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Doctoral Thesis

Crosslinking and Ageing Of Ethylene-vinyl Silane Copolymers

Síťování a stárnutí etylen-vinyl silanových kopolymerů

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1

ABSTRACT

Nowadays, polyethylene is one of the most produced polymers due to its low price and useful properties. It is one of the oldest synthetic polymers and the development of its structure and properties is closely connected with important discoveries in the field of polymer synthesis and modification. Crosslinking of polyethylene is a modification allowing significant improvement of thermal and mechanical properties that are necessary for advanced applications. Without crosslinking, polyethylene does not have sufficient thermal, mechanical and weather resistance required for the safety of products, such as wire insulation, hot water pipes and others. For this reason, research of crosslinked polyethylene is important, particularly the study of the influence of crosslinking performed at different conditions on the morphology, mechanical and thermal properties of the polymer.

This work investigates the behavior and property evolution of ethylene-vinyl trimethoxysilane copolymers upon crosslinking and thermal ageing in the oven at two different temperatures. The influence of additives (crosslinking catalyst and antioxidant) and temperature on the chemical structure, morphology and mechanical properties was investigated. The silane crosslinked copolymers used in this work have properties similar to LDPE and is usually used for the production of cable insulation.

It was found that two parallel processes influence the final properties: (1) crosslinking reactions and (2) improvement of crystalline order. These two processes play different role depending either the ageing proceed below melting temperature or above melting temperature. Chemical structure of EVTMS copolymers has an impact on molecular arrangement and changes of morphology due to melting and crosslinking then significantly influence the final mechanical properties. Behavior of EVTMS copolymers under these conditions can seriously affect the safety and durability of the products.

Keywords: silane crosslinked polyethylene, ethylene-vinyl trimethoxysilane copolymer, thermal ageing, silane crosslinking, morphology, chemical changes, cable insulations.

ABSTRAKT

Polyetylen je jeden z nejvíce používaných polymerů v dnešní době, zejména z důvodu jeho nízké ceny a využitelných vlastností. Je jedním z nejstarších syntetických polymerů a vývoj jeho struktury a vlastností je úzce spojen s významnými objevy v oblasti syntézy a modifikace polymerů. Síťování polyetylenu je jedna z modifikací, která umožňuje významnou změnu tepelných a mechanických vlastností, nutných v náročnějších aplikacích. Bez úpravy síťováním nemá polyetylen dostatečné tepelné a mechanické vlastnosti a odolnost vůči stárnutí, které jsou vyžadovány pro bezpečnost určitých výrobků, jako jsou např. izolace kabelů a teplovodní trubky. Z tohoto důvodu je důležitý i výzkum v oblasti síťování polyetylenu, zejména vliv různých podmínek síťování na morfologii, mechanické a tepelné vlastnosti.

Tato práce zkoumá chování a vývoj vlastností etylen-vinyl trimetoxysilanových kopolymerů při síťování a tepelném stárnutí v sušárně při dvou různých teplotách. Byl posuzován vliv aditiv (katalyzátor síťování a antioxidant) a teploty na chemickou strukturu, morfologii a mechanické vlastnosti. Silanem síťované kopolymery použité v této práci mají podobné vlastnosti jako LDPE a obvykle se používají pro výrobu kabelových izolací.

Bylo zjištěno, že dva paralelní procesy ovlivňují konečné vlastnosti: (1) síťovací reakce a (2) morfologické změny. Tyto dva procesy hrají různou roli v závislosti na tom, zda stárnutí probíhá pod teplotou tání nebo nad teplotou tání. Chemická struktura EVTMS kopolymerů má dopad na uspořádání molekul a změny v morfologii v důsledku roztavení a síťování pak výrazně ovlivňují konečné mechanické vlastnosti. Chování EVTMS kopolymerů za těchto podmínek můžou vážně ovlivnit bezpečnost a životnost výrobků.

Klíčová slova: Silanem síťovaný polyetylen, etylen-viny trimetoxysilanový kopolymer, tepelné stárnutí, síťování silany, morfologie, chemické změny, kabelové izolace.

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"There is a single light of science,

and to brighten it anywhere

is to brighten it everywhere."

Isaac Asimov

CONTENT

THEORETICAL BACKGROUND

1. INTRODUCTION

Plastics are undoubtedly one of the most important materials used in modern era. They are composed of polymers – substances of macromolecular nature. Although, we are literally surrounded by polymers of organic or inorganic origin, the history of development of synthetic polymers is relatively short.

First polymers utilized by human are dated back to a period of 15 000 years BC, when caveman created murals of colors from available natural materials such as eggs, blood, skin, bones, plants and others. It was unaware using of natural macromolecular substances and this trend essentially persisted until the early 19th century, when many researchers began experimenting with the available natural polymer substances in order to adapt their properties to actual needs.

Previously used natural polymers of botanical and animal origins, such as cellulose, natural rubber, gutta-percha, casein, keratin, shellac, silk and others, were modified by physical and chemical processes to produce final articles.

Crosslinking was one of the first chemical treatments, whereby resins were produced by using of proper crosslinking agent. At that time, crosslinking processes related entirely with thermosets (resins). In 1839, American Charles Goodyear discovered vulcanization (crosslinking) of natural rubber, which is one of the most important processes in rubber industry. The first successful synthetic thermoset was developed by Leo H. Beakeland in 1906 by the reaction of phenol and formaldehyde and products was named after the discoverer – Bakelite.

The origins of synthetic thermoplastic polymers can be dated to the same period. The first semi-synthetic thermoplastic was celluloid composed of nitrocellulose (Alexander Parkes, in 1862). Other synthetic polymers have been sufficiently explored and utilized in the early 20th century. Polyvinyl chloride, polystyrene, polyoxymethylene, polyethylene, polyamide, polypropylene and others were gradually discovered [1, 2].

The real expansion and development of plastics thus began in the 20th century and the plastics became an invaluable part of human life. Boundaries of their application possibilities have grown exponentially and they become dominant even in the industries where traditional materials such as glass, wood, paper and metal are used. It is not surprising that the production of plastics has an increasing trend, while the production of other materials more or less stagnates. The only exception was the global economic crisis in 2009, when rapid increase of plastics production was suspended (Fig. 1.1).

However, plastics production disproportionately increases to the world population growth, but this increase is much more significant mainly in

developed countries, where the consumption and waste rise with the standard of living.

Over the years, the development of new polymers has been stabilized, because it was easier and cheaper to modify polymers for required properties than to synthesize new polymers with a different chemical structure. Plastics were gradually divided into three basic groups: commodity, engineering and high performance plastics. The commodity plastics include polyethylene, polypropylene, polystyrene and polyvinyl chloride, which contribute about 70% to global production of synthetic plastics [3].

Volume of production and consumption of the commodity plastics is the highest due to the relatively low market price, easy production and extensive applications, moreover, they provide area for intensive research either in the basic or modified state. Their specific characteristics, such as low density and high variability of properties for "plastics tailoring", provide many possibilities to improve our living standard in different ways.

Crosslinking is one of the ways how to significantly affect the properties of plastic product. Process of crosslinking involves the formation of tri-dimensional structures – gels, which cause significant changes of material properties indispensable in numerous applications. Therefore, the crosslinking of polyethylene, the most widely produced polymer, is very important modification used in miscellaneous sectors from automotive to packaging industry.
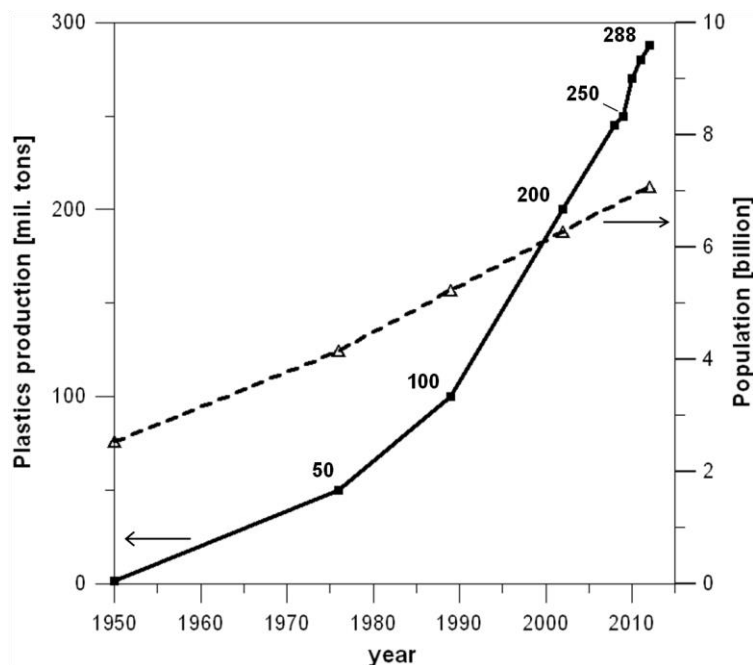

Fig. 1.1: Worldwide growth of population and plastics production (years 1950-2012) [3, 4].

8

2. POLYETHYLENE

2.1 History of polyethylene

For the first time, a flaky substance with chemical structure similar to polyethylene was made in 1898 by Hans von Pechmann. However, the origin of industrial production of polyethylene (PE) goes back to 1933, when branched, low density polyethylene (LDPE) was made in Imperial Chemical Industries, Ltd. (United Kingdom). This type of polyethylene was synthesized from gaseous ethylene by high-pressure and high-temperature polymerization in the presence of organic peroxide.

Synthesis of linear high density polyethylene (HDPE) was another important milestone. This synthesis directly relates with stereospecific catalysts, which were discovered in 1950s. They allowed the production of PE with linear molecular structure at substantially lower pressure and temperature. Several types of stereospecific catalysts had been discovered, such as Philips catalysts based on chromium catalysts supported on silica, or molybdenum catalysts on alumina. The most important invention of stereospecific catalysts were named after inventors - Ziegler-Natta (ZN) catalysts, which are based on titanium and organic aluminum substances.

In the next period, different types of PE with specific structure and morphology were gradually evolved. In 1970s, medium density polyethylene (MDPE) and subsequently linear low density polyethylene (LLDPE) were synthesized. At the end of 1970s, metallocene single site catalysts were discovered. Metallocene catalysts allow much better control of the macromolecular structure, such as better comonomer distribution, hyper-branching of monomers, bi-modal or narrow MWD and others. They consist of active metal complexes (Zr, Fe, Ti, Ni, Pd, etc.) surrounded by aromatic ligands.

Examples of polyethylene catalysts are in Fig. 2.1 [5-10].

a) di-t-butyl peroxide b) silica surface with CrO_3

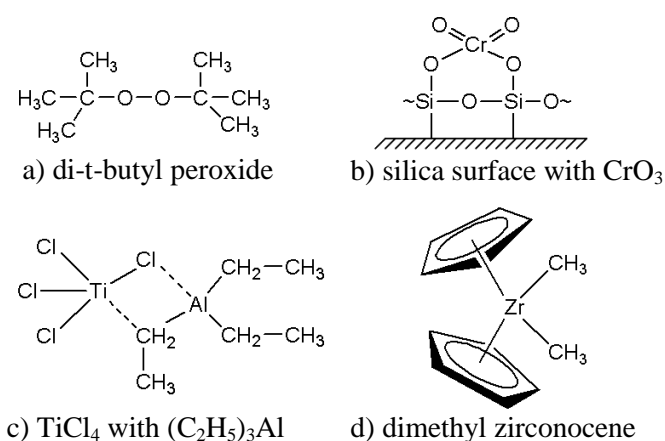c) $TiCl_4$ with $(C_2H_5)_3Al$ d) dimethyl zirconocene

Fig. 2.1: Examples of PE polymerization catalysts: a) organic peroxide, b) Phillips catalyst, c) Ziegler-Natta catalyst, d) metallocene single site catalyst [6, 8].

2.2 Basic types of polyethylene

Nowadays, the polyethylene is industrially produced by polymerization of ethene (ethylene) by using different types of catalysts and process conditions (temperature, pressure). Due to various synthetic technologies, it is possible to produce several grades of PE with different structures and properties, which vary in short or long chain branching, average molecular weight, MWD, comonomer content and others. These polyethylene grades are mainly classified according to their density, which directly relates to crystallinity and thus to the mechanical and thermal properties.

The basic grades of polyethylene are:

- LDPE, low density PE (0,910-0,925g/cm^3),
- MDPE, medium density PE (0,926-0,940 g/cm^3),
- HDPE, high density PE (0,940-0,965 g/cm^3).

These grades are not defined sharply. Depending on the density, the structure of macromolecules and the molecular weight distribution, further types are:

- ULDPE, VLDPE – ultra/very low density PE,
- LLDPE – linear low density PE,
- LMDPE – linear medium density PE,
- HMW-HDPE (or HMWPE) – high molecular weight-high density polyethylene,
- UHMWPE – ultra high molecular weight PE.

Further, the categorization of PE includes special catalyst types (mPE - metallocene PE), copolymers (vinyl acetate - EVA, vinyl alcohol – EVOH, acrylic acid - EAA, cyclic olefins - COC), filled grades, bimodal grades and others.

It should be noted, that except for LDPE, HDPE and UHMWPE, all the types of polyethylene are produced by copolymerization with a certain amount and type of α-olefins (up to 12%), such as butene-1, hexene-1, octene-1, usually by using ZN catalysts. All PE grades and their production conditions are summarized in Fig. 2.2.

Crosslinked polyethylene (XLPE, PEX) is a special grade, which theoretically can be prepared from each types of polyethylene [6, 11]. Crosslinked polyethylene is discussed in detail in the next chapters.
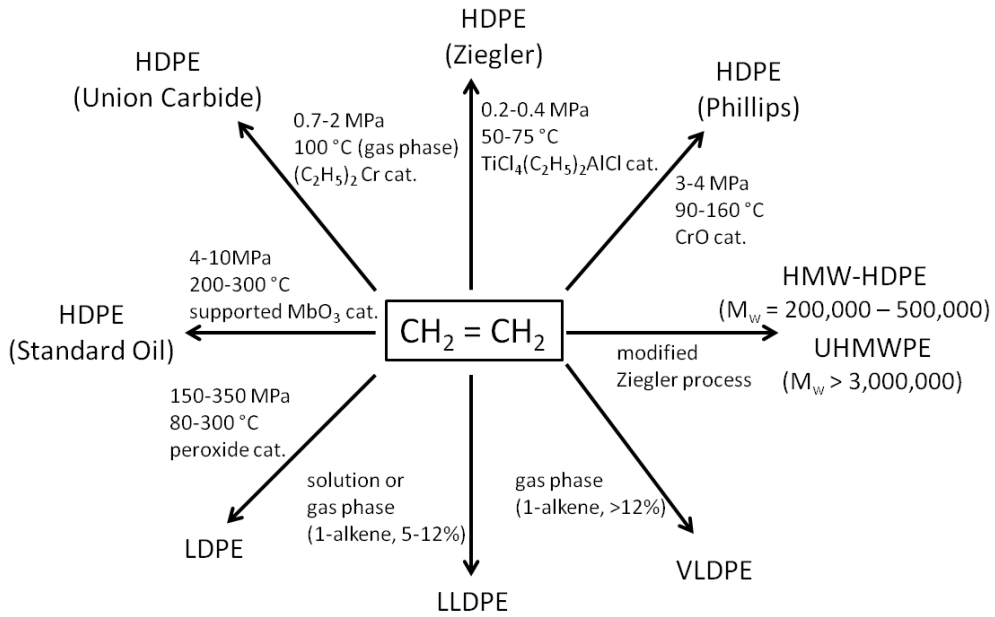
HDPE
(Ziegler)

HDPE
(Union Carbide)

HDPE
(Phillips)

0.7-2 MPa
100 °C (gas phase)
$(C_2H_5)_2$ Cr cat.

0.2-0.4 MPa
50-75 °C
$TiCl_4(C_2H_5)_2AlCl$ cat.

3-4 MPa
90-160 °C
CrO cat.

HMW-HDPE
(M_w = 200,000 − 500,000)

4-10MPa
200-300 °C
supported MbO_3 cat.

HDPE
(Standard Oil)

$CH_2 = CH_2$

modified
Ziegler process

UHMWPE
(M_w > 3,000,000)

150-350 MPa
80-300 °C
peroxide cat.

solution or
gas phase
(1-alkene, 5-12%)

gas phase
(1-alkene, >12%)

LDPE

VLDPE

LLDPE

Fig. 2.2: Production conditions of different PE grades [11].

2.3 Structure and properties of PE

Polyethylene has many attractive features, such as excellent electrical insulation properties over a wide range of frequencies, very good chemical resistance, good processability, toughness, flexibility and low price which make it the world's most produced polymer.

Structure and properties of PE can be presented through the three basic types, which differ in production and macromolecular structure. Fig. 2.3 shows the basic molecular structure of LDPE, LLDPE and HDPE.
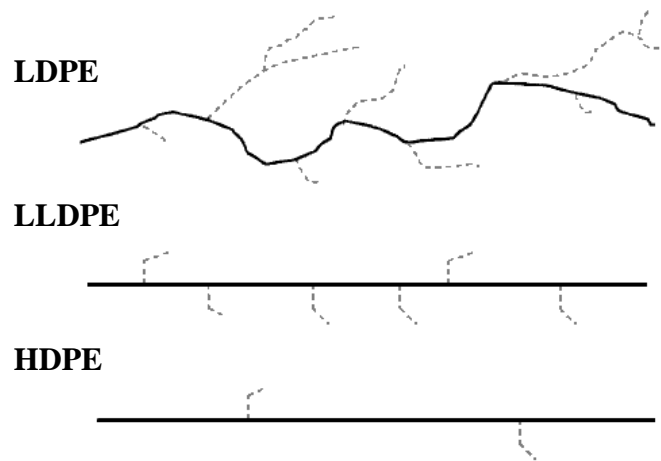

LDPE

LLDPE

HDPE

Fig. 2.3: Molecular structure of major types of polyethylene, where solid lines represent the backbone and dashed lines represent branching [6].

11

Synthetic methods of these types are different and lead to various macromolecular structures which have a direct impact on the density, crystallinity and consequently on the mechanical, thermal, processing and other properties.

In addition to the average molecular weight and molecular weight distribution, these polymers differ in intensity and sizes of side chains (branches). The presence of branch points correlates with crystallization ability. HDPE and LLDPE are both referred to linear polymers. However, LLDPE contains a significantly larger number of short branches (due to comonomer) than HDPE causing an obstruction in periodic folding of macromolecules during crystallization, and hence density and crystallinity of LLDPE are lower than that of HDPE. On the other hand, LDPE has long and frequent branching which is not limited to the main chain only, but continues in the side chains. Such branching in LDPE has similar effect to crystallinity as short branches in LLDPE, but significantly affects the rheological behavior. LDPE has the lowest density, the least opacity and a lower melting point, yield point, surface hardeness and Young's modulus. Furthermore, lower crystallinity leads to the greater permeability to gases and vapors. However, while LLDPE has improved physical properties, LDPE can be processed much better, for instance by blow molding, due to lower viscosities at similar molecular weight. This is also the reason, why the production of LDPE, the oldest type of polyethylene, is still indispensable [12, 13, 14].

Overview of the characteristics of three PE types is in Tab. 2.1.

Tab. 2.1: Properties of LDPE, LLDPE a HDPE [11, 15].

	LDPE	LLDPE	HDPE
Production	Radical polymerization of ethylene initiated by organic peroxides	Copolymerization of ethylene with α-olefins initiated by ZN, chromium or metallocene catalysts	Polymerization of ethylene initiated by ZN or Phillips catalysts
Density (g/cm^3)	0,910-0,940	0,915-0,95	0,940-0,965
Glass transition temperature (°C)	-110	-110	-110
Melting temperature (°C)	105-120	105-120 (depends on branching)	120-130
Tensile strength (MPa)	10-17	8-20	20-35
Elongation at break (%)	200-600	500-900	180-1000
Young's modulus (MPa)	96-262	250-700	413-1241
Flexural modulus (GPa)	0,245-0,335	0,35	0,75-1,575

3. CROSSLINKING OF POLYETHYLENE

3.1 Polyethylene crosslinking methods

Crosslinking can be considered as one of the most important modifications of the polymers. During the crosslinking, the macromolecules are linked by crosslinks and the three-dimensional network is formed. Polyethylene is saturated polymer without any reactive functional side-groups, thus the crosslinking process differs from the curing of liquid resins or unsaturated rubbers. Therefore, it is necessary to create reactive sites on the macromolecules, which enable a formation of covalent carbon-carbon bonds or other types of bridges, such as siloxane bonds.

Different procedures may be employed for the initiation of PE crosslinking. These procedures are either physical or chemical nature. The main crosslinking methods are:

- crosslinking by radiation,
- crosslinking by peroxides,
- crosslinking by silane compounds.

