shields the nucleus slightly from external magnetic fields. The exact amount depends on the chemical surrounding of the atom: which atoms it is attached to and to what those atoms are attached to as well as which special structures and bonds are nearby. These kinds of changes alter the frequency required for exciting the specific nucleus slightly. For example, for a 300 MHz spectrometer, commonly used in ^1H NMR, changes in the realm of thousands of Hz are expectable leading to a relative difference of a few ppm in the Larmor frequencies. This change in frequency is called *chemical shift*, denoted by δ , and the interpretation of NMR spectra is based on the relative intensity of signal spikes around different chemical shifts. For ^1H NMR, tetramethylsilane, or TMS, is used as a reference substance due to its clear spike and high shielding of its protons as well as a

variety of other benefits. [9] One of the benefits is the equivalence of all the hydrogens in the molecule due to the spatial symmetry of the molecule, as seen in figure 7.

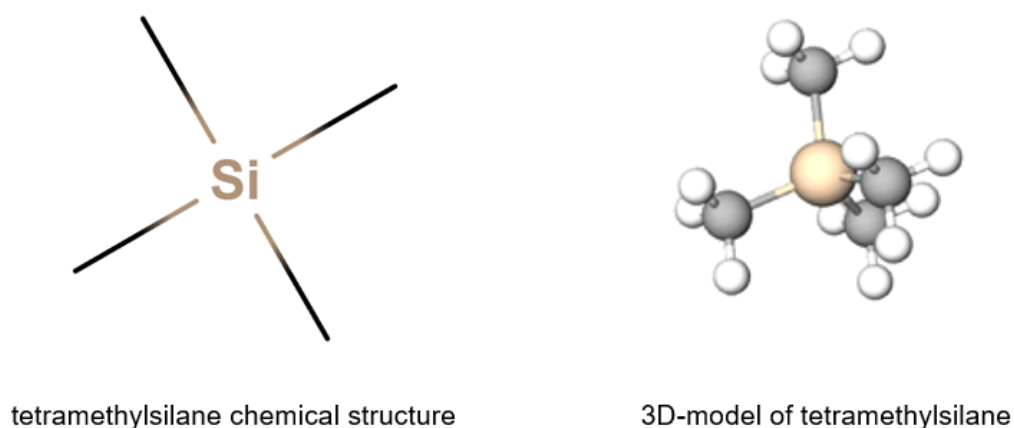


Figure 7. *The chemical structure and a 3D-model of TMS [5] to show the spatial symmetry of the molecule.*

The NMR spectra are constructed in such a way that on the very right of the spectrum there is the chemical shift of zero ppm, and chemical shift increases to the left. This means that signals from less shielded nuclei appear more left in the spectrum than those with high shielding. The spectra can then be interpreted according to the locations of different spikes on the δ -axis and the relative integrals of the spikes. The exact methods depend greatly on the nucleus in question.

3.2.3 Solid-state NMR

In a liquid sample, the individual molecules move and tumble around freely leading to different orientations of molecules being equally present. This averages all the effects that molecular orientations might have. It turns out that the molecular orientation influences the signal, and this is a problem for solid-state NMR. Unlike in the liquid phase, particles in the solid phase are mostly stationary with limited movement, leading to possible symmetry breaking structures existing in notable fractions. Such interactions as electric quadrupolar and magnetic dipolar interactions have anisotropic properties, but the erratic and random movement of molecules in solutions averages these out to zero while other properties can also be reduced to isotropic values. Alas, solid samples cannot be inspected on a molecular basis, but on a basis of a unit cell. [12]

It is important to remember that solid substances vary in the amount of order in their structure. Some materials, like metals, tend to be highly crystalline, whereas materials such as glasses or some polymers are mostly amorphous. This contributes to the symmetry of the material, as amorphous substances are more symmetric on a macroscopic scale and without a clear structure, a unit cell is impossible to define. Overall, for crystalline materials notable factors are that identical chemical positions can be oriented differently in an external magnetic field, and that intermolecular and intramolecular arrangements of atoms have effects as nearby atoms can affect the chemical surroundings of identical molecules [12].

With the various difficulties relating to solid-state samples many techniques have been developed to gain better information out of the spectra. When not using ^1H NMR, heteronuclear coupling has a large line broadening effect on the spectra in solid-state as well as in solution-state. They have analogous methods of *high-power proton decoupling* (HPPD) and *proton decoupling* respectively. The anisotropic shielding effects of crystals also cause line broadening. The effects of different orientations can be largely mitigated by *magic-angle spinning* (MAS), where the sample is spun rapidly at the 'magic' angle of $54^\circ 44'$. With some nuclei the relaxation times can be inefficiently long, slowing the measurement down significantly, or the nuclei may have low sensitivity towards the magnetic field. In such cases, the method of *cross polarisation* (CP) is used for transferring magnetisation from ^1H , or similar, nuclei to any given spin- $\frac{1}{2}$ nuclei enhancing the resulting signal. [12]

3.2.4 Practical process of an NMR measurement

Solution-state NMR works the best, as it has the highest sensitivity and resolution. For this reason, the samples need to be in a solution state, either liquid or suspended, for best results, unless specifically information about the solid-state structure is wanted. This usually means dissolving the sample in a solution, of which solvent has been deuterated, and placing it in a small glass tube. The sample tube is then spun at 10-20 Hz in a machine with strong permanent or electromagnets as well as various coils for the different radio frequency applications [9]. For solid-state NMR the samples are packed into ceramic capsules in powder form and spun at the magic angle at 3-30 kHz [12] to imitate the moving and tumbling of molecules in solution state. A computer interface streamlines the process and records the resulting spectrum. The interpretation of the peaks is done using existing models or reference spectra possibly aided by computers. A simplified schematic of the assembly used for an CW NMR measurement is shown in

figure 8. A FT NMR spectrometer follows roughly the same principles but is noticeably more complex [9].

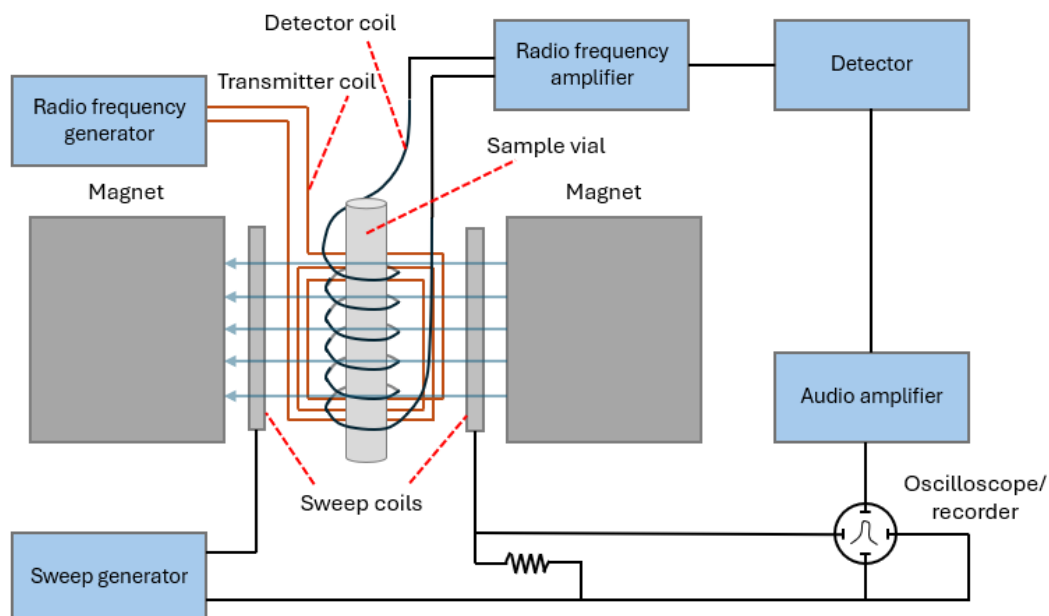


Figure 8. A simplified model of an CW NMR measuring assembly [9].