Overview of the crosslinking methods of polyethylene is shown in Fig. 3.1 [16, 17].
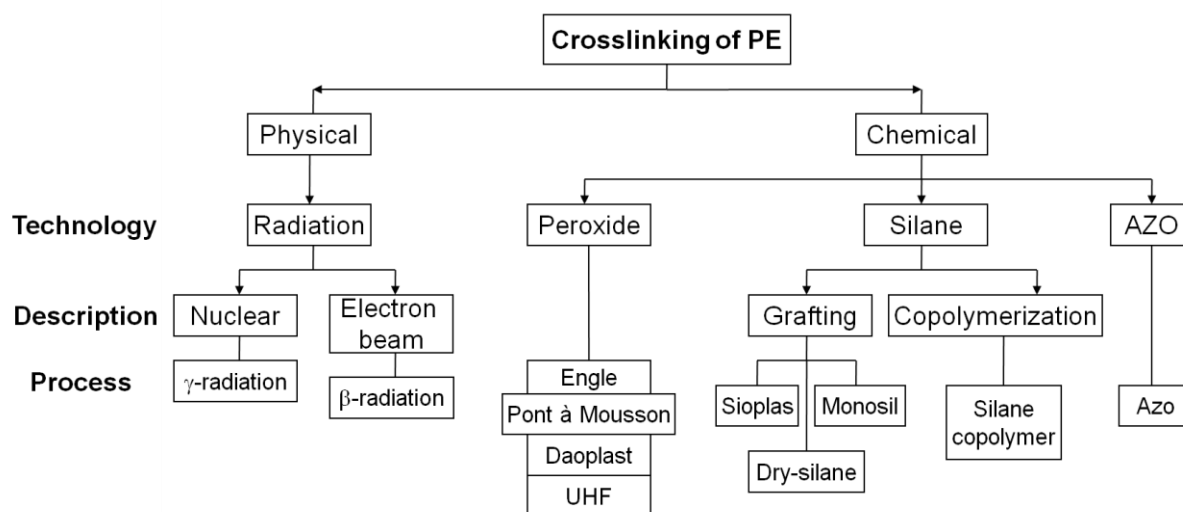

Fig. 3.1: Scheme of crosslinked PE production [16, 17].

Historically, the oldest industrially used method is radiation crosslinking (1950s). Consequently, crosslinking by peroxides was introduced in 1955 and at the end of the 1960s, the technologies for crosslinking by silane compounds began to promote. It should be noted that crosslinking by radiation is a physical method, while the others, crosslinking by peroxides and silane compounds, are known as chemical methods. Benefits and drawbacks of these methods are summarized in Tab. 3.1.

Tab. 3.1: Benefits and drawbacks of PE crosslinking methods [16, 24].

	Radiation crosslinking	Peroxide crosslinking	Silane crosslinking
Benefits	• post-processing crosslinking, • one step process in solid or molten state, • variable crosslinking conditions, • pure process without additives.	• the most uniform and homogeneous crosslink distribution in whole volume, • high gel content, • crosslinking of thick-walled articles.	• post-processing crosslinking in solid state, • polar nature of crosslinks, better compatibility with fillers, • variable crosslinking conditions depending on composition, • crosslinking is without free radical formation.
Drawbacks	• heterogeneous network, • side reactions altering a polymer structure, • free radical accumulation, • difficult to crosslink thick article with irregular shapes, • safety precautions against ionizing radiation, • high initial investment cost.	• crosslinking proceeds only in molten state, • peroxide is needed, • possible side reactions, • decrease of crystallinity, • sensitive to impurities, • energy intensive process, high scrap rates and low outputs.	• heterogeneous network, • additional compounds is needed for crosslinking, • degree and uniformity of crosslinks is highly dependent on catalysts and water diffusion, • curing time is very high, • grafting involves free radical formations and possible side reactions, • possible premature crosslinking of pellets during storage.

3.1.1 Radiation crosslinking

Radiation crosslinking of PE has been known for several decades and it belongs to the economically most successful products of radiation chemistry research. Radiation technology is a physical method which allows generating active intermediates in the solid, as well as in the molten polymer within a large temperature interval. There are several techniques intended for free radical formation in polymer, mostly involving high energy waves or particles. The radiation, such as UV, X-ray and ultra high frequency radiation can be used for crosslinking, however the industrially most employed method are electron beam

and gamma irradiation. While gamma irradiation is usually more economical at lower doses and for large high density parts, electron beam is commonly used for small low density parts and linear products processed reel to reel usually with limited thickness (wires, cables, tubes).

Radiation crosslinking seems to be cleaner process opposite to peroxide or silane crosslinking, since no additives and catalyst are required to initiate the reaction, although there is a possibility to use some co-agent for increasing the efficiency of radiation. Furthermore, radiation dose can be varied in a wide range and thus the reaction can be controlled more precisely. On the other hand, high energy radiation can cause not only alteration in the chemical structure of polymer through mechanisms such as crosslinking, chain scission, oxidation, double bonds formation, long chain branching, but also can cause trapping of charge within the polymer leading to deterioration of long-term and electric properties.

However, the main radiation-initiated reactions include crosslinking and scission due to absorption of energy which initiates a free radical process (Fig. 3.2). The crosslinking mechanism involves the cleavage of a C-H bond in the polymer chain to form hydrogen atom and polymer radical. Then two adjacent polymer radicals combine to form a crosslink. On the contrary, scission is the opposite process in which the cleavage of C-C bonds occurs. While crosslinking increases the average molecular weight, scission reduces it. Gas release can occur during these reactions due to hydrogen liberation and release of small amount of aliphatic organic compounds.
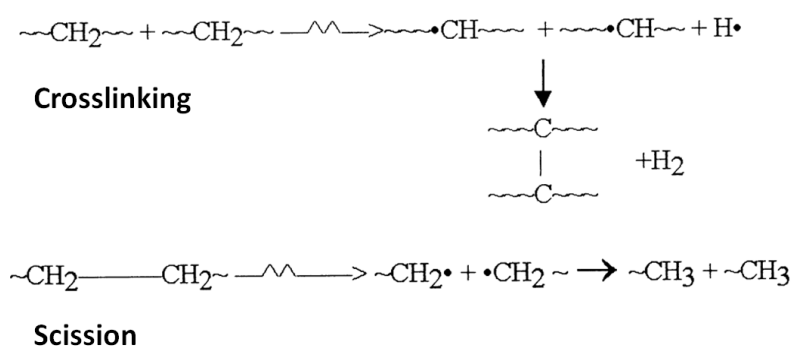
$$\sim\!CH_2\!\sim + \sim\!CH_2\!\sim \longrightarrow \sim\!\bullet CH\!\sim + \sim\!\bullet CH\!\sim + H\bullet$$

Crosslinking

$$\sim\!C\!\sim$$
$$|\qquad +H_2$$
$$\sim\!C\!\sim$$

$$\sim\!CH_2\!\!-\!\!-\!\!-\!\!-\!\!CH_2\!\sim \longrightarrow \sim\!CH_2\bullet + \bullet CH_2\sim \longrightarrow \sim\!CH_3 + \sim\!CH_3$$

Scission

Fig.3.2: Two basic mechanisms within the radiation crosslinking process [21].

Radiation dose is an important parameter. At low doses, crosslinking proceeds mainly in amorphous region. At medium doses, crosslinks are formed on the lamellar surface and between individual lamellae. Further increase of radiation dose can lead in breaking or crosslinking inside the crystallites leading to amorphization and loss of deformation properties.

The crosslinks density at a given radiation dose depends on the amorphous fraction of polymer, especially if the crosslinking takes place in the solid state [16, 18-23].

3.1.2 Peroxide crosslinking

Peroxide crosslinking is a method, in which organic peroxide initiator, such as dicumyl peroxide or tert-butyl cumyl peroxide, is used to generate free radicals. Crosslinking takes place through the connection of polymeric radicals and formation of carbon-carbon bonds. Peroxide crosslinking gives the highest and uniform degree of crosslinking (up to 90%), since the chemical reaction proceeds in the molten state above decomposition temperature of peroxide. Thus, peroxide crosslinking leads to the more homogeneously crosslinked material with uniform properties. On the other hand, crosslinking reactions in the molten state leads to a significant drop of crystallinity and melting temperature opposite to virgin polymer, due to subsequent recrystallization of less mobile polymer chains and formation of less perfect crystals with distorted unit cell. Therefore, the crystallinity, the melting temperature as well as the crystallization temperature decreases as peroxide level and gel content increases [19, 24-28].

Chemical reaction of peroxide crosslinked PE is in Fig. 3.3. Free radicals are formed by abstraction of hydrogen atoms from polymer chains. This reaction continues until all peroxide is consumed or the temperature falls below the decomposition temperature of peroxide. Reaction of peroxide radical with polymer chain proceeds mostly on tertiary carbon, i.e. on the side of chain branching, due to better stabilized radical. Thus, LDPE is more prone to crosslinking than HDPE.
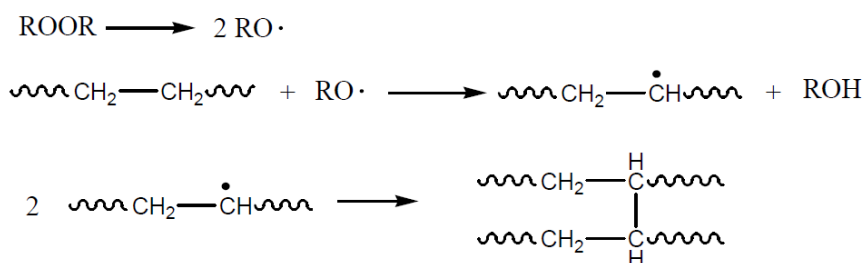

Fig.3.3: Chemical reactions within the peroxide crosslinking process.

Similarly to radiation crosslinking, some unwanted reactions can occur depending on the polymer composition, the presence of impurities, additives, oxygen and others, leading to the reduction of crosslinking effectiveness. Particularly, antioxidants cause depletion of peroxide due to the consumption of free radicals. In many cases, it was reported that during the peroxide crosslinking (as well as radiation crosslinking), an unambiguous increase of vinylene bonds has been observed [29].

There are several commercially available peroxide crosslinking methods, such as *Engel* method and *Pont à Mousson* method. *Engel* method is the oldest process, whereby a mixture of polyethylene (HDPE) and peroxide is fed into extruder and subsequently melted, crosslinked and shaped in one piece of

equipment. *Pont à Mousson* method includes two steps, in which the mixture of polyethylene and peroxide is extruded, followed by the crosslinking in a salt bath above the decomposition temperature of peroxide [30, 31, 19].

3.1.3 Silane crosslinking

Silane crosslinking is a chemical method which involves incorporation of silane coupling agents into the polymer chains. There are many silane coupling agents, mostly vinyl silane chemicals with methoxy or ethoxy groups on Si are used for the crosslinking of polyethylene, due to their double bonds and ability of rapid crosslinking. These substances can be incorporated into the polymer structure by two main ways:

- radical grafting of vinyl alkoxysilanes into the polymer chains by using a small amount of peroxide,
- copolymerization of ethylene with vinyl alkoxysilanes.

Crosslinking chemical reactions consist of two reaction steps (Fig. 3.4):
1) Hydrolysis of alkoxy group to a silanol group in the presence of water and an alcohol is released as a by-product.
2) Condensation of two silanol groups into siloxane crosslink and regenerate water.

Because water is needed for the reactions, this kind of crosslinking is often referred to moisture, water or humidity crosslinking. Water, released during second step, can hydrolyze another alkoxy group.
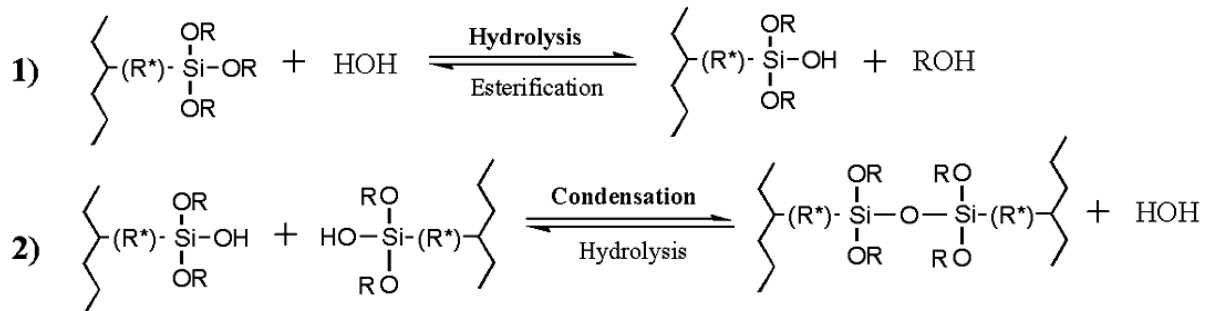

Fig. 3.4: Scheme of silane crosslinking reactions, where R is usually -CH$_3$ or -CH$_2$CH$_3$, and R* depends whether silane compound was incorporated by grafting (R* is -CH$_2$CH$_2$-) or by copolymerization (R* is missing).

There are five main factors which influence reaction rate and crosslinking: catalysts concentrations, silane content, water concentration in polymer, temperature and sample geometry.

Generally, there are several types of silane crosslinking catalysts for enhancing the rate of condensation reactions. Organotin compounds, such as dibutyltin dilaurate, acidic or basic compounds are usually used for catalysis.

Therefore, pH level of polymer blend is also an important factor for reaction kinetics.

Content of vinyl silane influences both, gel content and crosslinks density which results in different morphological and mechanical properties. There is also evidence of the increased flame retardation of polymer with increasing concentration of siloxane crosslinks [32].

The temperature as well as sample geometry (thickness) influence the diffusion of water (water concentration) and by-products into or from the polymer and they play a significant role in reaction rates. Maximum thickness for moisture crosslinking is limited to a few millimeters. Furthermore, the density or crystallinity has a significant impact on diffusivity of reaction species, thus tightly packed lamellar structure of HDPE is less prone to crosslinking. For the same reason, the effect of temperature on crosslinking reactions is complicated, since the temperature affects not only the diffusion of species and the reaction rate of hydrolysis and condensation, but higher temperature can also lead to the morphological changes, which can slow down the crosslinking (typical temperature for hot water crosslinking is 90 °C, which is close to the melting temperature of LDPE). The diffusion of water is believed to be the rate-determining step in the crosslinking process [33].

Crosslinking can occur slowly in the presence of atmospheric moisture at ambient temperature or can be accelerated by hot, moisture rich environment, for instance in autoclave, water bath or sauna [34, 35].

Crosslinking reactions or degree of conversion of polar alkoxy or hydroxyl groups into siloxane bonds can be followed by analytical methods such as infrared spectroscopy. Vinyl alkoxysilanes consist of three alkoxy groups which are capable of creating siloxane bonds. Therefore, some internal conversion of alkoxy groups can occur even if maximal gel content was reached, because each alkoxy side can link several chains together [25]. Multiple reactivity of silane compounds also supports a heterogeneous network formation during condensation reaction.

Silane-grafting method

Even a small amount of grafted vinyl alkoxysilane (1 to 2 wt%) into PE chains by using of peroxide gives possibility of crosslinking and therefore enormous changes in physical and chemical properties. On the other hand, decomposition of peroxide takes place in the melt due to free radical formation, which can lead to undesirable side-reactions involving scission, branching, inter- or intra-molecular hydrogen abstraction from main chain or grafts, oligomeric grafting, carbon-carbon crosslinking and others [36, 37, 38]. For this reason, the optimal concentration of vinyl alkoxysilane and peroxide must be found.

Furthermore, grafting can lead to a heterogeneous distribution of grafts producing a polymer with silane rich (preferentially amorphous fraction) and silane depleted (crystalline fraction) molecules. Then, crosslinking in the solid

state takes place preferentially in amorphous region on silane rich molecules which lead to overall more heterogeneous network. This is probably the reason why peroxide crosslinking (homogeneous network) results in a relatively high gel contents in comparison to silane crosslinked PE [27]. According to available literature, the increase of gel content with peroxide concentration is not linear. At first, the gel content increases rapidly and then increases slightly with peroxide concentration (for dicumyl peroxide it is beyond 0.1 phr) [39, 40].

After the grafting process, polyethylene is shaped into the final product and it is ready for crosslinking via the exposure to hot water or steam (special silane-modified PE is capable to crosslink even at ambient conditions).

Two main processes are known for production of silane crosslinked products: *Sioplas* and *Monosil*.

Sioplas process consists of two separate blending, where polyethylene is firstly separately grafted by silane with peroxide initiators and pelletized. Then, grafted PE can be stored in a dry place for several months, usually in sealed vacuum bags. During subsequent processing, grafted PE is mixed together with the pellets of masterbatch containing catalyst and other additives, such as antioxidants, scorch retardants, fillers, metaldeactivators, drying agents and others, in a typical weight ratio of 5:95. Final product is usually shaped by extrusion and then crosslinked by water.

Monosil process involves mixing of polyethylene with additives, catalyst, silane and initiator in one step into the shaping device where the article is produced. Consequently, as in previous case, the article is crosslinked by water.

Ethylene-vinyl silane copolymers

Another method for production of silane crosslinkable PE involves copolymerization of ethylene with a small amount of vinyl alkoxysilane (usually vinyl trimethoxysilane or vinyl triethoxysilane) in a reactor. By copolymerization, distribution of silane groups is significantly improved. The utilization of copolymer is similar to *Sioplas* process. Ethylene-vinyl silane copolymer (EVS copolymer) is stored in vacuum bags due to short shelf life (about 9 months). When it is intended to produce the final product, EVS copolymer is mixed with catalysts masterbatch, shaped and finally crosslinked by water. Processing of EVS copolymer does not involve free radical formation, thus selection of additives and antioxidants is less limiting. Furthermore, no undesirable side-reactions can occur during processing, therefore EVS copolymer is more suitable for industry requiring high quality level and stability, for instance in cable industry.

EVS copolymer can contain up to 30 wt% of silane groups, although content of vinyl silane comonomer is preferably from 0.1 to 5 wt%. Furthermore, EVS copolymer can be modified with other comonomers, such as acrylic acid, butyl acrylate and others, to enhance crosslinking rate due to their acidic character and self-catalyzing mechanism [41, 42, 43].

Significant drawback of silane crosslinkable PE is possibility of premature crosslinking by moisture, for instance during storage, and formation of defects related with creation of insoluble gel (inhomogenities, rough surface, increase of viscosity and others). These defects can have undesirable impact on processing conditions, mechanical and electrical properties. For this reason, additives, such as dry agents, scorch retardant and others are added to prevent premature crosslinking [44].

Silane polar groups can act as a compatibilizer in filled PE blends. Furthermore, crosslinking provide improved adhesion to organic and inorganic surfaces, like in the case of wood-plastic or silica composites leading to improved mechanical properties, creep and weather resistance [45-48].

3.2 General properties of crosslinked polyethylene

As was mentioned before, crosslinking is a process, in which carbon atoms of same or different polyethylene chains are joined together to form the three-dimensional network structure (Fig. 3.5). Because of this connection, the mobility of molecules is restricted, especially in the amorphous area of polymer, which results in higher polymer elasticity. At the same time, molecular weight is significantly increased and the flow behavior is also considerably changed, resulting in increase of viscosity, mixing torque and the reduction of melt flow index and elongation at break.

On the other hand, crosslinking leads to the formation of insoluble and infusible polymers that has great impact on the final properties of products, even at low network density. Crosslinked polyethylene (XLPE) behaves more as soft rubber, while thermoplastic PE has not significant strength above melting point.

By crosslinking, some important properties are significantly improved, such as impact resistance, abrasion resistance, crack propagation resistance, weather resistance and resistance to high temperature, light, chemicals and solvents. Furthermore, crosslinking provides the shape stability of final articles and crosslinked PE is capable to absorb high loadings of additives (reinforcing, electrically conductive fillers and fire retardants), contrary to thermoplastic PE which become brittle and unusable upon the addition of fillers [16, 24, 41, 49-52].

In the cable industry, PE and crosslinked PE is used as an insulation of power cables. The use of virgin PE has been restricted as cable insulation due to inherent defects, such as a low operating temperature, rapid dissolution in hydrocarbon solvents and tendency to crack under stress. Power cable insulation from XLPE can withstand operating temperature of 90-120 °C and short-circuit temperature of 250 °C. Furthermore, beyond the ability of XLPE to withstand higher electric loading, XLPE, in some cases, could improve resistance against defects caused by the effects of electric tension, such as water treeing.

According to *Nilsson et al.* [53], the degree of crystalinity is the most important factor for water treeing, i.e. it depends whether the crosslinking proceeds in the melt or in the solid state. Therefore, silane crosslinked PE could have better insulation properties than peroxide crosslinked PE [54].

Furthermore, crosslinking process involving free radicals formation can negatively affect quality of insulation. The insulation efficiency of radiation crosslinked PE falls remarkably with increasing temperature up to the melting point, where a recovery to the level of non-crosslinked PE is observed [55-58].

Similarly to cable insulations, XLPE is more suitable for plastic piping system than non-crosslinked PE. In this area, XLPE can be used for many applications, such as, cold- and hot-water distribution systems, natural gas distribution and others. In general, the typical maximum service temperature for thermoplastic HDPE pressure pipe applications is 60 °C, while for crosslinked HDPE the temperature can be raised to 82 °C and more, depending on density, crosslinking degree and crosslinking method. [59]

In the biomedical area, crosslinked UHMWPE is widely used as a total joint and hip replacement, because crosslinking can dramatically reduce the wear rate, creep and abrasion of UHMWPE. Radiation (gamma and electron beam) and peroxide crosslinking has been mainly used to obtain highly crosslinked network (up to 80 %). Peroxide crosslinked UHMWPE exhibits improved wear rate in the hip simulator, which can be around 20 times better than that of non-crosslinked UHMWPE. Radiation crosslinking of UHMWPE may improve wear rate more than 100 times, depending on process conditions and dose level.