A standard NMR spectrometer setup contains a magnet that produces a homogeneous field, an emitter and a receiver of RF signals, a console to control the measurement, and software to interpret the data [13]. The console is usually a separate computer used to run the experiment.

3.3 Obtainable data from single and combined processes

As mass spectrometry reveals the spectrum of mass to charge ratio in the sample, the masses of various substances in the sample can be deduced. The ionisation methods as well as fragmentation of the molecules tend to result in predictable charges for the sample ions, so the masses of specific sample ions can be calculated. In the case, where only a few different masses are present the ratios of these specific ions can be calculated or with suitable ions the chemical composition of these ions can be estimated, since the masses of elemental nuclei as well as electrons are known. Though as the mass of an ion increases, likely so will the proportion of mass being bound to intramolecular bonds as energy increase. This means that for larger sample molecules, using the whole mass of the ion is not a good way to determine the chemical composition. In

this case methods as ICP can be useful, as for pure samples the proportion of various elements is easy to calculate. For larger molecules, such as polymers, the exact masses are not that important, as the repeat structure is known, and the exact length of the chains tend to vary. Much more useful information is the distribution of various masses now directly corresponding to specific chain lengths. Since chain length affects the mechanical properties of the material, it is important to know how widely the chain length varies. A narrow length distribution means similar properties throughout the material and a wide distribution means that the mechanical properties can vary noticeably within the material decreasing reliability. Regardless of whether the exact chemical composition can be deduced with MS, the information about the included elements is valuable when combined with other methods of analytical chemistry.

An NMR measurement produces a graph of signal intensity against chemical shift. Certain types of nuclei, differentiated by the shielding provided by nearby nuclei and the chemical surroundings as a whole, appear differently in the graph. For example, in hydrocarbons a signal varies according to what atom the ^1H is bonded to and to what atoms that atom is bonded, and even their neighbouring atoms can have an effect [9]. Additionally, specific structures, such as benzene, have easily recognisable typical spikes in the graph. In ^1H NMR the graph can be integrated to get relative proportions various types of protons. With this information as well as knowing the relation of various elements, with for example MS, the chemical structure of a given sample can be deduced. As substances produce a graph specific to them it is possible to compare known graphs to a measured one to determine the sample substance. Assuming that the measured graph is a linear combination of various graphs, information about mixed substances could be acquired as well.

As discussed, the chemical surroundings of the nuclei have an effect on the produced signal. Namely the crystal structure in a solid sample tends to affect the signal. This way solid-state ^{13}C NMR can be used to evaluate the crystallinity of polymers. As crosslinking and branching are dissimilar to the basic structure of polymers. They cause differences in chemical surroundings in the material and can thus be detected by NMR methods.

3.4 Choice of specific methods of analysis

As the samples of interest can vary largely, it is important to understand how to choose the correct method depending on the sample. Important factors in selecting the method or methods are the type of sample, desired information, speed, and cost. Speed

and cost often increase with more measurements, more complex measurements, and more accurate measurements. In some cases, the use case might require relatively quick results and so fast methods providing enough information are needed. As an example, DART coupled with some analysis method is a vastly applicable method for fast MS, and even suitable for field work.

For mass spectrometry to be possible the sample must first be ionised. For this, there exists a multitude of methods for varying types of samples. The most obvious first step to determining the proper ionisation method is to see in what state does the sample exist in. For solid samples it is often possible to dissolve the sample and use the solution for tests as it separates the molecules and makes many ionisation methods possible. Gaseous samples are commonly ionised with either electron impact ionisation or chemical ionisation depending on whether hard or soft ionisation is wanted. Volatile liquid samples can be vaporised to be treated as gaseous samples.

When a sample cannot be tampered with by for example dissolving it or otherwise the internal structure of the material or the molecules is wanted, NMR methods can prove useful. As the signal depends on the intramolecular bonds, NMR can be used to follow the progress of chemical reactions. For solid samples it is often important to study the structure as is, so the non-invasive solid-state NMR can provide valuable information.

3.5 Other noteworthy methods

While MS and NMR are powerful tools, they are not always necessary, nor can they always provide all the information needed. Various other methods exist for studying the composition and structure of substances while materials have a lot of various important properties that might require separate tests to properly quantify. For polymeric composite materials the most important information is the composition of the matrix polymer and the nature of the dispersed phase or the compositions of various layers in the case of layered films. Due to the wide use of polymer composites, their chemical and mechanical properties are widely known, though variance in results are easily possible as molecular mass, and thermal history can alter polymers' properties noticeably.

When studying polymer composites with MS, the focus is on learning about chemical composition, while another property that is often studied is chain length distribution. Notably, while MS seems like a practical way to measure chain length distribution, can the overlap of charges lead to a difficult-to-read spectrum as MS measure mass to charge

ratio instead of mass. This way, to get usable results can be laborious and other well-established methods may be more practical. Such a method for chain length distribution is gel permeation chromatography (GPC), where the polymer is dissolved and let permeate through a porous gel. The chain size affects the retention time in the gel and such different sizes of molecules can be separated for measurement [14]. Also, chemical composition and structure have other methods for their study. A commonly used method is infrared absorption spectroscopy (IR), which is based on how atoms and bonds can absorb photons with specific energies.

As for NMR, when studying polymer composites and the polymer matrices specifically, the obtained data provides information about different forms and the conformations of the materials such as tacticity and crystallinity. In composites the information about material or phase boundaries, available via NMR, can prove valuable. There are various other methods to acquire similar information. For polymers, there exists a method called differential scanning calorimetry (DSC), in which the temperature of the sample is scanned over a range and the heat flow into the material is measured. When the crystallization energy of the polymer is known, crystallinity of the polymer can be calculated. Another common method used with polymers and polymer composites is x-ray diffraction (XRD), where the intensity of diffracted infrared light is measured as a function of angle. XRD can provide information about the crystal structure as well as the phases of the material.

As the idea of composites is to combine some wanted properties of multiple materials or to achieve new properties unique to the composite, it is important to measure how well these properties were achieved. This can be anything from standard mechanical tests to thermal and electrical property tests depending on what the composite is designed to do and what properties are relevant in its environment of use.

4. EXAMPLES OF CURRENTLY USED PROCESSES FOR THE ANALYSIS OF VARIOUS POLYMER COMPOSITES

While standard methods exist and are widely in use, there are also numerous other and more specialised methods for studying the wanted information. Understanding the important underlying phenomena in a given study can help decide the best method for a specific case. This chapter goes briefly over examples various methods used in studies about polymer composites and highlights the vast range of possible ways to approach the study of these specific materials via the use of NMR and MS.

4.1 Applications relating to wood

As wood is widely used from structural applications to biofuel, it is important to understand its microstructure as well as its components' derivatives. Wood and synthetic cellulose composites can be used for various structural applications. Paper and cardboard structures are commonly used in packaging, and waste from their manufacturing, such as lignin, can be used as biofuel. Optimising the process from production to application and recycling is important in terms of creating a sustainable industry.

As the exact structure of cellulose is not yet understood [15], further research on the subject is relevant for possible synthesis of cellulosic materials. As natural materials, cellulose structures with hemicellulose and lignin have complex structures but extracting them from a sample can prove harmful to the integrity of the original structure. Thus, a non-invasive, non-destructive method is required. For this reason, solid-state NMR is an apt method for studying cellulosic structures. This subchapter contains discussion about some use cases of NMR and MS in the study of various wooden materials.