Despite the evidence of improved wear resistance of radiation crosslinked UHMWPE, the long-term stability to oxidative degradation is questionable due to concentration of free radicals resulting from ionizing radiation. Oxidative degradation may change the physical properties for years after crosslinking due to chain scission and drop of molecular weight. Density and toughness increase during this period, while strength, ductility and toughness are reduced, with an adverse effect on wear and fatigue endurance. In order to decrease the free radical concentration, the thermal treatment after crosslinking can be employed to enhance the mobility of residual radicals and promote their recombination before oxidation. On the other hand, such a treatment can lead to the reduction of the mechanical and fatigue strength. An alternate method for obtaining oxidative stability in radiation crosslinked UHMWPE is stabilization of these free radicals by an antioxidant without post-radiation thermal treatment [60, 61, 62].

As was mentioned, XLPE is infusible in terms of its flow properties, which are significantly restricted above the melting point, although there is a small crystalline portion in XLPE, which can be melted from a morphological point of view. Therefore, XLPE deforms easily above melting point and this deformation can be fixed by cooling. Thus, crosslinked PE has been put into practical use as the so-called shape memory material, particularly in packaging and cable

industry. A thermoresponsive shape-memory PE is able to change a shape depending on the temperature. High energy radiation crosslinking is usually used for these applications, although this technology is limited to articles of thin cross-section. At this process, PE is firstly crosslinked for fixing its initial shape. Then, the polyethylene chains are oriented upon an application of mechanical stress above the melting temperature. During cooling under the stress, new polyethylene morphology is formed and new temporary shape is fixed. Subsequent heating of material above melting temperature leads in the material return to its permanent, initial shape, which was fixed during the crosslinking. The heat shrinkage depends on the gel content; with the increasing gel content, the heat shrinkage increases as well, but chemical fixation of molecules is of the same importance as the physical. Crystallization ability of molecules decreases with increasing gel content, especially after the melting and recrystallization. Therefore, it is necessary to find the optimum between gel content and crystallinity for the best heat shrinkage [63-66].

On the other hand, crosslinking can be used for fixing the shape of articles, which leads to remarkable reduction of undesirably shrinkage at higher temperature. This can be particularly important in the cable industry, where the heating of PE insulation to high temperature may cause undesirable shrinkage and deterioration of mechanical and electrical properties [67].

Crosslinked polyethylene foams are other commercially available products, mainly in automotive industry, sports, protective packaging and others, due to their improved properties opposite to virgin PE foams. PE foams exhibit superior ability to absorb mechanical impact, low permeability to water vapours and resistance to weathering and chemicals compared to polystyrene and polyurethane foams. Crosslinked PE foams represent about 24% of all PE foams and production is expected to grow. The silane crosslinking system allows the use of conventional blowing agents, such as hydrocarbons and halocarbons, but water has also been used successfully as a blowing agent [11, 35].
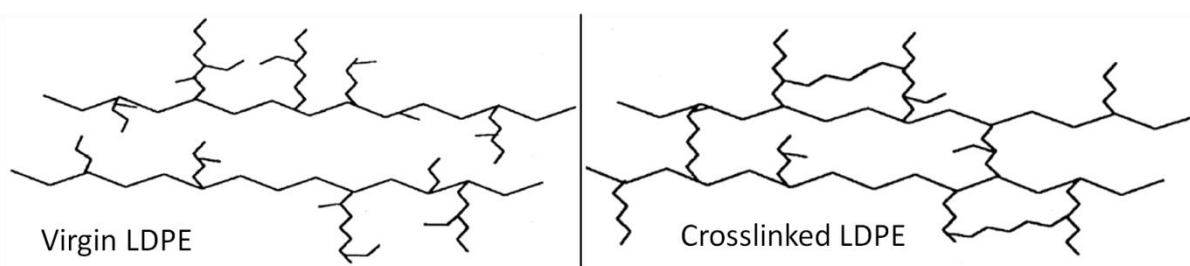

Fig.3.5: Schematic view of non-crosslinked virgin LDPE and crosslinked LDPE [24].

3.3 Morphology of crosslinked polyethylene

During the radiation and peroxide crosslinking, the formation of radicals on the macromolecules takes place and the covalent carbon-carbon (-C-C-) crosslinks are created through their combination. Crosslinking via silane compound leads to the formation of siloxane (-Si-O-Si-) crosslinks. These

crosslinks have different physicochemical properties. Lower electronegativity of Si results in highly polar Si-O bond with higher binding energy (452 kJ/mol) than that of C-C bond (356 kJ/mol). In contrast, the binding energy of Si-C has only a slightly lower value, 318 kJ/mol. These values indicate a high resistance of Si-O bond to homolytic cleavage. On the other hand, heterolytic cleavage occurs relatively easily, especially in the presence of acids or bases [68].

The crosslinks also vary in their rigidity; rotation energy of Si-O bond is close to 0 kJ/mol (free rotation) opposite to C-C bond (about 13.8 kJ/mol), and thus it is much more flexible [69].

Narkis, et al. [52] suggested that different crosslinks may affect the ability of polyethylene crystallization. Thus, more rigid carbon-carbon crosslinks may cause higher decrease of crystalinity than the flexible siloxane bonds.

Generally, even a low crosslink density has a significant effect on the final morphology and crystallinity of the product. There are many parameters influencing the final properties, such as crosslinking method and conditions, structure of polymer (branching, molecular weight) and others. These parameters have a great impact on the temperature of melting and crystallization, crystallization rate, specific heats and other physical properties due to introduction of irregularities into the polymer chains. Typically, crosslinking makes the polymer chains less flexible which leads to more difficult crystallization, and thus crystallinity, crystallization temperature and rate decrease. Furthermore, less flexible molecules are connected with increasing of tensile strength, but at the same time, decrease of crystallinity caused by crosslinks influences the tensile strength oppositely. Thus, crosslinking does not necessarily mean an increased tensile strength at room temperature [18, 39, 70].

In general, branched PE is more feasible for crosslinking compared to linear PE due to better stabilization of radicals on tertiary carbons of the polyethylene chains. Furthermore, double bond residues in polymer chains, as well as higher gyration radius of polymer coils may support radical formation and crosslinking. On the other hand, less accessibility of polymer backbone to peroxide and/or silane initiators would negatively influence a radical formation and gel content at PE grades with higher molecular weight and high chain branching [71].

The final morphology is further dependent on whether the crosslinking takes place in the melt (peroxides) or solid state (radiation, moisture). Crosslinking in the melt leads to a homogeneous distribution of crosslinks, while the process in the solid state proceeds mostly in amorphous regions or at the crystallite boundaries, thus amount of amorphous fraction (i.e. crystallinity) in solid state can play an important role in crosslinking rate and gel content, especially in the case of silane crosslinking.

Venkatraman and Kleiner [72] studied different properties of silane grafted HDPE prepared via the moisture, peroxide or radiation crosslinking. The results are depicted in Fig. 3.6. Crystallinity as a function of the gel content evaluated

from first melting is unchanged for samples crosslinked in the solid state, i.e. moisture and radiation crosslinked. On the other hand, a significant drop of crystallinity of peroxide crosslinked HDPE is clearly seen. Since the peroxide crosslinking must proceeds above the decomposition temperature of the peroxide, i.e. in the melt, a new arrangement of macromolecules take place during the solidification and crystallization. This new arrangement also causes DSC melting peak broadening due to existence of the sol and gel fractions. However, after the second melting and subsequent crystallization, a similar decrease in crystallinity can be observed also for moisture and radiation crosslinked samples, while the crystallinity of peroxide crosslinked HDPE does not change. Similar results reached *Khonakdar et al.* [19].

Lyamkin et al. [73] examined the thermomechanical properties of several cable insulations crosslinked by all three methods. They found that there is consistent relation between the values of the thermal strain at 200 °C and the network density. At the beginning, thermal strain rapidly decreases with the increasing of network density, but then it is stabilized at the certain value. The most stable structure of the XLPE network can be find at network density values in a range of $n_c = 7\text{-}11 \times 10^{-5}$ mol/cm^3, irrespective of the crosslinking method. Furthermore, radiation, peroxide and silan crosslinking occurs usually under the different temperature conditions, which can have impact on the thermomechanical properties of cable insulations in the molten state. As can be seen in Fig. 3.7, the peroxide crosslinking showed the highest values of strength (at 130 °C) at equal network density. This is probably connected with the homogeneous crosslinks distribution as crosslinking takes place above melting temperature.
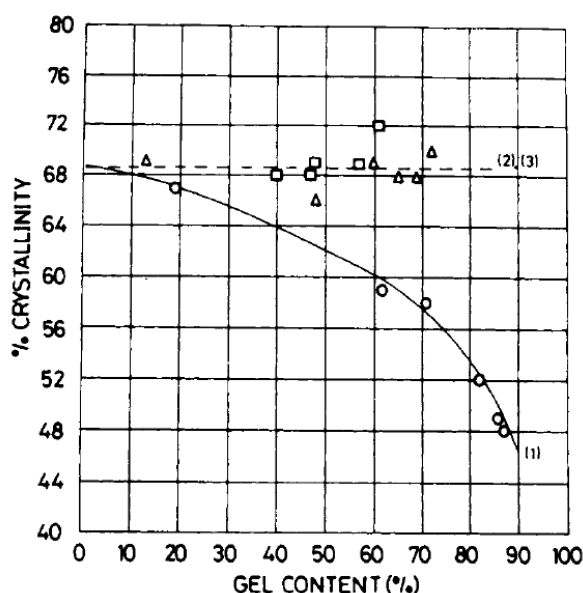

Fig.3.6: The degree of crystallinity, measured from the heat of fusion during the first heating step, plotted as a function of gel content for the three types of crosslinked HDPE. Heating rate was 20°C/min; (○) peroxide crosslinked [curve (1)]; (Δ) electron crosslinked [curve (2)]; (□) moisture crosslinked [curve (3)] [72].
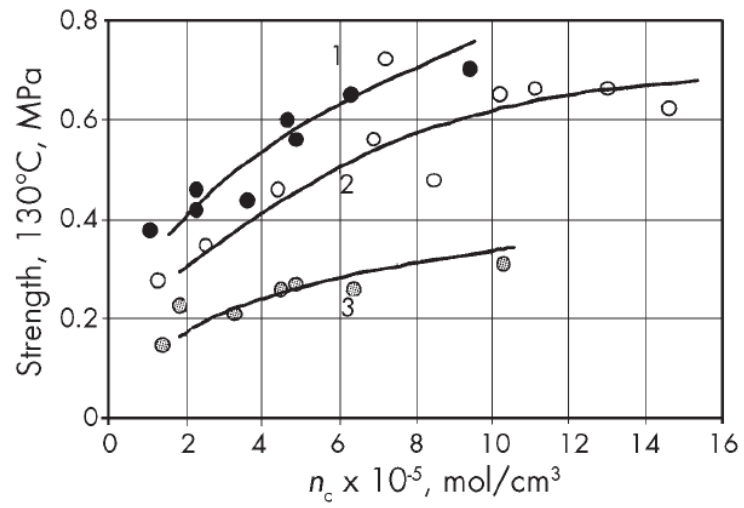
Fig.3.7: The dependence of strength at 130 °C of PE cable insulations crosslinked by the peroxide method (1),silan method (2), and by radiation method (3) on the network density [73].

4. THE AIMS OF RESEARCH WORK

The main goals of the doctoral research study are the description, understanding and explanation of the relation between the preparation, structure and properties of the final products of crosslinked and thermally aged polyethylene. The aim of the research is to contribute originally to the development of silane crosslinked polyethylene, especially the EVTMS copolymer crosslinked in hot water bath or at room conditions and it is focused on the changes of properties during the crosslinking and thermal ageing at different temperatures, which is important for the safe use of polymer, for instance as cable insulation.

The main examined properties and principal analytical methods are:
- chemical changes, analysed by Fourier transform infrared spectroscopy,
- morphological changes, indirectly investigated by Differential scanning calorimetry and X-ray diffraction,
- mechanical properties, evaluated by Mechanical tensile testing and Dynamic mechanical thermal analysis.

5. EXPERIMENTAL PART

5.1 Materials

Copolymers of ethylene with vinyl trimethoxysilane (EVTMS copolymer) were used for study of properties during the crosslinking and/or ageing at different conditions. All the materials were produced by Borealis AG.

Major study was focused on the specific type of copolymer of Visico^{TM} series, which have properties similar to LDPE and it is used for production of low voltage insulation. This copolymer must be mixed with catalyst masterbatch for sufficient crosslinking. The catalyst masterbatch is from Ambicat^{TM} series and it is usually mixed with copolymer in a ratio of 95 wt% of copolymer and 5 wt% of catalysts masterbatch according to Sioplas process, i.e. masterbatch is added directly prior an extrusion. Some physical properties of these materials from Borealis data sheet are given in Tab. 5.1.

Visico^{TM} contains a permanent scorch retardant additive which ensures safe processing and using of highly active crosslinking catalyst. Ambicat^{TM} contains patented crosslinking catalyst based on sulphonic acid, which is environmentally friendly opposite to the traditional tin-based catalysts. Furthermore, Ambicat^{TM} contains antioxidant, metaldeactivator and drying agent for better processing and preventing of premature crosslinking. Mixed and extruded polymers of Visico^{TM} and Ambicat^{TM} composition require crosslinking at higher temperature in water bath or sauna, although crosslinking at ambient conditions is also possible.

For the purpose of presented Ph.D. research, the samples with different amounts of catalyst were added in order to find out the interrelation between network density and final properties of crosslinked and aged EVTMS copolymer.

Second type of material, denoted as DEX1 and DEX2 copolymers, was chosen for the purpose of research. These EVTMS copolymers have different composition than Visico to ensure more efficient crosslinking. The crosslinking reactions of DEX copolymers proceed reasonable even at room temperature and room humidity, although mixing with Ambicat^{TM} is still needed.

Tab. 5.1: Physical properties of sufficient crosslinked Visico^{TM}/Ambicat^{TM} (95:5)

Property	Typical value	Unit	Test method
Density	923	kg/m^3	ISO 1872-2 / ISO 1183-2
MFI	1,0	g/10 min	ISO 1133 (190 °C, 2.16 kg)
Tensile strength	> 15	MPa	ISO 527 (250 mm/min)
Elongation	> 300	%	ISO 527 (250 mm/min)
Hardness	52	Shore D	ISO 868
Brittleness temp.	< -76	°C	ASTM D 746

5.2 Preparation of samples

The mixtures of Visico^{TM} and Ambicat^{TM} were extruded using a Brabender extruder with temperature setting 120 °C, 135 °C, 165 °C in barrel and 165 °C in die. A rotation speed was 20 rpm, compression ratio of screw was 4:1. The extruded tape was approx. 20 mm wide and about 2 mm thick. Concentration of Ambicat in mixtures varied; the samples were prepared with 5 or 7 wt% of Ambicat, as well as without this catalysts masterbatch (0 wt%).

After extrusion, the tapes were cut off into pieces with length of 230 mm and subsequently crosslinked in water bath at 90 °C for 4 hours, although a few non-crosslinked samples from each series were put aside for testing.

Subsequently, the crosslinked samples were aged in an oven with airflow at two temperatures, 90 °C and 135 °C. After certain time, the samples were successively collected from the oven and tested; the maximal ageing time was 240 hours. The procedure of samples preparation is summarized in Tab. 5.2.

For the purpose of results and discussion, the samples are sometimes denoted as: Visico (*X*% Amb), where *X* means concentration of Ambicat. Thus, Visico without Ambicat can be denoted as *Visico (0% Amb)* and Visico with 5% of Ambicat as *Visico (5% Amb)*.

Two EVTMS copolymers, DEX1 and DEX2, were extruded at the same conditions as Visico copolymer. Crosslinking, on the other hand, was performed either in water bath at 90 °C for 4 hours, or in the storage room at ambient temperature (25 °C) and humidity (50 %RH) up to 10 days, since these polymers are able to crosslink even at room conditions. However in both cases, the ageing in an oven with airflow at 90 °C or 135 °C took place after crosslinking period. As in the case of Visico, the samples for testing were taken during crosslinking at room temperature, as well as during ageing. The procedure of samples preparation is summarized in Tab. 5.3.

Tab. 5.2: Procedure of Visico samples preparation.

Mixture	Visico™ + Ambicat™					
Concentration of Ambicat™	0 wt%		5 wt%		7 wt%	
Conditon of crosslinking	90°C/4 hours in water bath		90°C/4 hours in water bath		90°C/4 hours in water bath	
Temperature of ageing	90 °C	135 °C	90 °C	135 °C	90 °C	135 °C
Time of ageing (hours)	0 to 240	0 to 240	0 to 240	0 to 240	0 to 240	0 to 240

Tab. 5.3: Procedure of DEX1 and DEX2 preparation.

Mixture	DEX1 + Ambicat™				DEX2 + Ambicat™			
Concentration of Ambicat™	5 wt%				5 wt%			
Conditon of crosslinking	90°C/4h in water bath		room temp. up to 10 days		90°C/4h in water bath		room temp. up to 10 days	
Temperature of ageing	90 °C	135°C	90 °C	135°C	90 °C	135°C	90 °C	135°C
Time of ageing (hours)	0 to 240	0 to 240	0 to 240	0 to 240	0 to 240	0 to 240	0 to 240	0 to 240

5.3 Characterization methods

5.3.1 Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) is a technique based on the vibrations of the atoms in a molecule. An infrared spectrum is commonly obtained by passing infrared radiation from the source through the sample and detector determines absorption of radiation of particular energy in a broad range of wavelengths (wavenumbers), usually from 4000 cm^{-1} to 400 cm^{-1}. Infrared radiation activates vibration-rotation changes in energetic states of molecules. The position of absorbed energy peak corresponds to a vibration of particular chemical bond. FTIR method is the most sensitive to polar chemical groups with high dipole moment, such as OH or CO groups, although non-polar compound, such as polyethylene, can still exhibits significant selective absorption of hydrocarbon chain. Intensity of absorption peak is proportional to concentration of characteristic bond. Thus, the basic information about chemical composition

of the sample can be revealed by finding of position and intensity of absorption peaks in spectrum and/or comparing measured spectrum with the database [74].

The transmission infrared spectra were obtained in the range of 4000 cm^{-1} – 550 cm^{-1} with a resolution of 2 cm^{-1} and 32 scans by Perkin-Elmer Spectrum 2000 or Nicolet Avatar 320 FTIR spectrometers. Thin slices of specimens were prepared by using of microtome. The surface of specimens, through which the IR radiation penetrated, was cross-section of extruded tape, so the specimens were approx. 2 mm wide and 20 mm high. Thickness of specimens was about 100 μm.

For interpretation of crosslinking and ageing progression from IR spectra, the relative intensities of characteristic bands were involved. Peak intensity was calculated by measuring the heights of peaks from baseline in transmittance spectrum. In order to get quantitative results, the heights of characteristic bands were normalized by the height of skeletal rocking C-H vibration at 715 cm^{-1} in order to eliminate the influence of specimen thickness. This C-H vibration remains stable during treatment and does not suffer by total absorption. Calculated values were expressed as relative band intensity (RBI) I_x/I_{715}. The list of characteristic bands and the interval of baselines, whereby the heights (intensities) of peaks were obtained, is in Tab. 5.4.

Tab. 5.4: Characteristic bands for evaluation relative bands intensities.

Charact. band [cm^{-1}]	Chemical group	Baseline points [cm^{-1}]	Used for samples
1095	Si-OCH$_3$	1230-972	all
795	Si-OCH$_3$	827-767	all
1025	Si-O-Si	1230-972	Visico with Ambicat, DEX1, DEX2
1015	Si-O-Si	1230-972	Visico without Ambicat
1735	C=O	1781-1662	Visico with Ambicat, DEX1, DEX2
1715	C=O	1838-1660	Visico without Ambicat
715	C-H	767-675	all

5.3.2 Differential scanning calorimetry

Differential scanning calorimetry (DSC) is a technique where difference in energy input to a small weighted sample and reference material is measured, while the sample and reference are subjected to a controlled temperature program, which includes heating and cooling at defined rate, as well as isothermal step. Temperature is measured continuously and the heat flow into the sample is assessed for determination of heat gains or losses accompanied by physical or chemical endothermic or exothermic processes, such as melting,

crystallization, glass transition, vaporization, oxidative degradation and others. For study of polymers, the technique is most often used for characterization of T_g, T_m, T_c, and specific heats (enthalpies). The technique can also be used for study of the kinetics of chemical reactions and crystallization. The heat of fusion can be converted to a % of crystallinity. [75, 76]

The melting and crystallization behavior of the samples was mostly measured by PerkinElmer Pyris-1 and Mettler Toledo DSC-1 differential scanning calorimeters. Standard thermal program used in our work includes first heating from 20 °C to 150 °C, cooling from 150 °C to 20 °C and second heating from 20 °C to 150 °C at scanning rate 10 °C/min. Each of scans proceeded under nitrogen atmosphere with flux 20 ml/min. The samples of weight about 7 mg were cut from the extruded tapes and placed into standard aluminum pans.