Polysaccharides and lignin form larger structures called lignin-carbohydrate complexes (LCC) by covalently bonding to each other. Understanding these bonds is important for biorefining processes and structural understanding of wood, as almost all lignin in wood is bonded to polysaccharides, such as hemicellulose, with covalent bonds. [16] The use of 2D NMR methods allows for the detection of specific bonds where the

bond is formed between specific atoms in lignin and polysaccharide structures. By studying samples of certain pine and birch species, Balakshin et al. [16] presented a method for directly quantifying these bonds. In addition, they found a difference in specific bonds in these samples, namely pinewood having more benzyl ether bonds and birchwood having more phenyl glucoside and γ -ester linkages. It was also found out that the use of high field NMR and a cryogenic probe improved the results.

Lignin not only bonds to carbohydrates around it, but as its structure is made up of various lignin units covalently bonded to each other, understanding and quantifying the bonds proves to be a useful insight. Like cellulose, lignin has high potential for biofuels, so understanding the degradation behaviour can lead to more efficient utilisation of the resource. Sheng et al. [17] conducted a study with oligomers comprised of lignin G- and S-units, where using ESI with linear quadrupole ion trap and FT ion cyclotron resonance MS fragmentation the patterns of the oligomers were studied. Multi-stage tandem MS was also used in the study. The study led to finding pathways for fragmentation of the oligomers. In certain positions functional groups were susceptible to breaking off easier and forming other molecules such as H_2O and CH_2O [17]. As the exact masses of possible combinations of the lignin units are known the specific point where the molecule breaks can be determined leading to understanding of strengths of various bonds and structures in lignin.

The main component of wood is cellulose. Cellulose itself is found in a few forms: amorphous, semicrystalline, and various crystalline forms. The most important allomorphs are the naturally occurring I_α and I_β crystal structures as the cellulose fibres themselves are composites of these phases. [18] To gain a better understanding of the allomorphs, as pure samples as possible are needed. Kono et al. [18] approached this by biosynthesising cellulose with bacteria, algae, and small marine animals to acquire reproducible samples. Plants can also be used for acquiring cellulose samples. In the study, a cellulose sample could be annealed to increase the prominence of I_β in the sample. While these samples were not perfect, the resulting spectra from CP/MAS ^{13}C NMR studies could be interpreted as linear combinations of spectra from different phases. Then according to the portions of the phases, correcting terms could be deducted. With the results from the study, the signal spikes for different carbons in I_α and I_β cellulose crystals could be assigned furthering the understanding of the structure of the material [18].

When cellulose is dissolved and coagulated, it tends to form cellulose II crystals in a material dubbed *regenerated cellulose*. As cellulose is a fibrous material, the orientations of the molecules have important effects on the mechanical properties of the material. This can be examined with *rotor synchronised magic angle spinning* (ROSMAS) NMR by investigating *chemical shift anisotropy* (CSA) and comparing it to an analytical model. [19] This way differences in stretched and unaltered cellulose CSAs were found giving understanding about molecular orientation within the materials.

Sometimes it is not necessary to understand the exact microstructure of a wooden material, but knowing more general information about it is. Recognising the species is a practical way to achieve this. Plant cells contain metabolites and the exact metabolites, and their relative amounts vary species by species. Declerck et al. [20] present a method using DART ToF-MS with a sorting algorithm to identify several different species of wood. The use of DART streamlines the process by simplifying sample preparation. This way the species of the sample can be recognised or at least narrowed down with high accuracy [20] using a small sliver of material. While recognising metabolites in the material does not directly tell anything about the structure, this kind of roundabout way can be sufficient, as reference data about known species can be utilised.

4.2 Applications relating to various polymer composites

More traditional polymer composites are used for a multitude of different uses. These can vary from multilayer polymer films in packaging to high performance fibre composites as a lightweight structural material. As such, relevant structural information usually changes for each instance. Common subjects of study include adhesion between different parts of the composites as well as the nature and amount of particulates in the composite. Often there is not a universal method for studying a given property, so the methods vary according to the restrictions of the material of interest. In this subchapter, some of such methods are discussed in more detail.