Thermal fractionation was chosen as a complementary method for supporting of several statements resulting from standard thermal scans. This method is able to non-physically fractionate the polymer starting from the melt, and then carefully designed thermal program induces molecular segregation and crystallization as a function of the ability of chain segments crystallization at specific temperatures. In this particular method, named as step crystallization, isothermal steps alternate with cooling steps, from the melt down to temperature, where crystallization is highly restricted. Then, the final DSC heating reveals distribution of melting points [77].

Thermal fractionation used here involves (Fig. 5.1):
heating 40 °C–120 °C at 10 °C/min,
cooling 120 °C–113 °C at 1 °C/min, isothermal at 113 °C for 30 min,
cooling 113 °C–110 °C at 1 °C/min, isothermal at 110 °C for 30 min,
cooling 110 °C–107 °C at 1 °C/min, isothermal at 107 °C for 30 min,
cooling 107 °C–104 °C at 1 °C/min, isothermal at 104 °C for 30 min,
cooling 104 °C–101 °C at 1 °C/min, isothermal at 101 °C for 30 min,
cooling 101 °C–98 °C at 1 °C/min, isothermal at 98 °C for 30 min,
cooling 98 °C–95 °C at 1 °C/min, isothermal at 95 °C for 30 min,
cooling 95 °C–40 °C at 10 °C/min,
heating 40 °C–120 °C at 10 °C/min.

All thermal fractionations proceeded in standard aluminum pans and under nitrogen with flux 20 ml/min.

Evaluation of the crystallinity (X_c). The basic equation for the calculation of X_c for polymer via DSC is:

$$X_c = \frac{\Delta H_m}{\Delta H_m^0} \cdot 100 \qquad (\%) \qquad \text{(eq. 5.1)}$$

where ΔH_m is the integral melting enthalpy (heat of fusion) calculated from DSC scan (J/g), and ΔH_m^0 is the melting enthalpy of 100% crystalline PE. Since ΔH_m^0 varies depending on the branching and comonomer content of PE, and

$\Delta H_m{}^0$ of EVTMS monocrystal is unknown, the melting enthalpy of 288 J/g was chosen for calculation [78, 79].
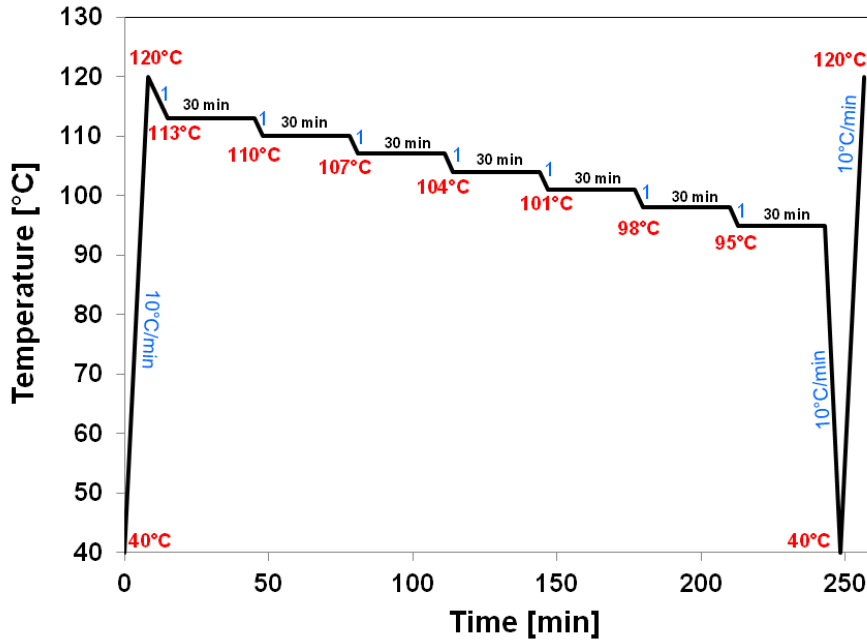

Fig. 5.1: Scheme of DSC thermal fractionation scans.

Gibbs-Thomson equation can be used for calculation of lamellar thickness from the melting temperatures of a crystalline lamella. Lamellar thickness (L) derived from Gibbs-Thomson equation is expressed as:

$$L = \frac{2\sigma_e}{\Delta H_m^0} \cdot \frac{T_m^0}{T_m^0 - T_m} \qquad \text{(eq. 5.2)}$$

where $T_m^0 = 141.4$ °C is equilibrium melting temperature of the infinite crystalline lamella, $\sigma_e = 90$ mJ/m² is the basal surface free energy of the crystalline lamella, $\Delta H_m^0 = 288$ J/cm³ is the melting enthalpy of PE crystal and T_m is a melting temperature from DSC heating scan in °C.

This equation is only suitable for the lamellae whose lateral dimensions are much larger than their thickness [80, 81, 82].

5.3.3 X-Ray diffraction

X-ray diffraction techniques (XRD) are widely used in the field of materials characterization to obtain information about atomic arrangement of various crystalline or semi-crystalline compounds. X-ray diffraction involves measurement of the intensity of X-ray scattered from electrons in atoms. Monochromatic X-rays impact on the sample surface at given angle, they are scattered by atoms at different positions and arrive to the detector with a relative phase shift. If the arrangement of atoms is regular and the scattered waves

possess Bragg law, an increase of intensity of a scattered light occurs. This phenomenon is called diffraction.

Thus, diffraction patterns are recorded as numerical function of a single independent variable, the Bragg angle. From the position, intensity and shape of diffraction peaks, information about crystalline structure, composition and texture can be obtained. [83, 84, 85]

Wide-angle X-ray diffraction patterns were obtained by using PANalytical X´Pert PRO with theta-theta goniometer and Ni-filtered CuKα radiation (0.1542 nm). All the measurements were performed at laboratory temperature in reflection mode, at 40 kV and 30 mA with automatic divergence and anti-scatter slits in the range of angles from 10 to 35° (2θ) and step size 0.0263°, counting time 38 s per step.

Crystallinity of samples was evaluated by using softvare X'Pert HighScore. The diffraction pattern from 12° to 30° (2θ) was first aligned by subtraction of constant background and then the amorphous halo was determined. Crystallinity is calculated as a ratio of the integral area above this amorphous halo to the total area of diffraction pattern.

5.3.4 Mechanical tensile testing

The mechanical properties are important characteristics of end-use polymer applications. There are several mechanical tests which involve some degree of mechanical loading. Mechanical tensile test involves uniaxial stretching of test specimen [86]. The conditions of tests, test specimen types, evaluation of characteristics such as tensile modulus, tensile strength and other aspects of the tensile stress/strain relation, are given in international standard ISO 527-1:2012.

Mechanical tensile testing was performed in accordance with standard CSN EN ISO 527-1 using a Zwick Materialprüfung Z030 tensile testing machine equipped with an external extensometer or Alpha Technologies Tensometer T2000. Testing rate for the determination of modulus (0.05-0.25 % of elongation) was 1 mm/min. After one percent of elongation, testing rate was adjusted to 250 mm/min. The testing specimens had a dog-bone shape with thickness of 2.15 mm and width of 5.90 mm. Initial gauge length was 20 mm. All measurements were performed at room temperature and humidity. The mechanical stress was calculated as a ratio of measured force to initial cross-section area.

5.3.5 Dynamic mechanical thermal analysis

Generally, dynamic mechanical analysis (DMA) is a method invented for evaluation of the complex viscoelastic behavior of polymers, whose mechanical behavior exhibits characteristics of both, solid and liquid. DMA is used to study molecular relaxation processes in polymers and to determine inherent mechanical or flow properties as a function of time and temperature. There are several DMA techniques, which varies in a type of deformation and/or type of measurements under oscillatory mode (frequency sweep, strain sweep, time sweep, temperature sweep). Dynamic mechanical thermal analysis (DMTA) is a temperature sweep measurement of the dynamic modulus (in-phase or out-of-phase) in an oscillatory mechanical deformation experiment during a programmed temperature scan at controlled frequency [76, 87, 88].

The temperature sweep dynamic measurements were performed in accordance with standard ISO 6721-1 & 7. The specimens were rectangular above 40 mm long, 10 mm width and 2 mm thick. The temperature program was set from -130 °C to 160 °C at heating rate 2 °C/min. A mechanical loading was performed as a torsional deformation at constant frequency of 1 Hz.

6. RESULTS AND DISCUSSION

6.1 Chemical reactions of EVTMS copolymers during crosslinking and thermal ageing

Infrared spectroscopy (IR spectroscopy) is a powerful tool for monitoring of EVTMS copolymers, because unlike the radical crosslinking by radiation or peroxide, EVTMS copolymers contain silane groups which are visible in IR spectrum due to different chemical composition than covalent C-C bond. Furthermore, virgin polyethylene is relatively infrared transparent material with simple spectrum of basic C-H vibrations; therefore silane groups frequencies are visible even at low concentration. It is necessary to mention that copolymers and catalytst masterbatch, supplied for this research contain various additives which can influence a final IR spectrum and restrict proper analysis.

According to the reaction scheme of crosslinking (Fig. 3.4), crosslinking site contains three reactive methoxy groups which can react with water to create silanol groups. In the second step, two silanol groups of different chains react together to form siloxane group. Because each silicon atom is connected to the three methoxy groups, this single crosslinking site is capable of linking several chains together and, in extreme case, forms cyclic oligomers [25]. This is also the reason, why crosslinking reactions can continue further even when the maximal gel content was reached.

Siloxane bond Si-O-Si exhibits two stretching vibrations – asymmetric and symmetric, as well as deformation vibration. Symmetric vibration is visible in Raman spectrum and deformation vibration is below 180 cm^{-1}, thus the asymmetric vibration is the most significant for evaluation of crosslinking from IR spectra. The band of asymmetric Si-O-Si stretching vibration is in the region 1100-1000 cm^{-1}. Due to the great ionic character of Si-O group, as well as mass and size of silicon atom, this band is about five times more intense than the band from the corresponding carbon linkage.

The spectra of linear, branched or crosslinked siloxanes are similar in the case of identical substituents and it is difficult to distinguish between linear or cyclic siloxane structures. However, due to the influence of ring strain, cyclic siloxane trimers absorb at 1020-1010 cm^{-1}, which is about 60 cm^{-1} less than other cyclic siloxanes. Thus, tetramers and higher cyclic siloxanes absorb at 1090-1070 cm^{-1} [89].

The O-H stretching bands of Si-OH groups can be observed in the same region as alcohols, i.e. 3700-3200 cm^{-1}. Deformation vibration could appear in the same region as siloxane band, but opposite to siloxane band, it is a weak vibration [74, 89].

The Si-O-C bands of methoxysilanes can be observed in the region of 1115-1090 cm^{-1} (asymmetric) and 850-640 cm^{-1} (symmetric). Trimethoxysilane in

grafted PE or EVTMS copolymer exhibits three main absorption bands at 1190, 1095 and 795 cm^{-1} [90].

Characteristic C-H vibrations of polyethylene chains do not change during crosslinking reactions, therefore some characteristic C-H vibration can be taken as a constant value for evaluation of relative band intensity (RBI).

The other interesting bands, which can be followed in IR spectra of copolymer mixture, include vibration of oxygen groups, such as carbonyl group vibrations C=O in aldehydes, ketones and carboxylic acid, or C-O- vibrations of esters, ethers, anhydrides, alcohols and others. These vibrations can be significant for additives and catalyst, as well as in the case of oxidation-induced degradation. During degradation, a chain scission related with a formation of unsaturated alkene group can occur.

All mentioned characteristic bands are summarized in Tab. 6.1.

Tab. 6.1: Frequencies of infrared characteristic groups related with EVTMS copolymer/catalyst masterbatch mixture [89]. Absorption intensities: v – very, s – strong, m – medium, w – weak, str. – stretching vibration, def. – deformation vibration.

Wavenumber [cm^{-1}]	Chemical group
~1190 s (str.), ~1100 (1095) vs (str.), 850-640 m-s (str.)	**Si-O-CH$_3$** (methoxysilane group)
1100-1000, 1065, 1025 vs (str.)	**Si-O-Si** (siloxane group)
3700-3200 (str.)	**Si-OH** (silanol group)
2975-2950 m-s (str.), 2885-2865 m (str.), 1465-1370 m (def.),	**-CH$_3$** (alkane aliphatic)
2940-2915 m-s (str.), 2870-2840 m (str.), 1480-1350 m (def.)	**-CH$_2$** (alkane acyclic)
725-720 w-m (def.)	**-(CH$_2$)$_n$-** (alkane skeletal vibration)
1680-1600 w-m (str.)	**C=C** (alkene stretching vibration)
~1740-1700 vs (str.)	**C=O** (carbonyl group)
~1300-1100 s (str.)	**C-O-C** (ether group)

6.1.1 VISICO/AMBICAT copolymer

Infrared spectra of pure Visico and Ambicat are in Fig. 6.1. Both spectra exhibit strong C-H vibrations, mainly in the region of 3000-2800 cm^{-1}, where total absorption of peaks occurs due to relatively thick specimens (100 μm). Nevertheless, this phenomenon does not spoil the analysis, because the most important differences are apparent in the fingerprint region, where other C-H vibrations are visible at 1464 and 720 cm^{-1}. It is obvious that catalyst masterbatch Ambicat exhibits the same C-H vibration as Visico; this is probably

due to presence of polyethylene, which is mixed with an additives and catalyst for better manipulation and homogenization with Visico during extrusion. The additives in Ambicat cause brown color of pellets, while Visico pellets have opaque polyolefin appearance.

In the case of Ambicat, C=O and C-O-C vibrations are visible at 1735 cm^{-1} and 1166 cm^{-1} respectively, due to additives, such as antioxidants and acidic catalytic agent. On the other side, pure Visico does not contain such additives, thus the differences opposite to virgin PE spectrum are mainly in the region of 1235-765 cm^{-1}, where silane chemical groups absorb IR radiation. The most significant bands belong to three methoxysilane groups at 1190, 1095 and 795 cm^{-1}. Intensities of these bands are changing during crosslinking as they react and form siloxane bonds.

IR spectrum of mixed Visico and Ambicat in ratio of 95:5 is shown in Fig. 6.1.b. In comparison to pure Visico (Fig. 6.1.a), the intense C=O band appears as an influence of Ambicat. Furthermore, the band at 1166 cm^{-1} deforms methoxysilane band at 1190 cm^{-1} what makes it difficult to analyze. Thus, the most important bands used for analyzing of chemical changes are methoxysilane groups at 1095 and 795 cm^{-1}, siloxane bands at 1100-1000 cm^{-1}, as well as carbonyl group at 1735 cm^{-1} which could be used to study of thermo-oxidative reactions.
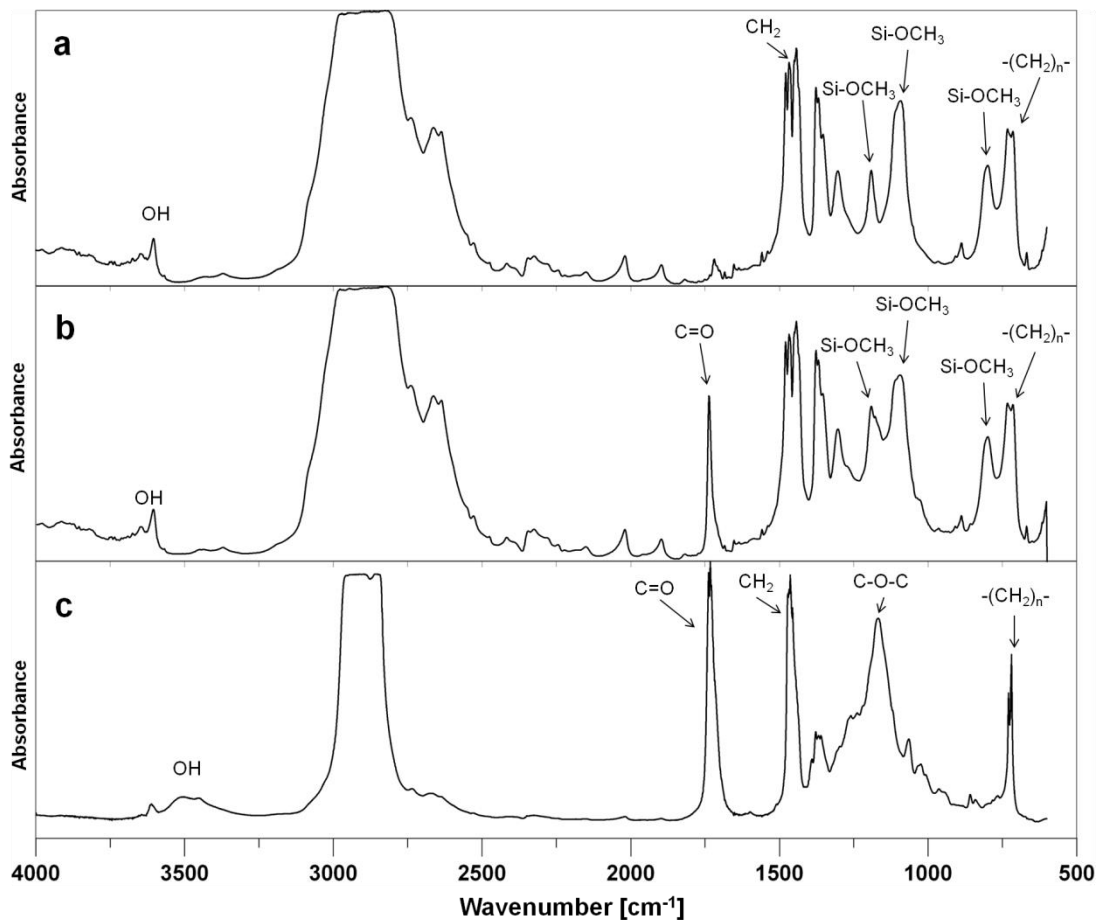
Fig. 6.1: Infrared spectra of a) Visico (0% Amb), b) Visico (5% Amb), c) Ambicat.

Visico without Ambicat

After the extrusion, all samples were put into the water bath at 90 °C and subsequently aged at 90 °C or 135 °C. Fig. 6.2 shows selected spectra of Visico without Ambicat (0 wt%) at different stages of treating, focused on the regions of carbonyl and silane bands (all spectra are baseline corrected). Spectrum of non-crosslinked sample is similar to spectrum of crosslinked and non-aged sample. Since this material does not contain a catalyst masterbatch, the crosslinking reactions proceed slowly in water bath at 90 °C. Only small peak at approx. 1050 cm^{-1} is visible and relate with siloxane band. Furthermore, the spectrum of sample Vis (0% Amb) aged in oven at 90°C up to 240 hours is basically identical with non-aged sample. The peaks in carbonyl region remain also unchanged.

However, dramatic changes in intensities occur when the material is aged at 135 °C. Decrease of peaks at 1190, 1095 and 795 cm^{-1} (methoxysilane) and development of peaks at approx. 1065 and 1015 cm^{-1} (siloxane) suggests that crosslinking reactions proceed rapidly at this ageing temperature even in the oven with air flow, despite of previous crosslinking in water bath which did not have any effect. These rapid changes can be seen in Fig. 6.3, where relative band intensities (RBI) are depicted versus ageing time (There are not shown all characteristic bands, since evolution of bands at 1060 and 1190 cm^{-1} were very similar to evolution of band at 1025 and 795 cm^{-1}, respectively). In all characteristic bands, the RBI remains constant in the case of crosslinking and ageing at 90 °C. In the case of ageing at 135 °C, the RBIs are dramatically altered and the greatest changes occur within 96 hours. The reasons for rapid changes relate not only to the higher temperature, but it is important to note, that temperature of 90 °C is below melting temperature and 135 °C is above melting temperature of Visico copolymer. Therefore, different diffusion rates of reaction species together with higher macromolecules motion takes place. However, changes of band heights in the region of 1250-690 cm^{-1} are not simply caused by crosslinking, it is rather a combination of crosslinking and degradation: dramatical decrease of methoxysilane bands and increase of siloxane bands suggest crosslinking but, at the same time, the carbonyl band increases at significant rate up to 240 hours. Thus, it can be assumed that degradation of samples continues, even when the crosslinking reactions were stopped.

Rise of carbonyl peak (1719 cm^{-1}) during ageing at 135 °C can be seen also in Fig. 6.2. The position of peak is slightly shifted to lower wavenumbers than in Ambicat. Furthermore, the complexity of carbonyl band area suggests that several oxygen-specific groups are formed during ageing. Thus, pure Visico without Ambicat and without antioxidant considerably degrades at this temperature. The images of crosslinked and aged samples are shown in Fig. 6.4. There is clear color change related with degradation, mainly visible in samples aged for at least 96 hours. Furthermore, it cannot be excluded that the carbonyl

and/or other polar groups, such as carboxyl groups created during degradation, can catalyze crosslinking, therefore elevated temperature does not have to be the only factor influencing the crosslinking reactions.

Visico with 5% of Ambicat

Visico with 5 % of Ambicat reveals completely different IR spectra which can be seen in the same Fig. 6.2. A presence of antioxidant and catalyst has considerable impact on the crosslinking reactions what clearly reflects in IR spectra. It can be assumed that crosslinking reactions proceed with appreciable rate in water bath as well as during ageing in the oven. This process can be clearly seen and the evolution of peaks associated to silane groups occurs for samples prepared at 90 °C as well as at 135 °C in oven. It should be noted that the crosslinking at 135 °C proceeds at higher extent as can be derived from higher decline of methoxysilane peaks, especially at 1095 cm^{-1} and 795 cm^{-1} and reversely, higher increase of siloxane peak at 1065 cm^{-1} and 1020 cm^{-1}. An observation of two siloxane bands at 1065 cm^{-1} and 1020 cm^{-1} suggests that formation of crosslinks is not constrained only on connection of two silanol groups but silanol groups probably create oligomeric structures which absorb IR radiation at higher wavenumbers. However, the most significant changes occur during crosslinking in water bath, which can be seen from the initial drop of methoxysilane and growth of siloxane peak intensity in Fig. 6.3. This is caused by presence of catalyst because, opposite to pure Visico where basically no changes occur during crosslinking in water bath, Visico with Ambicat crosslinks mainly during first 4 hours in water bath and crosslinking further continues another 2 hours. However, after 2 hours there are only slight changes suggesting that the crosslinking is almost finished. It should be noted that the chemical changes are more visible in samples aged at 135 °C, which can relate with already mentioned better diffusion and molecular motion, but this changes are not as dramatic as in Visico without Ambicat.

The peak in carbonyl region is considerably high even for non-crosslinked samples, and it is assigned to the Ambicat composition. Furthermore, this peak remains constant during the crosslinking and ageing (see Fig. 6.3). It can be assumed that the possibility of degradation of material followed by the evolution of the carbonyl groups can be excluded. Degradation that was evident in pure Visico samples is suppressed due to stabilization of copolymer mixture. Aged samples are shown in Fig. 6.5. Brownish color of initial samples is caused by addition of Ambicat (the pellets are brown). The color changes occurred only during ageing at 135°C after 2 hours, but this color change to browner hue relates rather with migration of substances toward the surface than with thermo-oxidative changes. This conclusion is supported by images of cross-section from optical light microscope, where separation of two phases of distinct colors near surface can be visible.
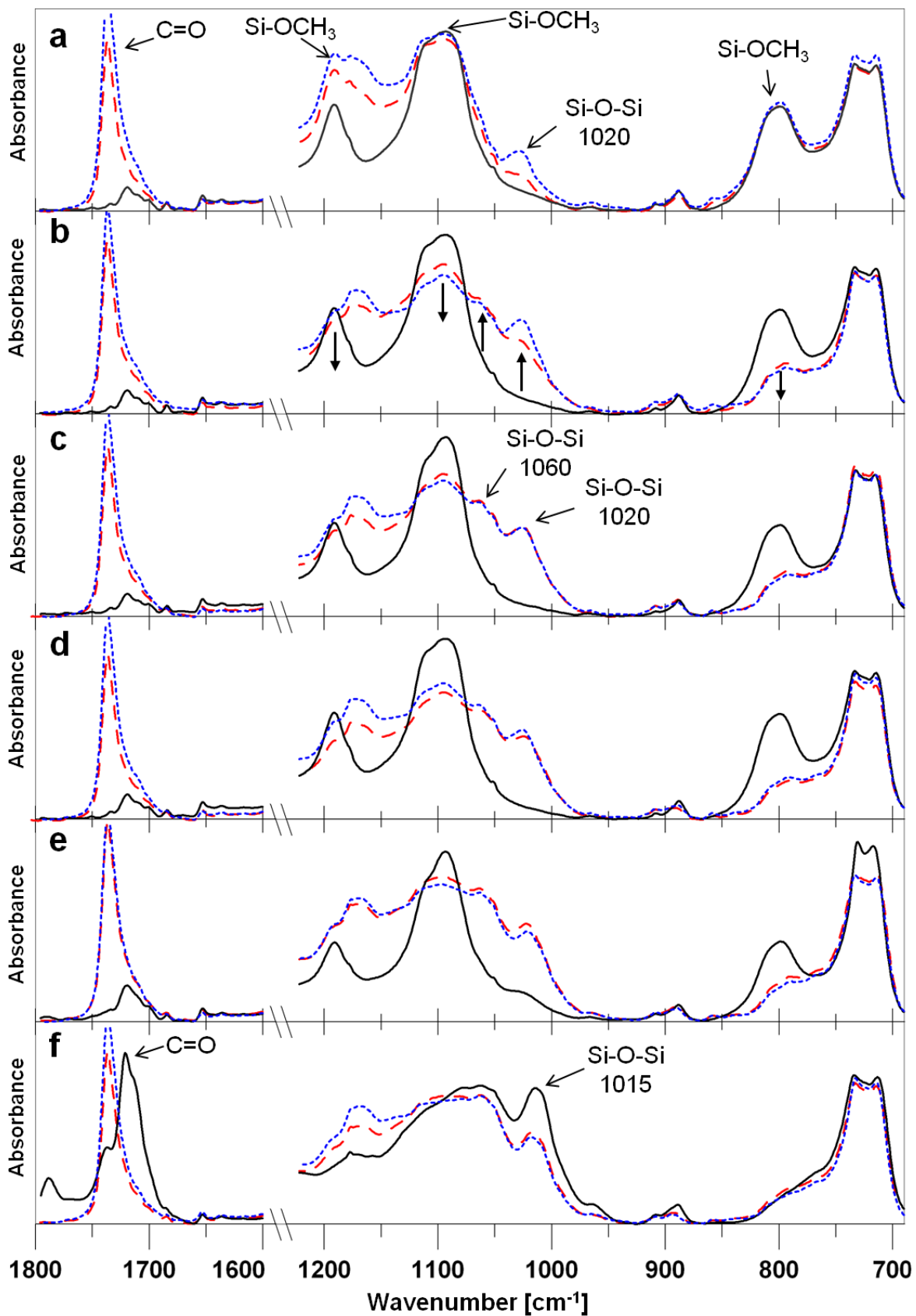
Fig. 6.2: IR spectra of Visico (0% Amb) (——), Visico (5% Amb) (— —) and Visico (7% Amb) (▪▪▪), in the range of 1800-1600 cm^{-1} and 1250-690 cm^{-1}: a) non-crosslinked, b) crosslinked, c) aged at 90 °C/24 h, d) aged at 90 °C/240 h, e) aged at 135 °C/24 h, f) aged at 135 °C/240 h.
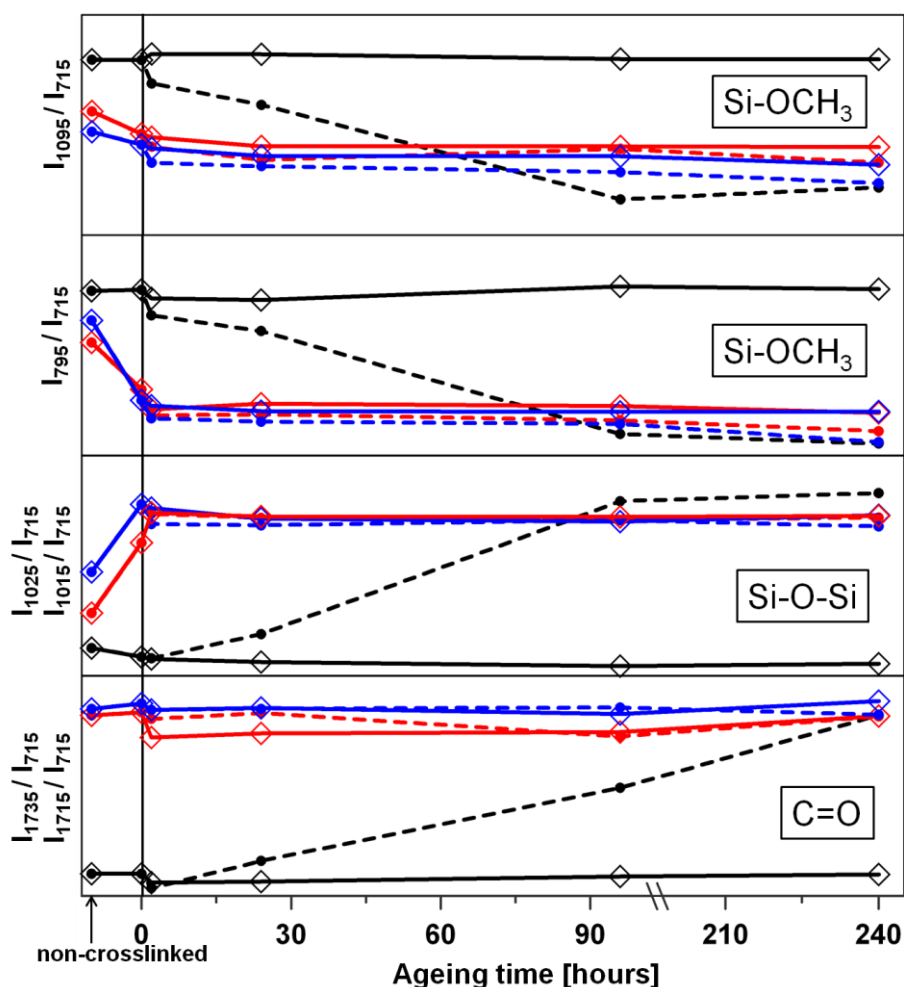
Fig. 6.3: Relative IR bands intensities of samples crosslinked in water bath and subsequently aged. First symbol represents non-crosslinked sample and second symbol crosslinked sample with no ageing: Visico (0% Amb), aged at 90 °C (━━━); Visico (0% Amb), aged at 135 °C (━ ━); Visico (5% Amb), aged at 90 °C (━━━); Visico (5% Amb), aged at 135 °C (━ ━); Visico (7% Amb), aged at 90 °C (━━━); Visico (7% Amb), aged at 135 °C (━ ━) . In the carbonyl and siloxane region, different peaks were chosen according to Tab. 5.4.

Visico with 7 % of Ambicat

Visico with 7 % of Ambicat has very similar bands evolution as Visico with 5 % of Ambicat, although there are some differences. First at all, the crosslinking reactions continue during ageing as in previous case, but it seems that crosslinking is more intense, which can be derived from the higher decline of methoxysilane bands (see Fig. 6.3). Furthermore, ageing at 135 °C induce even faster crosslinking and the decline is the highest. These results are not surprising due to higher catalyst content. However, these differences between Visico with 5 wt% and 7 wt% of Ambicat are not significant, since the most significant changes occur before ageing, i.e. during crosslinking in water bath. The conditions in water bath are sufficient to ensure that the greatest chemical changes occur during 4 hours in water at 90 °C and they seem to be more

41

efficient for the samples with higher catalyst content as can be assumed from the band intensities.

Carbonyl band in Visico with 7 % of Ambicat remains constant during ageing although the intensity is higher as in Visico with 5% of Ambicat. Furthermore, the color changes of samples during ageing were similar as in Fig. 6.5, although the initial color was even browner due to higher Ambicat content.

It is necessary to note, that there is a risk of premature crosslinking instantly after or during extrusion. The higher catalyst content can promote the chemical reactions which can lead to the processing problems. In Fig. 6.2 it is evident that in the case of Visico with Ambicat, the premature crosslinking on extruded samples takes place before crosslinking in water bath (non-crosslinked samples), which can be derived from the increase of band intensity at 1025 cm^{-1}. This premature crosslinking occurs mainly in Visico with 7 % of Ambicat due to higher catalyst content, whereas Visico without Ambicat does not exhibit any premature crosslinking.

As can be seen in Fig. 6.6, dependence of carbonyl band intensity on the concentration of Ambicat is nearly linear, therefore this carbonyl peak evidently relates to Ambicat composition and it is difficult to assign any changes in carbonyl region to the thermo-oxidative induces degradation. However, due to presence of antioxidant in masterbatch it is assumed that the degradation is highly restricted.

Fig. 6.4: Aged samples of Visico (0% Amb). Color changes start after 24 hours of ageing at 135 °C.
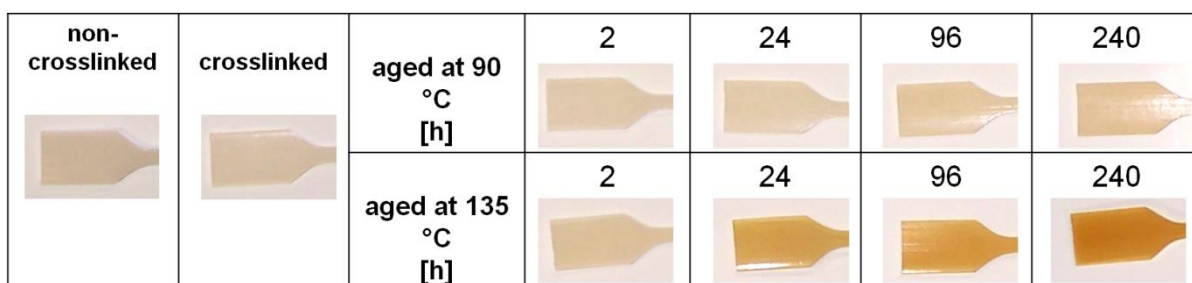
Fig. 6.5: Aged samples of Visico (5% Amb). Color changes start after 2 hours of ageing at 135 °C.
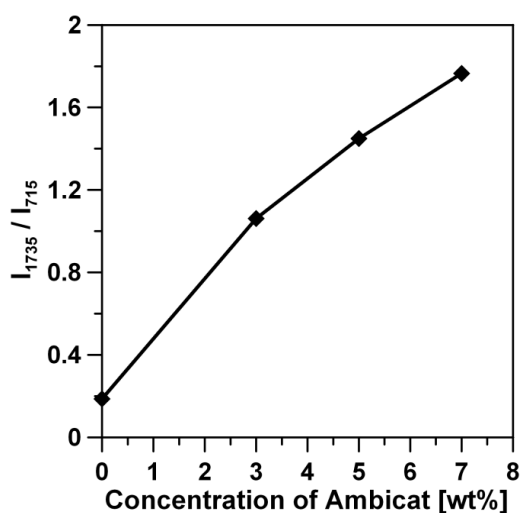
Fig. 6.6: Dependence of carbonyl RBI on the concentration of Ambicat in mixture.
RBIs originate from non-crosslinked samples.

6.1.2 DEX1 and DEX2 copolymers

DEX1 and DEX2 are other two EVTMS copolymers are capable to crosslink in reasonable time at room temperature and humidity opposite to Visico with Ambicat. Chemical nature of these copolymers determined by IR spectroscopy can be seen in Fig. 6.7. At first sight, chemical composition of DEX copolymers is clearly different than pure Visico (Fig. 6.1.b). First, pure DEX copolymers absorb in the region of carbonyl group (1735 cm^{-1}) and ether group (1169 cm^{-1}). A presence of these groups enables faster crosslinking than in the case of Visico. It is generally known, that acidic or basic compounds influence silanol reaction rate. As was published in the work of *Palmlöf et al.* [42, 43], significant increase of reaction rate could be achieved by addition of Brønsted acid, such as dibutyltin dilaurate, polymerization of EVTMS with third acidic monomer and preparation of terpolymer or blending of EVTMS copolymer with polymer-bound carboxylic acid, such as ethylene-acrylic acid copolymer (EAA). All the three modifications significantly increase crosslinking reaction rates as well as enable crosslinking at lower temperature. Since there is a strong effort of producers to prevent premature crosslinking of EVTMS copolymer before processing, composition of pure DEX materials is rather terpolymer variant.

However, oxygen vibration band at 1169 cm^{-1} as well as band contributed from Ambicat, restrict analysis of crosslinking reactions due to hindering of methoxysilane and siloxane region at 1100-1000 cm^{-1}. The methoxysilane band at 800 cm^{-1} remains untouched.

It is necessary to note that comparison of IR spectra of pure DEX polymer and DEX with Ambicat reveals drop of band at 1092 cm^{-1} what indicates premature crosslinking during extrusion.
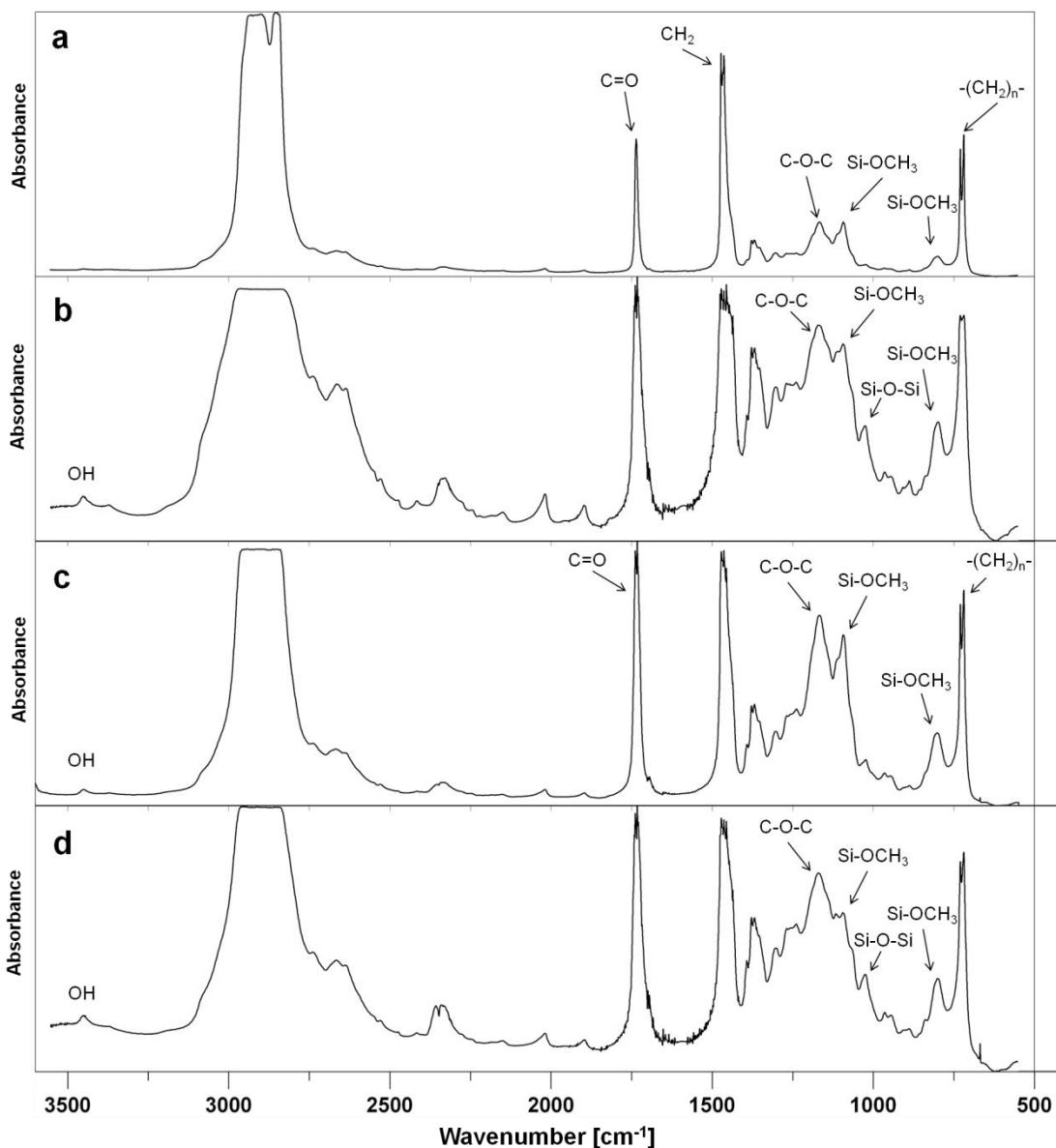
Fig. 6.7: Infrared spectra of a) pure DEX1, b) DEX1 with 5% of Ambicat, c) pure DEX2, d) DEX2 with 5% of Ambicat.

Both copolymers, DEX1 and DEX2, were mixed with catalysts masterbatch Ambicat and crosslinked either at room conditions or they were crosslinked as in the case of Visico, i.e. in water bath. After crosslinking, ageing at 90 °C or 135 °C takes place. As can be seen in Fig. 6.8, crosslinking at the room temperature proceeds mainly within 240 hours. In fact, crosslinking experiment at the room temperature continued up to 528 hours, however equilibrium state, in which relative bands intensities remain stable, was estimated to be in 240 hours. Therefore, crosslinking time of 240 hours was taken as a starting point for ageing in the oven. As was mentioned before, evaluation of relative band intensity of DEX materials is more difficult opposite to Visico due to hindering of characteristic bands; therefore the results are not as obvious as in Visico and accurate estimation of equilibrium state is also

difficult. Methoxysilane band at $800 \, cm^{-1}$ appears to be the best band for investigation of crosslinking reaction.