In a study conducted by Lyu et al. [21], improvements to matrix-fibre adhesion in an aramid-epoxy composite were studied. The improvements were achieved by copolymerising the poly-p-phenylene terephthalamide (PPTA, known by its commercial name Aramid) with 5-amino-2-(4-aminophenyl) benzimidazole (PABZ) creating poly-p-phenylene-benzimidazole terephthalamide (PBIA). This copolymer was then treated with aqueous HCl protonating the double bonded nitrogen atom in the imidazole ring leading to stronger interactions between the fibre surface the epoxy matrix. With the use of H^1 NMR

the protonated and unprotonated polymers could be compared and the protonation of the material could be confirmed. Additionally, information about the assimilation of the hydrogen atoms in the imidazole ring was acquired. The findings of the NMR measurements were supported by IR spectroscopy.

MXenes are a fairly new group of materials with promising properties and as such, viable methods to utilise them are studied. Structurally MXenes are two-dimensional sheets of early transition metals and either carbon or nitrogen in a planar arrangement. MXenes are made by etching MAX phases leading to a loose stack of MXene sheets. MXenes are difficult to use by themselves so a way to utilise them is to disperse them into a polymer matrix. However, agglomerated stacks of MXene sheets fall short of the potential of the material. In a study conducted by Yi et al. [22], a proposed solution to the aforementioned problem was to mechanically wet grind the material to acquire sheets of only one or few layers. As the surface of the MXene used is hydrophilic, it can be bonded well to polyvinyl alcohol (PVA) due to the hydroxyl side group in PVA. By dispersing the fine MXene to PVA in a water suspension, good dispersion of the sheets in the solution and thorough interaction between the sheets and the matrix could be achieved. This water suspension is also a good form to study the material's intermolecular interactions with NMR. Low field nuclear magnetic resonance (LF-NMR) was used to study the suspension as a specific relaxation time is dependent of dipole interaction characteristics of intermolecular protons. With the LF-NMR measurements changes in the interactions could be noticed and from that changes in the microstructure could be deduced. The information gathered about the change in microstructure was supported by rheological studies. The change in microstructure confirmed by NMR and rheological studies could then be connected to improvements in electrical and thermal conductivity as the MXene was now better dispersed in the matrix leading to better pathways for electron movement and less randomness in the polymer composite structure.

Carbon fibres are widely used due to their desirable properties and as such, many manufacturing methods exist for different specific circumstances. For fast curing methods, for example vinyl esters are used as they have desirable properties for a matrix with the downside of weak interfacial adhesion with the fibre. The adhesion can be improved by the use of sizing agents to roughen the fibre surface and adding functional groups to the interface. In a study by Jiao et al. [23] a sizing agent was designed for specifically carbon fibre-vinyl ester interface. The agent was synthesized by reacting glycidyl methacrylate (GMA) and 4'4-diaminophenyl methane (DDM) creating N-(4'4-diaminophenyl

methane)-2-hydroxypropyl methacrylate (DMHM). For the validity of the study the creation DMHM needed to be confirmed. For this purpose, ^1H NMR and ^{13}C NMR were used together with Fourier transform infrared spectroscopy (FTIR). Changes in the NMR spectra could be associated with the reaction as spikes relating to structure only present in the reactants or the product were measured thus confirming the success of the reaction. With the synthesis of the sizing agent confirmed its effects on the interface and interfacial adhesion could be measured with other methods.