Infrared spectra of DEX copolymers in the process of crosslinking and ageing are shown in Fig. 6.10. It is necessary to note, that experiments of DEX copolymers crosslinked in water bath were performed in different time, therefore IR spectra exhibit differences related with premature crosslinking. However, it seems that crosslinking in water bath at 90 °C for 4 hours is at least equally effective as crosslinking at room conditions for 240 hours. This claim is also confirmed by initial changes of RBI shown in Fig. 6.9 (Fig. 6.8 and 6.9 have identical y-axis scale). Furthermore, the changes of relative bands intensities during ageing are similar to Visico results.
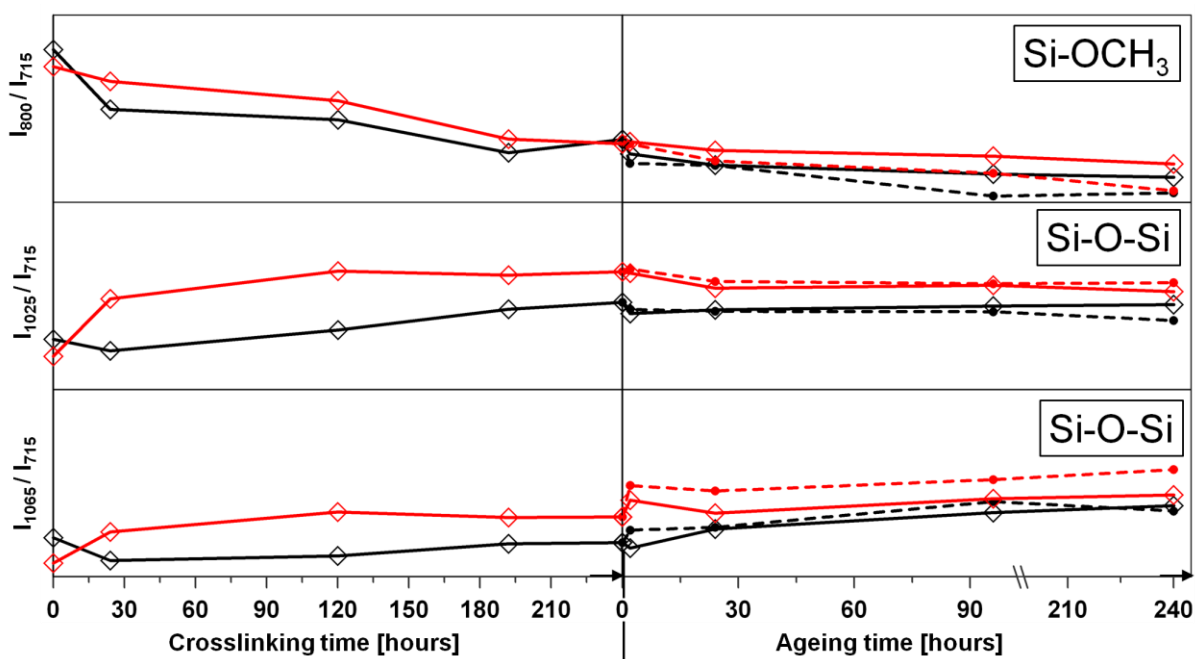
Fig. 6.8: Relative IR bands intensities of characteristic bands during crosslinking at room conditions (left part) and subsequent ageing (right part); DEX1 (——), DEX2 (——); ageing at 90 °C (solid), ageing at 135 °C (dashed).

In both cases, temperature of ageing plays an important role in terms of further crosslinking, thus, after initial chemical changes caused by crosslinking process either in the room or in water bath, the temperature of 135 °C causes higher chemical changes, although the results are not as clear as in the case of Visico. Decrease of methoxysilane RBI at $800 \, cm^{-1}$ suggests that crosslinking reactions proceed also during ageing, although siloxane bands at $1025 \, cm^{-1}$ and $1065 \, cm^{-1}$ seem to have constant development or even slightly decrease. In fact, the decrease of siloxane RBI is visible mostly at $1025 \, cm^{-1}$, which may relate to the further reactions of methoxysilane groups and formation of oligomeric structures of siloxane crosslinks. This process is more probable due to more extensive catalyst effect on chemical reactions than in the case of Visico.

Carbonyl band at 1735 cm^{-1} remains constant during crosslinking and ageing procedure indicating that this band completely relates with initial composition of DEX/Ambicat mixture, analogous to the Visico/Ambicat mixtures.

It is necessary to note that copolymer DEX2 has probably higher capability to crosslink than DEX1, which can be concluded from higher siloxane RBIs in Fig. 6.8 and Fig. 6.10. Furthermore, intensities of bands related to catalyst composition are higher, thus it can be assumed that crosslinking reactions proceed faster and to higher extent, which affects also other properties discussed in following chapters.
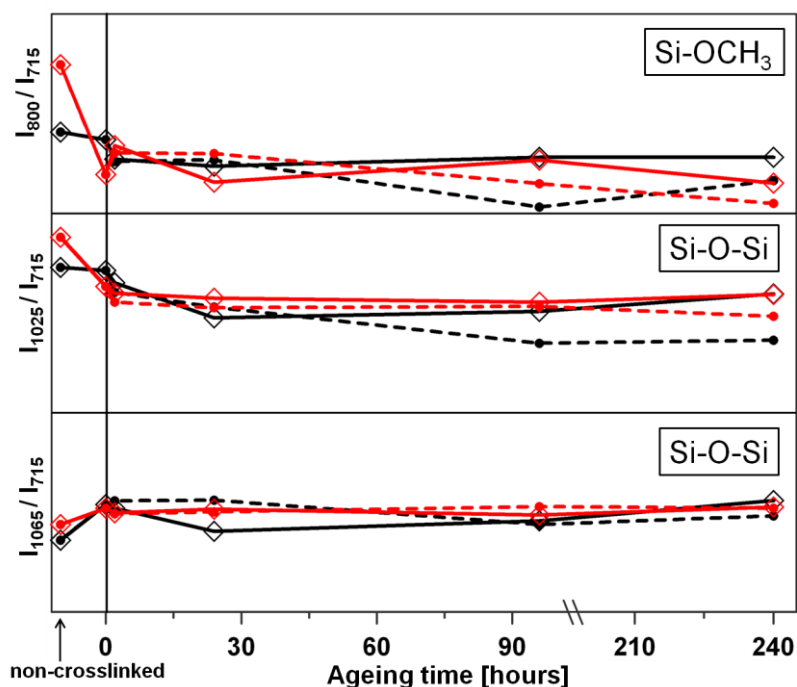
Fig. 6.9: Relative IR bands intensities of samples crosslinked in water bath and subsequently aged. First symbol represents non-crosslinked sample and second symbol crosslinked sample with no ageing: DEX1 aged at 90 °C (━━━); DEX1 aged at 135 °C (━ ━); DEX2 aged at 90 °C (━━━); DEX2 aged at 135 °C (━ ━).
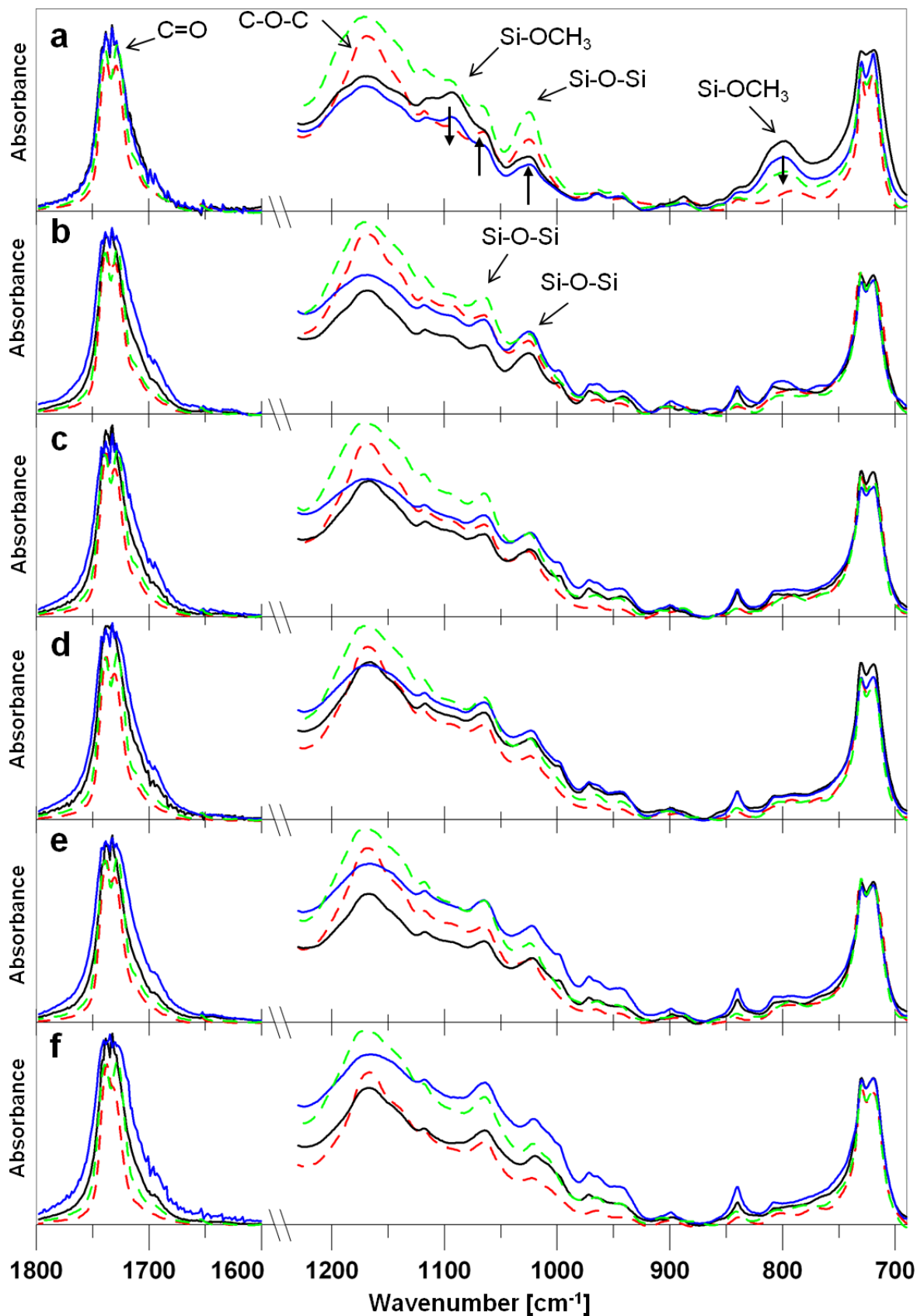
Fig. 6.10: IR spectra of DEX1 (——) and DEX2 (——) crosslinked at room conditions, and DEX1 (— —) and DEX2 (— —) crosslinked in water bath: a) non-crosslinked, b) crosslinked, c) aged at 90 °C/24 h, d) aged at 90 °C/240 h, e) aged at 135 °C/24 h, f) aged at 135 °C/240 h.

6.2 Morphology of EVTMS copolymers

Differential scanning calorimetry has been applied to observe the overall melting behavior and to study the influence of chemical reactions, such as crosslinking and degradation at elevated temperature on crystallization ability and morphology of polymers.

It is well known that chemical structure, size and flexibility of molecules, as well as temperature, pressure, time, presence of impurities and other parameters influence the final morphology of polymers which has enormous impact on mechanical properties. As was mentioned before, crosslinking makes the polymer chains less flexible which usually leads to decline of crystallization temperature, crystallinity as well as lamellae thickness [91-94].

The differences in thermal behavior of EVTMS copolymers are clearly seen in Fig. 6.11. In principle, DEX polymers have lower melting temperature and crystallinity opposite to Visico (Visico/Ambicat) copolymer (see Tab. 6.2), what is related to different chemical composition discussed in previous chapter. It is well known that irregularities, such as random comonomers and different chemical groups incorporated in polymer chains, restrict crystallization capability and decline melting and crystallization temperature, as well as crystallinity. Therefore, DEX2 has the lowest melting, crystallization temperature and crystallinity due to chemical composition enabling rapid crosslinking.

In fact, pure Visico has melting temperature (T_m) about 110 °C, what is similar value to T_m of LDPE. First heating scan of non-cosslinked samples reflects thermal processing history, thus the crystallization peak and melting peak during cooling and second heating, respectively, show more relevant results. However, the addition of Ambicat leads to the peak temperature decreases what can be connected with premature crosslinking and impurities present in Ambicat.

Crosslinking in water bath at 90 °C is basically connected with thermal annealing of partially crystalline copolymers since they melting temperatures are close to crosslinking temperature, and thus a recrystallization related with lamellar thickening occurs. This phenomenon can be clearly observed via the rise of secondary peak of crosslinked samples obtained from the first heating scan. Furthermore, the crystallinity slightly increases with annealing time below T_m and the most significant changes occur in Visico without Ambicat. It can be further expected that crosslinking occurs in amorphous phase preferentially and this is the reason why it does not influence first heating scan but the crosslinks interfere the crystallization process after melting during DSC experiment [95].
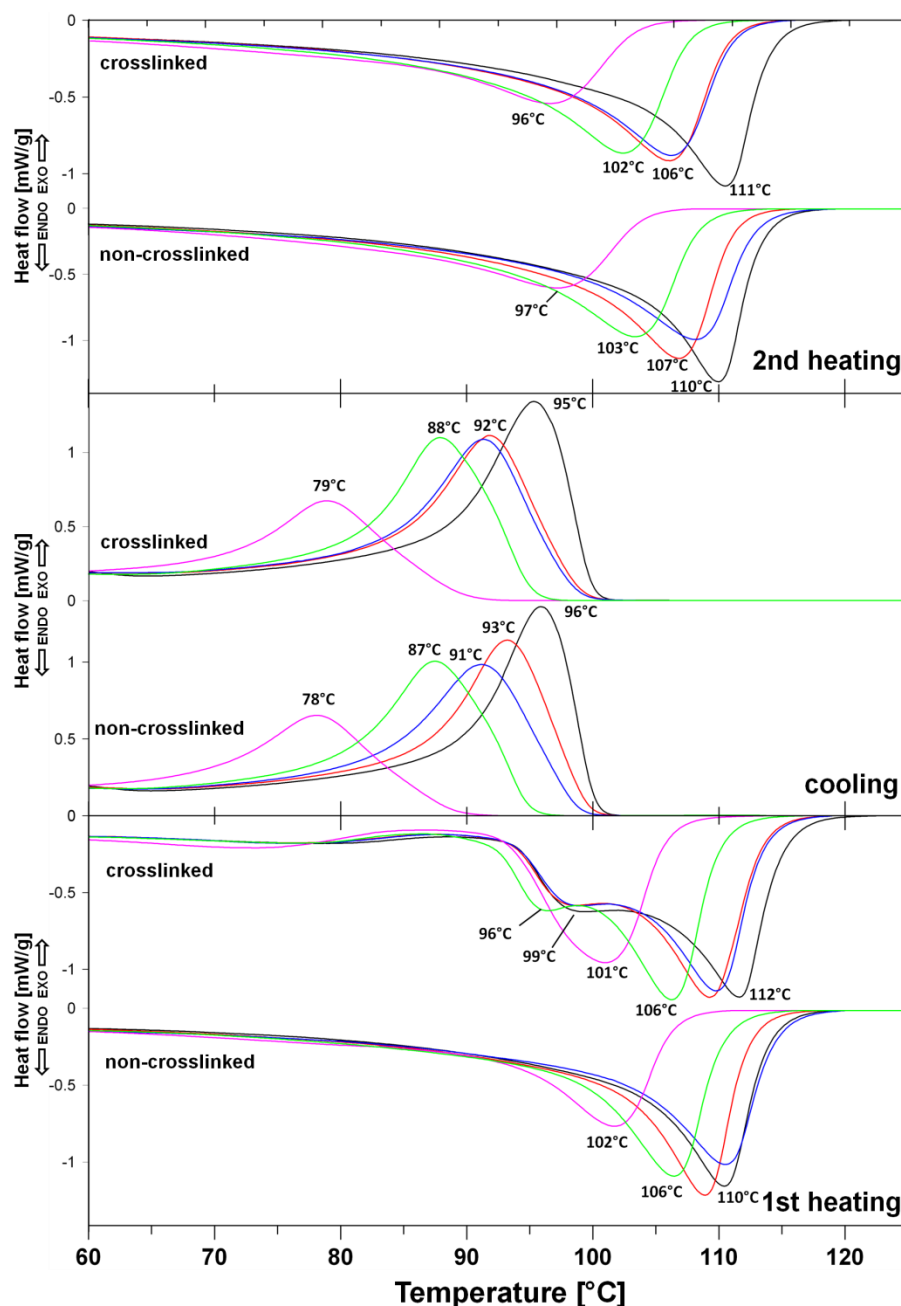
Fig. 6.11: DSC thermograms of EVTMS copolymers before and after crosslinking in water bath. The values represent peak temperatures. Samples: Visico (0% Amb) (━━━), Visico (5% Amb) (━━━), Visico (7% Amb) (━━━); DEX1 (━━━) and DEX2 (━━━).

A recrystallization process at 90 °C is visible also in DEX polymers, although DEX2 does not reveal a secondary peak due to low T_m, but peak broadening related with morphology improvement is obvious. After remelting of initial structure, the 2nd heating scans show only single peak. As can be seen, thermal curves of Visico with 5% and 7% of Ambicat were straightened and exhibit only small differences after crosslinking. However, Visico without Ambicat has still the highest crystallization capability and morphology improvement is the highest due to absence of siloxane crosslinks.

It is necessary to note, that DEX polymers crosslinked at room conditions did not exhibit morphology changes, because crosslinking proceeded at too low temperature for any recrystallization processes (they are not in Fig. 6.11)

Fig. 6.12 shows DSC thermograms of samples aged in the oven at 90 °C or 135 °C. The thermal characteristics are given in Tab. 6.2.

The Visico samples aged at 90 °C exhibit completely different thermal behavior as compared to those aged at 135 °C. In agreement with crosslinking process, it can be assumed further morphology improvement during ageing at the same temperature, i.e. at 90 °C. This process caused further lamellar thickening which leads to shifting of primary and secondary melting peaks to higher temperatures. The changes are more obvious for Visico without Ambicat than for Visico with 5% or 7% of Ambicat due to already mentioned crystallization capability. After melting of initial morphology, the crystallization occurs during cooling. The crystallization temperature is, of course, lower than melting temperature. However, the cooling scans are very similar, thus it can be assumed that any significant molecular changes do not occur at the ageing temperature of 90 °C, although there are some discrepancies which can relate to non-extensive crosslinking reactions, as well as with sample handling and preparation.

Subsequent heating of newly-crystallized material (2nd heating) shows only one peak with slightly lower melting temperature and crystallinity in contrast to initial peak, which proves that the second melting peak at 1st heating is fully connected with a specific morphological arrangement.

The scans of samples aged at 135 °C exhibit completely different evolution. First, the scans from the first heating samples are similar to the scans from the second heating. This is actually caused by ageing process, since 135 °C is above melting temperature leading to the remelting of initial (recrystallize) morphology and creating of new homogeneous morphological arrangement. This new arrangement is similar to arrangement created in peroxide crosslinked PE mentioned in [72]. Therefore, remelting of network structure, as well as further crosslinking in polymer melt must lead to the decrease of crystallinity and melting temperature due to introduction of crosslinks (molecular heterogeneities) to the polymer chains. The crystallization temperature decreases as well, as can be seen in Tab. 6.2.

However, Visico with 5% and 7% of Ambicat virtually does not exhibit significant changes in time of ageing at 135 °C, although other unpublished results indicate a tendency to decrease the melting and crystallization temperature in time. This is in good agreement with FTIR results, which show good thermal stability due to presence of antioxidant, as well as non-significant crosslinking reaction during ageing at 135 °C, although the crosslinking reactions run to higher extent than at 90 °C. On the other hand, ageing of Visico without Ambicat at 135 °C reveals completely different scans. The significant

drop of crystallinity and completely changed morphology in time relates to degradation processes suggested by FTIR. Pure Visico does not contain antioxidant, thus chemical changes and chain scission of molecules during degradation have a great impact on final morphology of copolymer.

Ageing of DEX copolymers that contain 5% of Ambicat has similar effect as in the case of Visico with Ambicat (Fig. 6.12). Temperature of 90 °C causes morphology improvement of both DEX polymers, although the shape of melting peak is different depending on the melting characteristics of polymers. DEX2 has significantly lower T_m and crystallinity than DEX1 due to different composition, as can be seen from Fig. 6.12 and Tab. 6.2,. Similarly as in previous case, morphology improvement continue during ageing at 90 °C what leads to shift of T_m to higher values and to increase of X_c in both DEX polymers, independently whether crosslinking proceeded in water bath or at room temperature. The remelting of initial morphology leads to homogenization of molecular arrangement with single crystallization and melting peak. This reorganization of morphological structure is slightly dependent on ageing time and temperature, which prove a good thermal stability of DEX polymers with catalyst masterbatch Ambicat. However, the morphological changes of DEX2 seem to be more extensive, what can be assumed from higher decrease of T_m and X_c during ageing at 135 °C. This is probably due to higher crosslinking capability of DEX2 confirmed by FTIR measurements.

Tab. 6.2: Thermal characteristics of Visico and DEX copolymers at crosslinking and ageing.

Sample	DSC first heating scan				DSC cooling scan		DSC second heating scan		
	T_{m1} [a] (°C)	T_{m2} [b] (°C)	ΔH_{m1} [c] (J/g)	X_{c1} [d] (%)	T_c [a] (°C)	ΔH_c [c] (J/g)	T_m [a] (°C)	ΔH_{m2} [c] (J/g)	X_{c2} [d] (%)
Visico (0% Amb)									
non-crosslinked	110.4	–	133.3	46.28	95.9	122.9	110.0	124.2	43.12
crosslinked in water	111.7	99.3	146.5	50.87	95.3	119.9	110.5	135.2	46.94
aged 90°C/240h	112.3	102.8	139.5	48.44	95.0	121.0	110.8	130.9	45.45
aged 135°C/240h	101.2	–	82.9	28.78	84.8	111.7	103.0	70.0	24.31
Visico (5% Amb)									
non-crosslinked	108.9	–	132.9	46.15	93.2	117.7	106.8	120.2	41.74
crosslinked in water	109.3	98.8	134.2	46.60	91.8	115.5	106.2	118.7	41.22
aged 90°C/240h	112.1	102.5	136.3	47.33	89.3	114.2	107.8	123.8	42.99
aged 135°C/240h	105.8	–	130.1	45.17	89.5	111.6	105.6	123.5	42.88
Visico (7% Amb)									
non-crosslinked	110.4	–	137.5	47.74	91.2	114.6	108.1	123.5	42.88
crosslinked in water	109.7	98.9	112.2	38.96	91.4	115.5	106.3	117.3	40.73
aged 90°C/240h	111.5	101.6	130.1	45.17	89.9	104.6	107.0	115.1	39.97
aged 135°C/240h	105.6	–	125.4	43.54	89.0	105.1	105.4	119.7	41.56
DEX1 (5% Amb)									
non-crosslinked	106.3	–	114.9	39.90	87.4	110.5	103.3	106.4	36.94
crosslinked in water	106.3	96.1	112.8	39.17	87.9	107.4	102.5	108.0	37.50
aged 90°C/240h	107.6	99.4	114.7	39.83	87.4	110.6	102.5	106.5	36.98
aged 135°C/240h	101.7	–	103.5	35.94	86.4	106.1	101.5	102.8	35.69
DEX2 (5% Amb)									
non-crosslinked	101.7	–	92.2	32.01	78.1	84.9	97.2	81.5	28.30
crosslinked in water	101.0	–	89.5	31.08	78.9	83.6	96.7	84.5	29.34
aged 90°C/240h	102.8	–	90.0	31.25	78.9	84.0	96.5	84.7	29.41
aged 135°C/240h	95.2	–	82.9	28.78	76.9	82.9	95.2	79.5	27.60

[a] *maximum temperature from the highest peak (primary peak),* [b] *temperature of secondary peak arising from thermal annealing,* [c] *specific heat calculated from the primary peak area,* [d] *crystallinity evaluated according to eq. 5.1.*
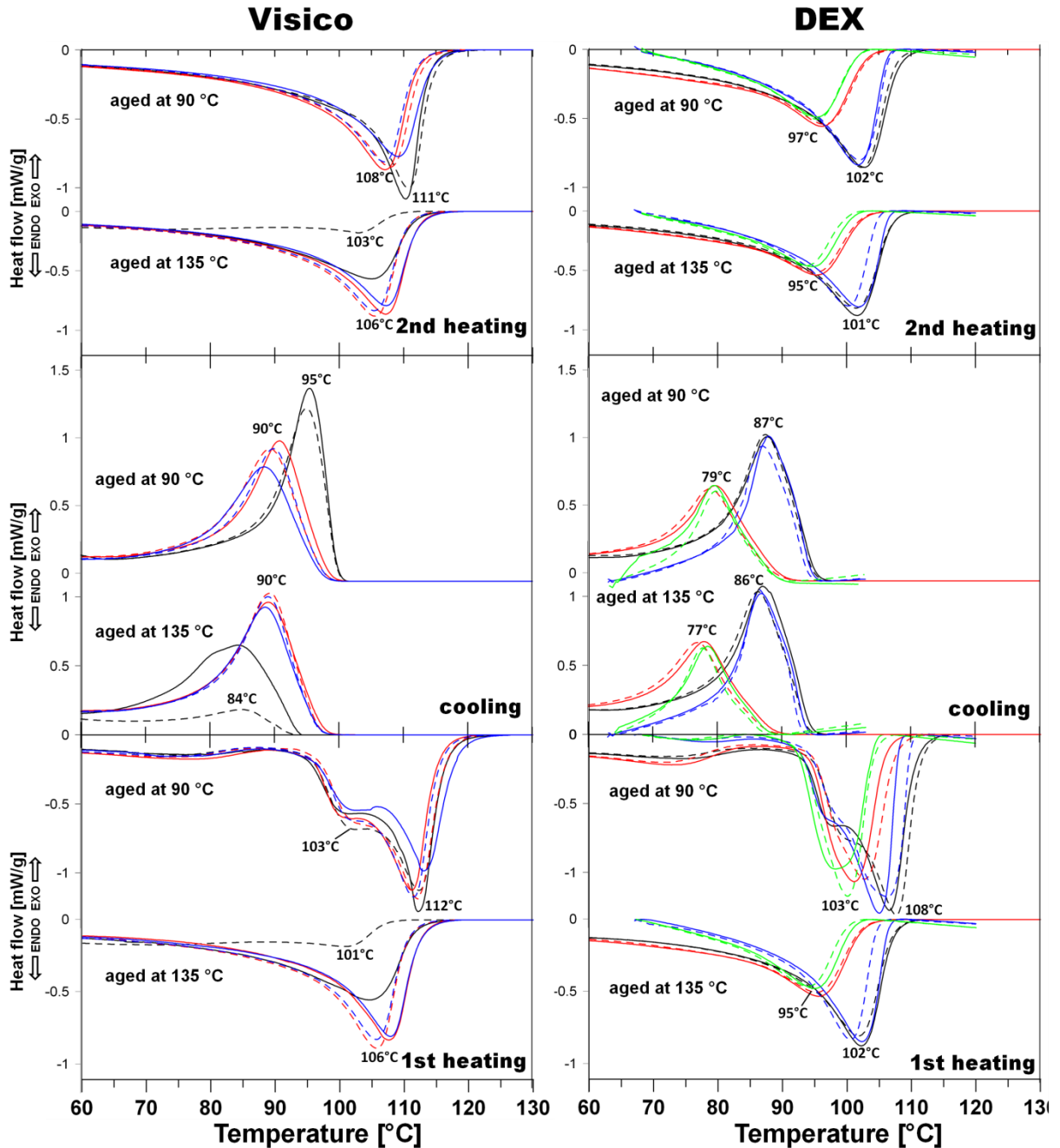
*Fig. 6.12: DSC thermograms of EVTMS copolymers during ageing in the oven. The values represent peak temperatures. **Left**: Visico (0% Amb) aged 24 h (━━━),Visico (0% Amb) aged 240 h (━ ━), Visico (5% Amb) aged 24 h (━━━),Visico (5% Amb) aged 240 h (━ ━), Visico (7% Amb) aged 24 h (━━━),Visico (7% Amb) aged 240 h (━ ━);*

***Right**: DEX1 (5% Amb) crosslinked in water, aged 24 h (━━━), DEX1 (5% Amb) crosslinked in water, aged 240 h (━ ━), DEX2 (5% Amb) crosslinked in water, aged 24 h (━━━), DEX2 (5% Amb) crosslinked in water, aged 240 h (━ ━), DEX1 (5% Amb) crosslinked in the room, aged 24 h (━━━), DEX1 (5% Amb) crosslinked in the room, aged 240 h (━ ━), DEX2 (5% Amb) crosslinked in the room, aged 24 h (━━━), DEX1 (5% Amb) crosslinked in the room, aged 240 h (━ ━).*

6.2.1 Thermal fractionation of Visico copolymer

It is well known, that a connection of two originally separated macromolecules through crosslink leads to a decrease of crystallization capability due to the introduction of irregularities which are usually excluded from the crystallized lamella, as well as due to restriction of segments mobility. According to crystallization kinetics theories, crystallization is controlled by two competitive processes: diffusion of molecules and formation of stable crystal nuclei. Thus, the PE molecules with more regular structure crystallize at higher temperature and vice versa. Furthermore, crystallization at higher temperature causes formation of thicker lamellae, which naturally have higher melting temperature. This fact is also supported by research, when crosslinked polyethylene was extracted by diluents to soluble sol and insoluble gel. Insolubility of gel results from a dense network structure. In comparison to original PE, higher content of structural irregularities in gel causes decline of melting temperature as well as different thermal fractionation behavior, since each melting peak is representative for distinct family of molecules with different structure [96].

Thermal fractionation technique can promote different structure units of EVTMS copolymer to form more stable equilibrium state during crystallization and melting process. For the purpose of explanation how the crosslinking influences a thermal properties, crosslinking of Visico copolymers in water bath at 90 °C up to 240 hours was performed. It is necessary to note that first four hours correspond to crosslinking in water bath employed in the common experiments.

DSC scans from thermal fractionation of Visico without Ambicat and Visico with 5% of Ambicat are shown in Fig. 6.13. At a first sight, there are clear differences between pure Visico and Visico with Ambicat at 0 hours suggesting different molecular structure which results probably from premature crosslinking of catalyzed Visico, although composition of Ambciat can also play a role (FTIR spectrum implies presence of polyethylene as a carrier of catalyst masterbatch) despite of low concentration. However, Visico without Ambicat shows four melting points corresponding to the temperatures of isothermal steps, while Visico with 5% of Ambicat has only three clear melting points. List of melting points, lamellar thicknesses and melting peak heights is in Tab. 6.3. Absence of fourth melting peak at about 110 °C relates to already mentioned lower crystallization capability caused by irregularities in molecular structure and restricted mobility of molecules.
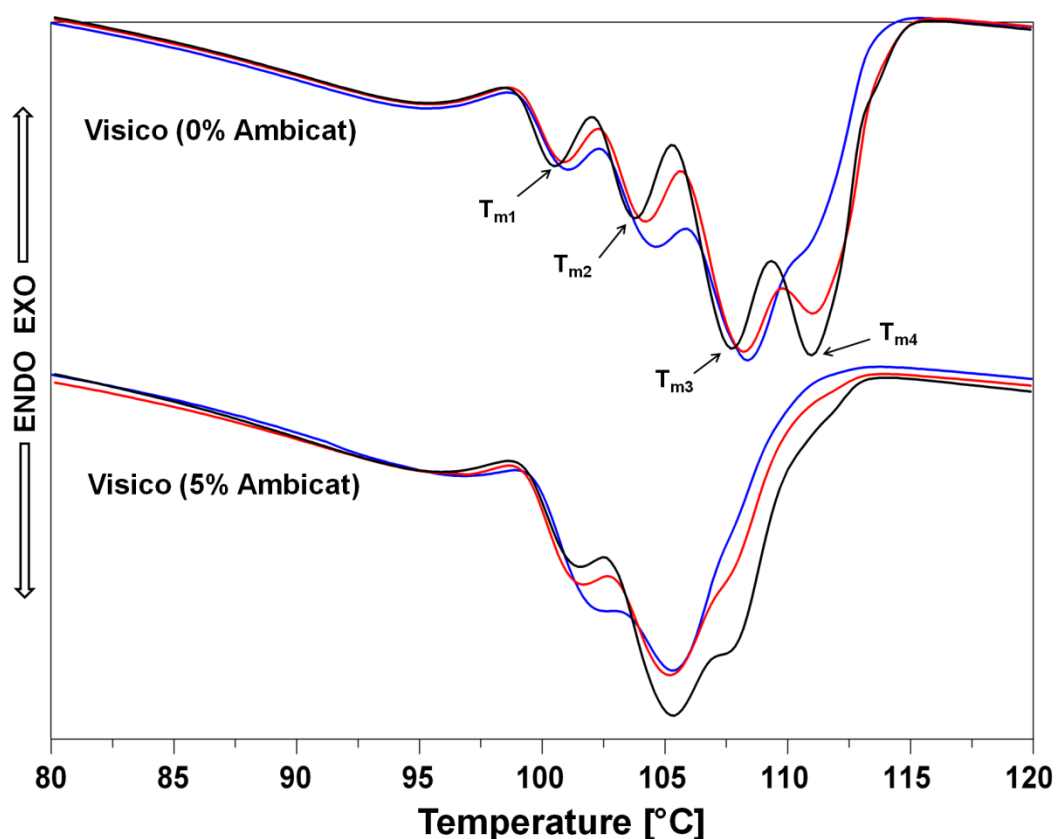
Fig. 6.13: Thermal fractionation of Visico copolymer crosslinked in water bath at 90 °C, up to 480 hours; non-crosslinked (———), crosslinked 4 hours (———), crosslinked 240 hours (———).

As can be further seen in both cases, molecular changes continue during crosslinking up to 240 hours, leading to gradual fall of peaks at higher temperatures while the peaks at lower temperatures increase. This fact corresponds with the gradual formation of network structure and thus lowering of crystallization capability of segments which, according to crystallization theory, crystallize at lower temperature and contribute to overall melting peak heights at lower temperature. Furthermore, the melting points have a tendency to shift T_m to higher values, therefore thicker lamellae are formed. However, the molecular changes are much more obvious in Visico with catalyst masterbatch than in Visico without catalyst. While Visico without Ambicat gradually loses only fourth peak, the melting points of Visico with Ambicat are reduced to two melting points. These results clearly prove that crosslinking causes decrease of melting and crystallization temperature as well as enthalpy of crystallization and melting, which was also observed in the samples during ageing in the oven at 135 °C.

The results from thermal fractionation confirm an importance of catalyst presence on crosslinking reactions, as well as significant changes of molecular structure and crystallization capability caused by crosslinks.

It is necessary to note that first DSC heating scans (not shown here) in this thermal fractionation experiment reveals initial structure corresponding with an

annealing at 90 °C, therefore a secondary peak appears. As a crosslinking in hot water proceeds in time, an annealing of solid copolymer causes shifting of secondary and primary peaks to higher temperatures (in agreement with previous observation), whereas morphology improvement was more significant in Visico without Ambicat probably due to less crosslinked structure. Furthermore, evolution of DSC thermal curves at cooling and second heating was in a good agreement with previous assumptions, i.e. crystallization and melting temperatures and enthalpies decrease with crosslinking time.

Tab. 6.3: Multiple melting temperatures, lamellar thicknesses and melting peak heights from DSC thermal fractionation scans.

Sample	Melting temperatrure [°C] /Lamellar thickness [nm] Peak height [mW/g]			
	T_{m1}	T_{m2}	T_{m3}	T_{m4}
Visico (0% Amb), crosslinked 0h	100.5 / 21.6 0.39	103.8 / 23.5 0.55	107.7 / 26.2 0.91	111.1 / 29.1 0.92
Visico (0% Amb), crosslinked 4h	100.8 / 21.8 0.40	104.3 / 23.8 0.56	108.2 / 26.6 0.92	111.0 / 29.1 0.82
Visico (0% Amb), crosslinked 240h	101.0 / 21.9 0.41	104.6 / 24.0 0.63	108.4 / 26.8 0.95	111.2 / 29.2 0.59
Visico (5% Amb), crosslinked 0h	101.5 / 22.1 0.53	105.4 / 24.5 0.94	107.5 / 26.1 0.77	110.5 / 28.6 0.20
Visico (5% Amb), crosslinked 4h	101.6 / 22.2 0.58	105.2 / 24.4 0.83	107.5 / 26.1 0.57	_____
Visico (5% Amb), crosslinked 240h	102.5 / 22.7 0.67	105.4 / 24.6 0.84	107.8 / 26.3 0.45	_____

* Lamellar thickness was calculated according to eq. 5.2. Peak height is a distance between linear baseline and maximal temperature of given T_m.

6.2.2 X-ray diffraction of Visico and DEX copolymers

Polyethylene is a semicrystalline material composed of amorphous and crystalline fractions and it behaves as polycrystalline solids in terms of X-ray diffraction. The crystalline area is characterized by a regular arrangement of chains. The chains form orthorhombic unit cell with a zig-zag conformation of molecules. Polyethylene shows two distinct reflection peaks at 21.3° and 23.5° (2θ) corresponding to the set of diffraction planes of (110) and (200), respectively.

Due to the semicrystalline nature, PE exhibits broad peak along the wide range of diffraction angles associated with amorphous portion of polymer. A ratio of the integral area of diffraction peaks above this amorphous halo to the total integral area is expressed as crystallinity. Information about crystallinity evaluated from X-ray pattern is of the same significance as of crystallinity evaluated from DSC, although the absolute value can be different.

Diffraction patterns of selected EVTMS copolymers are shown in Fig. 6.14. As can be seen, the samples exhibit typical PE pattern. Opposite to well-crystallized PE, the patterns of EVTMS copolymers have significant amorphous halo and less distinct diffraction peaks attributed to low crystallinity. The results of crystallinity evaluated from X-ray patterns are shown in Fig. 6.15. As can be seen, the absolute values of crystallinity are lower than those calculated from DSC scans due to differences between these two methods. However, the evolution of crystallinity is the same. Crystallinity of EVTMS copolymers decreases in the following order: Visico without Ambicat > Visico with 5% of Ambicat > DEX1 > DEX2 what agrees with the results from DSC method. The highest crystalline fraction in Visico without Ambicat can be also confirmed by intense peaks in X-ray patterns, especially the (200) peak and conversely, DEX2 aged at 135 °C for 240 hours with the lowest crystallinity has the less intense (200) peak. In comparison to DSC scans, crosslinking and ageing at 90 °C have a tendency to increase crystallinity, whereas ageing at 135 °C decreases crystallinity.