The use of graphene is increasing and being widely studied due to its desirable properties such as thermal, electric, and mechanical properties. However, due to the structure of graphene being a single-layer carbon lattice its production, and use as is, is difficult. In reality the name "graphene" is used for graphitic sheets as few layers thick as possible. To easier incorporate graphene into materials, it can be dispersed into a polymer matrix as graphene flakes. In a study by Brennan et al. [24], two different types of graphene from different sources were dispersed into a poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) matrix and a polymethyl methacrylate (PMMA) based matrix called MT46 to be able to characterize the distribution of graphene in the matrices. The samples were then placed on substrate surfaces made of polyethylene terephthalate (PET), or aluminium for various tests. When studying the electrical properties of the composites, the results varied a lot between graphenes and matrices and to better understand the underlying reasons for this, further studies into the structure of the composites was necessary. An important property of the composites to note is the fact that the matrices are high carbon content molecule chains and graphene is a carbon lattice, so the materials are not very dissimilar for many characterisation methods. The use x-ray photoelectron spectroscopy revealed a number of contaminant elements and so the use of ToF-SIMS was decided to gain more information. First the presence of contaminants was also confirmed by ToF-SIMS. Then more information about the dispersion of the graphene flakes in correlation to the contaminants was wanted. It was hypothesised that some of the contaminants, such as sodium, were related to surfactants used in the production of the graphene flakes. When comparing the MT46 matrix with and without graphene, an increase in the presence of sodium was noticed pointing at graphene introducing more sodium into the material. The same discrepancy was also confirmed by 'washing' the graphene as to remove any residue surfactants and studying it with ToF-SIMS again. By comparing the ionic maps produced by ToF-SIMS to optical micrographs it could be confirmed that the areas of higher Na^+ -content correlated with the presence of agglomerated graphene flakes. As the electrical discrepancies could be explained by

the contaminants the main goal of studying methods for discerning the dispersion of graphene in a polymer matrix was achieved by proving the usefulness of ToF-SIMS in this context.

When polymers form multilayer films, important information to gain includes layer thicknesses and interphase thicknesses, granted the polymers are already known. Wagner [25] studied the use of ToF-SIMS for measuring the layer and interphase thicknesses with thin polymer films. In the study, multilayer films were spin-cast onto silicon/silica substrates and the choice of polymers included PMMA, poly(2-hydroxyethyl methacrylate) (PHEMA), and trifluoroacetic anhydride-derivatised poly(2-hydroxyethyl methacrylate) (TFAA-PHEMA). The use of ToF-SIMS here was based on how the different polymers degrade and break down characteristically, when subject to primary ion bombardment. These broken off parts are the secondary ions of which are measured by the mass spectrometer. A problem faced by Wagner was that some of the characteristic ions were not completely unique and could break off from other polymers too. This was solved by data normalisation techniques. Another problem relating to the method is how monoatomic primary ions can damage the structure of the sample in a harmful way and lead to less information to be available. To solve this, the primary ion used was SF_5^+ , which due to its larger size caused less ion-induced damage of the sample area and more clean scission of the characteristic ions. The resulting intensities of the characteristic ions could then be plotted against the progress of the measurement, in this case the total ion dose. The thicknesses of the polymer layers were measured with ellipsometry. From the layer width and the ion intensity graphs the thicknesses of interfaces could be measured, though the interpretation of the interface from the graph had to be defined and it was set to specific relative values of the maximum intensity of a signal. The study proved the usefulness of ToF-SIMS in the measurement of thin polymer films.

As demonstrated by the given examples, the variance in specific methods and uses is vast. The methods used can often be standardised methods for better comparability or specifically designed methods as dictated by the needs of the study. The targets of the methods also change with the needs of a study. Studies can focus directly on the target structure, indirectly on the products of relevant reactions, or on the presence of various compounds to verify relevant processes. The information gained through MS or NMR are often useful as is but combined with other methods with varying levels of overlap in gained information, the methods are essentially always useful and often necessary. Having multiple methods providing evidence towards a hypothesis brings validity to the

study and cross-referencing data acquired through other methods can lead to finding correlation between properties of the subject of study.

5. SUMMARY

Polymers and polymer composites provide a wide range of possibilities as materials. Fibre reinforcements can be used to increase the strength of polymers while maintaining relatively low weight, various polymers can be layered on top of each other to create films serving many purposes, and wood is in use in a multitude of situations. The forms and tunability of polymer composites mean that they can be used almost anywhere.

There are numerous factors that contribute to how polymer composites can fulfil their intended purposes. An often-relevant factor is adhesion between various constituents of the composite. Other relevant factors are the dispersion of the dispersed phase, isotropy and homogeneity of the matrix, and simply the microstructure. For this reason, it is necessary to be able to determine how well these factors are achieved. Numerous methods for measuring various properties and determining information about the materials are possible and widely in use. Two promising and common methods are mass spectrometry and nuclear magnetic resonance spectroscopy.

Mass spectrometry can be used to study a wide variety of materials as the samples can be gaseous, liquid, or solid. Many options in the ionisation step of the process enable to choose the nature of the measured ions as information about just elements, complete molecules, or broken off parts of molecules might be wanted. With this the presence of certain compounds, breaking characteristics of compounds, or elemental data can be acquired, and much more. The style of measurement and the equipment can be highly tuned to fit a specific use case as the different methods can provide data of the sample as for example just a spectrum over the designated m/z range or a map of the materials surface showing the presence different elements. Depending on the needs of the task, the analysis method can be chosen and with that the equipment used for the measurements as some analysers can take up a whole room while some are small enough for field work.

Nuclear magnetic resonance offers a wide selection of possibilities for analysis of a variety of samples. Liquid-state measurements can be used for liquids, dissolvable compounds, or suspensions. Solid-state are also useful as many polymers and composites need to be studied whole. As the most common NMR spectroscopies are based on ^1H and ^{13}C nuclei, they are well suited for the study of polymers and polymer composites as

polymers are usually long hydrocarbon chains. As the NMR spectra give information the chemical surroundings of the nuclei, information about chemical bonds as well as intra- and intermolecular structures can be deduced. For composite structures, the properties of material in the finished form are often more relevant than those of its constituents. Thus, being able to study the material as is important and NMR is capable of that.

Usually, the information gained from a single method of study is not enough and supporting or other relevant information is needed. NMR and MS work together well as the elemental data available with MS helps interpret the NMR results and some MS methods can provide similar data as NMR to improve validity of the measurements. However, these two methods are not usually enough even together and other measurements can be necessary to get the required information. These methods usually give information different from the results of MS and NMR so correlations between the sets of data can be studied. Overlapping information is also sometimes wanted as many different sources pointing at the same result decreases the chance of errors.

Wood and wood-based materials are widely used natural materials. Wood-based industries have side streams of excess and unusable materials. There is value in recycling and refining these materials as well as improving and recycling the wood-based materials in their intended form. For example, understanding how lignin breaks down depending on the bonds between the repeat units can provide useful information. This can be achieved bombarding a lignin sample with ions and using mass spectrometry to measure the m/z of the ions that break off. Other in use methods include but are not limited to recognising wood species by their metabolites by DART MS and using NMR methods to study the crystal allomorphs and orientations of cellulose. The methods are highly tuneable for a wide range of use and enable detailed studying of many forms of wood-based materials.

For particle polymer composites it is important to study the dispersion of the particles in the matrix and interactions between the matrix and the particles. MS and NMR both provide ways to study these as particles can be directly or indirectly studied by MS and the change in chemical surroundings on the matrix-particle-interface can be seen in NMR spectra. For fibre reinforced polymers the most important interaction to study is the matrix-fibre-interfacial adhesion. A way to approach their study is to verify the synthesis or presence of sizing agents when fabricating the composite. With multilayer polymer films interfacial adhesion is also important but so are interphase properties. As an example, when knowing the characteristic ions of the polymers under ESI, SIMS can be used

measure the thickness of the layers as well as the interphase. Both NMR and MS proved useful in studying different polymer composites and they both can be tailored to specific needs on a case-by-case basis.

NMR and MS are powerful methods for studying polymer composites and their constituents. Both methods offer a wide range of variation to fit many kinds of situations as the materials and relevant properties vary largely. While both methods are powerful on their own, their use together with other methods is often necessary or at least useful.

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