It is necessary to mention that the differences in crystallinity values are minimal and crystallinity estimated from X-ray patterns may not to be as accurate as from DSC scans. Furthermore, the fine morphological changes of polymers could be hard to recognize from X-ray diffraction patterns, therefore DSC appears as a better tool for following morphological changes during crosslinking and ageing of EVTMS copolymers.
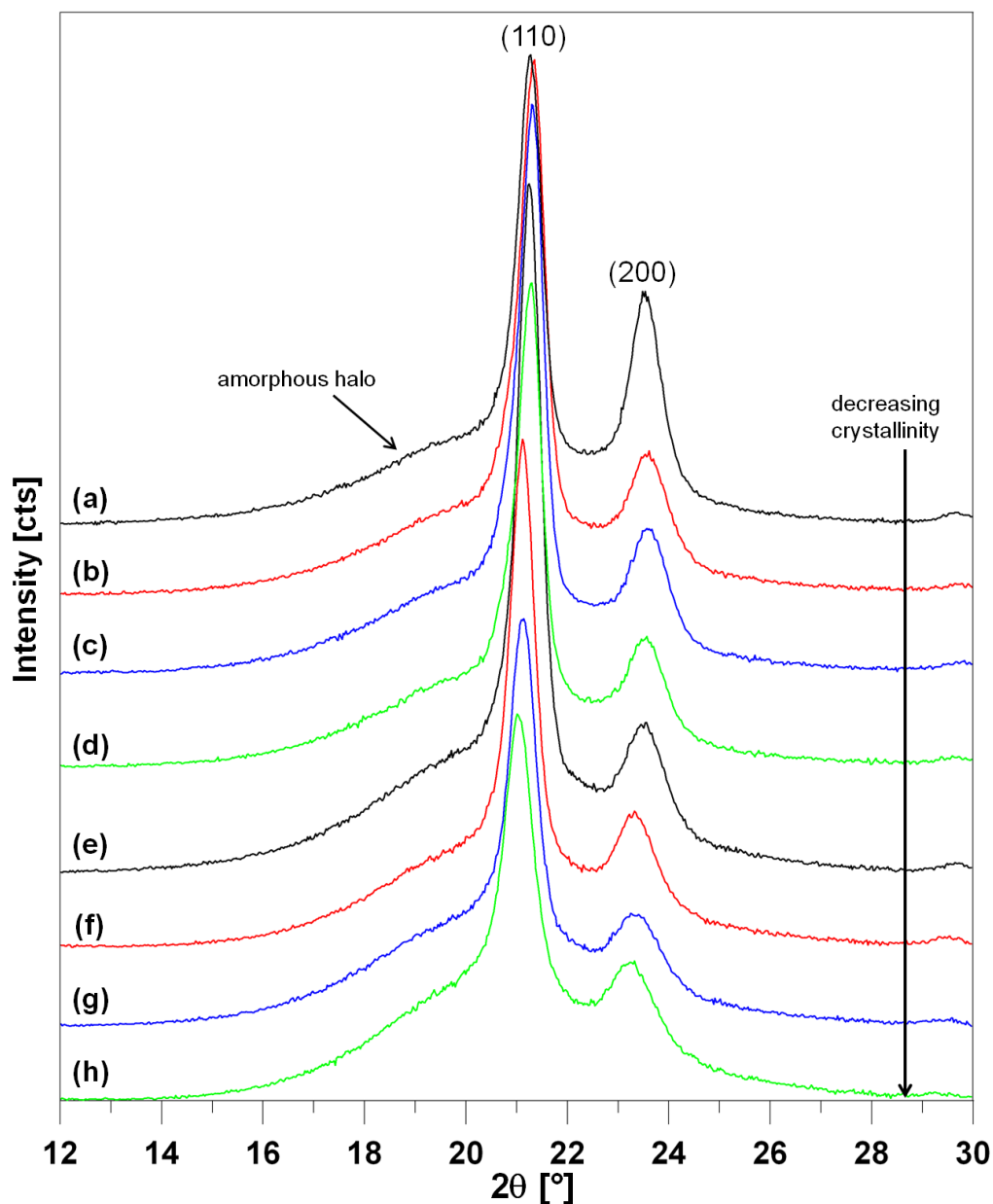
Fig. 6.14: Selected XRD patterns of Visico and DEX copolymers: (a) Visico (0% Amb) non-crosslinked, (b) Visico (5% Amb) non-crosslinked, (c) Visico (5% Amb) aged at 90 °C for 240 h, (d) Visico (5% Amb) aged at 135 °C for 240 h, (e) DEX1 (5% Amb) aged at 90 °C for 240 h, (f) DEX1 (5% Amb) aged at 135 °C for 240 h, (g) DEX2 (5% Amb) aged at 90 °C for 240 h, (h) DEX2 (5% Amb) aged at 135 °C for 240 h.
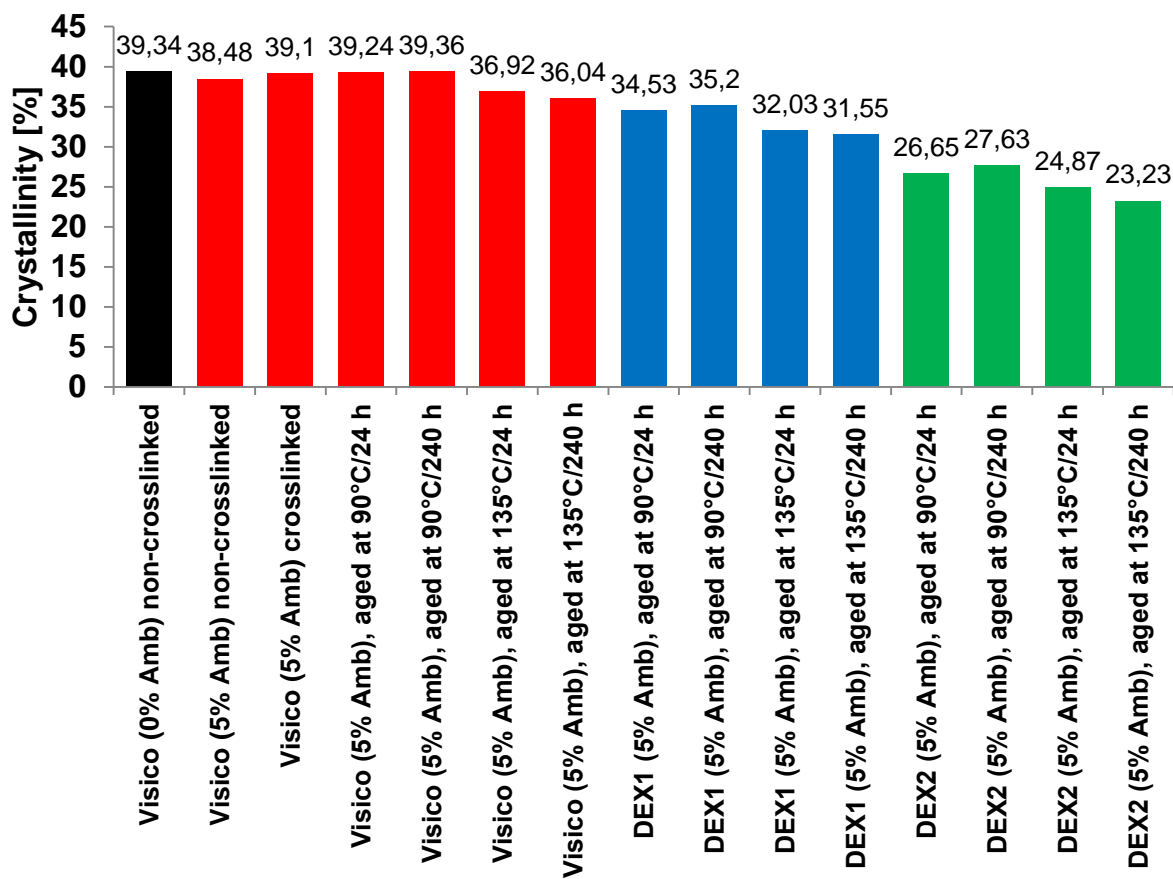
Fig. 6.15: Crystallinity evaluated from XRD patterns of EVTMS copolymers crosslinked in water bath and subsequently aged.

6.3 Mechanical properties of EVTMS copolymers

6.3.1 Mechanical tensile testing

The crosslinking of semicrystalline polymers influences the properties in the similar way as in the case of amorphous polymers, because crosslinking proceed mainly in amorphous state of polymers. If the crosslinking has an influence on the morphology of final products, the impact on mechanical properties is more complex. However, higher crosslinks density should basically leads to higher modulus and lower strain at break. On the other hand, drop of crystallinity causes decrease of modulus and material become more ductile.

The differences in tensile stress-strain curves significantly depend on the crosslinking capability, composition and morphology of EVTMS copolymers what can be seen in Fig. 6.16. The tensile stress-strain curves have similar development to ductile semi-crystalline polymer, although there are some differences resulting from specific composition and molecular structure of EVTMS copolymers. Each curve can be divided into the three main regions (first graph in Fig. 6.16). First region from A to Y represents uniform elastic deformation from which Young's modulus is evaluated. In the region Y and D, the stress drops with little plastic deformation of the sample. Point Y is called yield point and is closely connected to the specific morphology arrangement. In point D, the necking begins and the load passes through minimum and remains constant. Subsequently, new region from D to B is initiated, where the sample goes on stretching until it breaks at B point (breaking point). The increase of stress before breaking is attributed to a reinforcement caused by fibrillar rearrangement of molecules. Further deformation results in hardening until the chains become immobile. At this point B, the stress is concentrated to the defects and imperfections which leads to the rupture of polymer [97].

Visico without Ambicat shows the highest strain at break and distinct yield point. Mixing of Visico with Ambicat causes changes in curve development, which can be contributed to substances added in Ambicat as well as premature crosslinking of copolymers. However increase of strength and drop of elongation is clearly visible. Furthermore, the tensile curves vary according to ageing temperature. Visico with 5% and 7% of Ambicat exhibit similar deformation behavior. Conversely, copolymers DEX1 and DEX2 exhibit different deformation behavior, although behavior of DEX1 is close to Visico copolymers, what is related to analogous morphology resulting from DSC scans. On the other side, structure differences of DEX2 lead to low elongation without clear yield point.
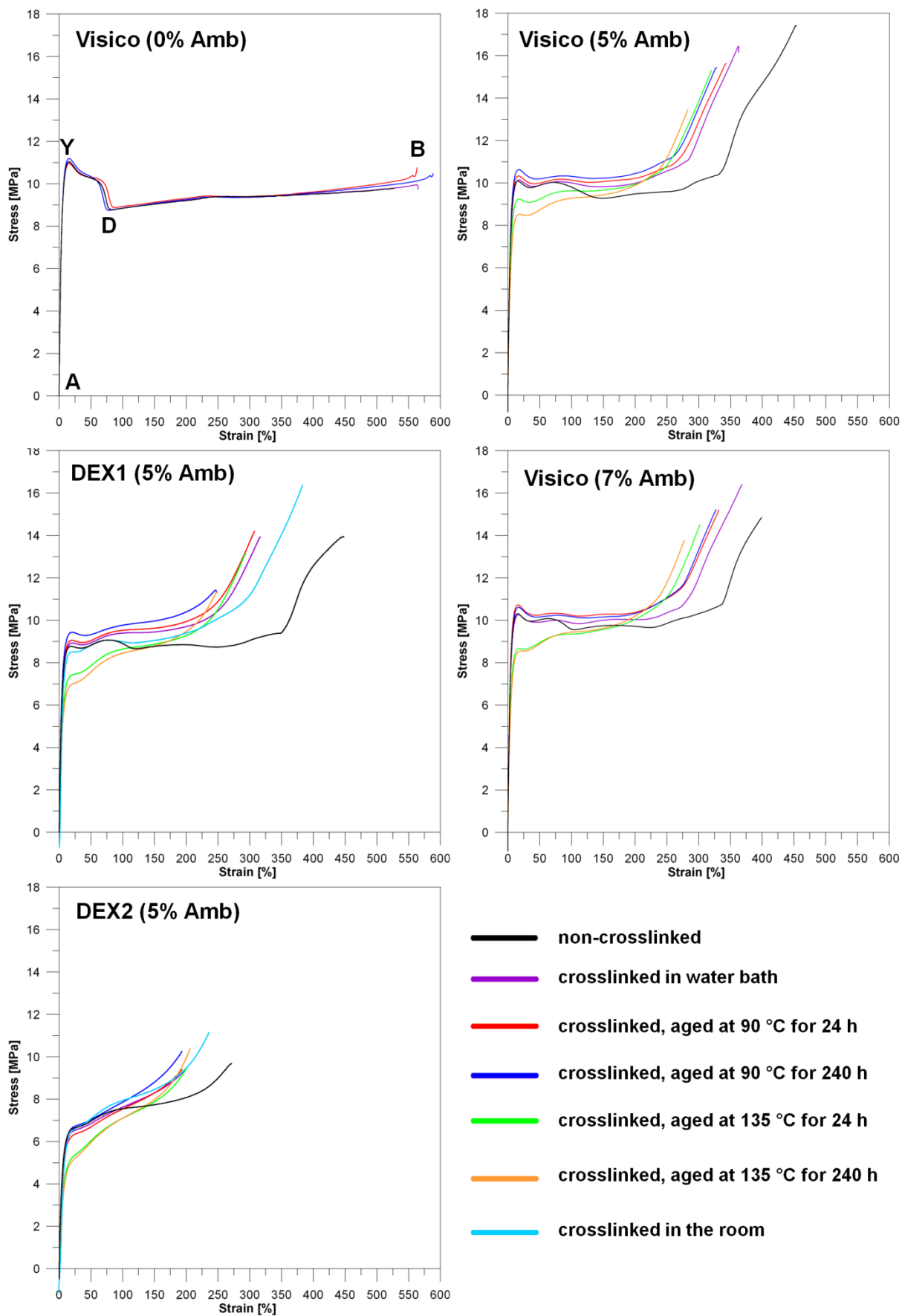
Fig. 6.16: Selected stress-strain curves of EVTMS copolymers. In the first graph, letter Y indicates yield point and B indicates breaking point.

It is necessary to mention that tensile behavior of Visico without Ambicat during ageing at 135 °C was not possible to measure, because the ageing temperature was higher than T_m of copolymer and specimens were unsuitable deformed due to melt flow. This was not a case of copolymers with Ambicat thanks to sufficient network density formed during crosslinking. Therefore, the crystalline portion of crosslinked samples can be physically melted, but high viscosity constrains a flow. However, degradation of Visico without Ambicat during ageing at 135 °C led to the rapid lost of mechanical properties irrespectively whether the tensile testing was performed or not.

Tensile mechanical characteristics are shown in Tab. 6.4. As can be seen, Visico without Ambicat has the highest modulus (227 MPa) which is similar to LDPE as well as the highest strain at break (about 500%). Visico with 5% and 7% of Ambicat exhibit lower modulus and strain at break due to already mentioned different composition and crosslinking. DEX2 exhibits the lowest values of these characteristics.

It is interesting that initial values of non-crosslinked samples are higher than the samples crosslinked in water bath. This observation could be attributed to molecular orientation formed during processing. It is well-known that the higher orientation, particularly in the surface layer, leads to higher modulus and strength values in extruded articles.

As was mentioned before, DEX2 has not clear yield point, thus yield properties could not be determined. This is also the case of DEX1 aged at 135 °C. Therefore, material becomes more ductile after remelting and loses toughness.

Generally, ageing at temperature of 135 °C leads to significant morphology changes, drop of crystallinity and melting temperature due to irregularities caused by crosslinking. As can be seen, ageing at 135 °C leads to the significant drop of modulus, as well as decrease of stress at yield and increase of strain at yield.

Complete evolution of tensile characteristics during crosslinking and ageing is shown in Fig. 6.17 for Visico copolymers, and in Fig. 6.18, 6.19 for DEX copolymers.

The modulus has a tendency to increase during ageing at 90 °C due to recrystallization processes (Fig. 6.17). This is obvious especially in the case of Visico without Ambicat (aged at 90 °C) due to faster morphology evolution as the chain mobility is less hinder by crosslinks compared to Visico with Ambicat. Stress at yield exhibit similar evolution since these characteristics are closely connected to polymer morphology. Melting and ageing of samples at 135 °C, followed by cooling to room temperature, leads to drastically changes of modulus and strain at yield due to completely different morphology. The fast decrease of modulus and stress at yield can be again attributed to this phenomenon rather than to crosslinking.

On the other hand, tensile properties such as stress and strain at break exhibit different evolution. First, the values of these characteristics vary with Ambicat content, what indicates the influence of composition and crossllinking on the strength and drawability. Lower strain at break of Visico with Ambicat is clearly connected with the sensitivity to croslinking: with increasing crosslink density, drawibility sharply decreases. On the other hand, since Visico without Ambicat is basically non-crosslinked, its strain at break is naturally higher. Slight increase in time can be caused by further recrystallization of initial morphology.

Visico with 5% and 7% of Ambicat aged at 90 °C does not exhibit significant changes in time (slightly decreasing trend only). Ageing at 135 °C lowers the strain at break in comparison to ageing at 90 °C, but in this case the change is rather moderate. On the other side, stress at break exhibit rather constant values which is still higher than for Visico without Ambicat, although the increase with crosslinking should be expected.
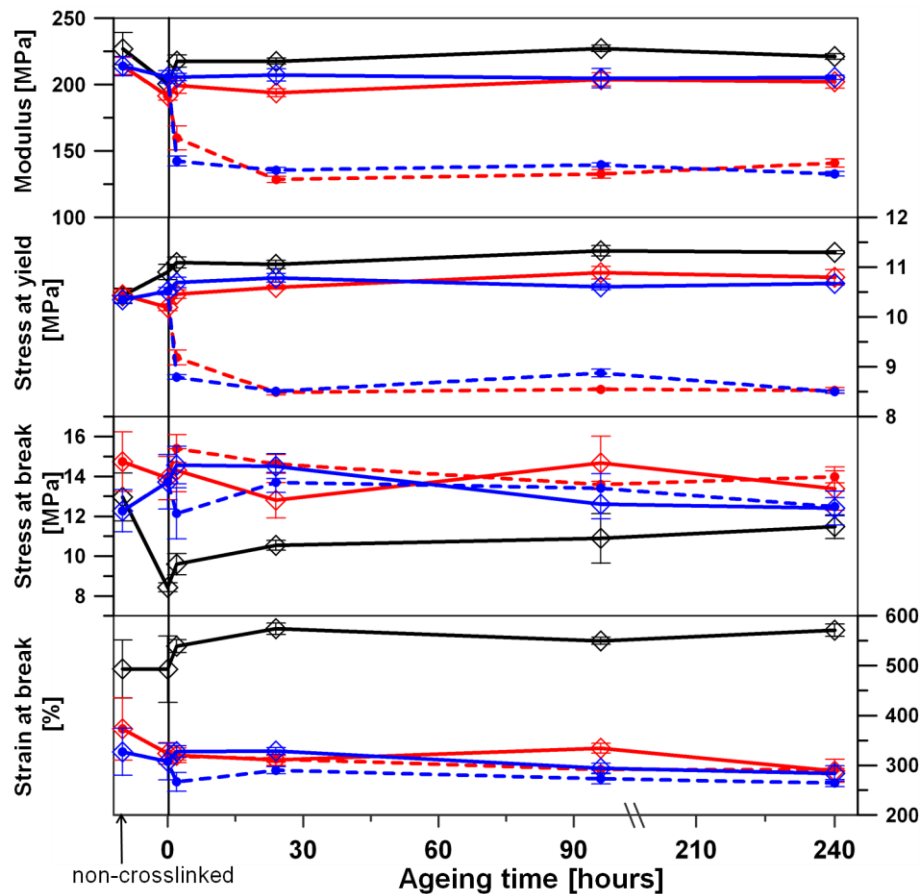
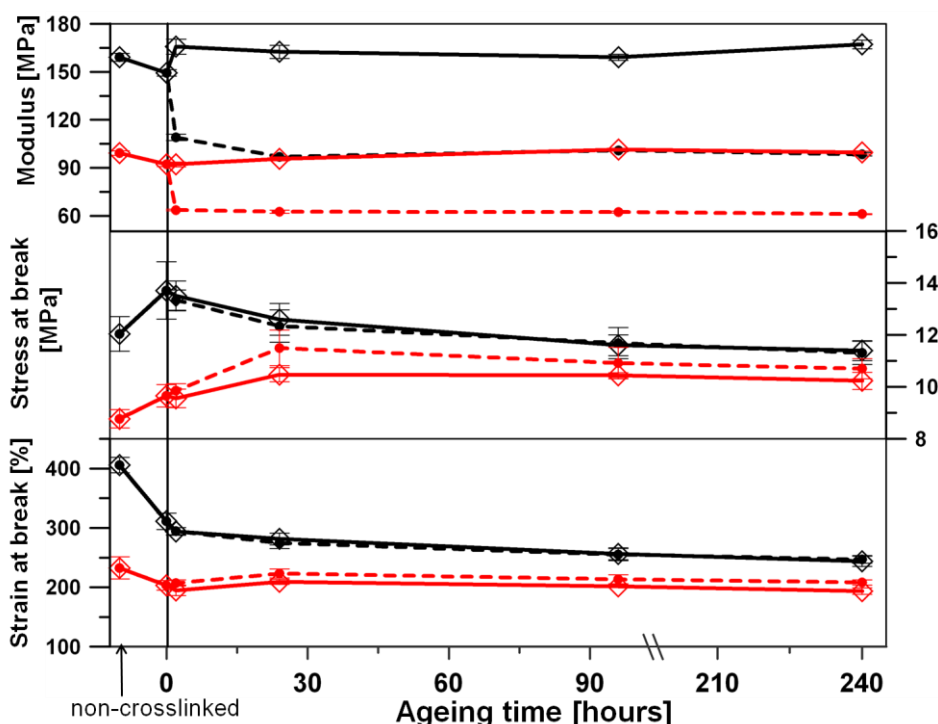*Fig. 6.17: Evolution of tensile mechanical properties during ageing of Visico copolymers. First symbol represents non-crosslinked sample and second symbol crosslinked sample with no ageing: Visico (0% Amb), aged at 90 °C (———); Visico (5% Amb), aged at 90 °C (———); Visico (5% Amb), aged at 135 °C (— —); Visico (7% Amb), aged at 90 °C (———); Visico (7% Amb), aged at 135 °C (— —).*

Tab. 6.4: Results of tensile testing of Visico and DEX copolymer (average values with standard deviation). E – Young's modulus, σ_Y – stress at yield, L_Y – strain at yield, σ_B – stress at break, L_B – strain at break.

Copolymer	Sample	Tensile mechanical properties				
		E (MPa)	σ_Y (MPa)	L_Y (%)	σ_B (MPa)	L_B (%)
Visico (0% Amb)	non-crosslinked	227.0±12.2	10.43±0.15	14.91±0.12	12.97±1.21	493.29±58.62
	crosslinked in water	200.5±6.2	10.90±0.15	15.70±0.21	8.43±0.23	493.15±66.65
	aged 90°C/240h	221.3±2.1	11.26±0.03	15.97±0.14	11.48±0.60	571.52±12.31
	aged 135°C/240h	n/a	n/a	n/a	n/a	n/a
Visico (5% Amb)	non-crosslinked	214.0±6.5	10.44±0.10	14.76±0.40	14.74±1.50	372.99±62.60
	crosslinked in water	191.5±3.2	10.19±0.07	16.91±0.19	13.92±1.09	324.05±21.58
	aged 90°C/240h	202.1±5.4	10.79±0.16	16.65±0.14	13.39±1.09	288.62±23.15
	aged 135°C/240h	141.0±3.2	8.52±0.06	18.39±0.14	13.98±0.30	291.14±2.20
Visico (7% Amb)	non-crosslinked	213.9±7.4	10.34±0.08	15.21±0.14	12.27±1.06	327.08±47.22
	crosslinked in water	205.7±4.7	10.52±0.07	16.23±0.17	13.73±1.36	307.64±36.63
	aged 90°C/240h	205.5±1.7	10.67±0.02	16.64±0.21	12.42±0.85	283.76±15.35
	aged 135°C/240h	132.8±1.8	8.50±0.03	21.45±0.22	12.48±0.46	264.17±6.95
DEX1 (5% Amb)	non-crosslinked	159.2±2.5	8.69±0.03	18.47±0.24	12.04±0.67	406.05±13.09
	crosslinked in water	149.3±2.0	8.99±0.11	21.15±0.57	13.72±1.11	311.25±13.96
	crosslinked in room 240 h	150.0±9.73	8.52±0.10	19.36±0.13	14.02±0.50	400.40±6.86
	aged 90°C/240h	167.2±2.6	9.42±0.04	19.71±0.21	11.40±0.38	243.98±8.83
	aged 135°C/240h	98.4±1.1	n/a	n/a	11.31±0.45	247.04±6.52
DEX2 (5% Amb)	non-crosslinked	99.23±1.3	n/a	n/a	8.78±0.35	232.87±18.49
	crosslinked in water	92.18±1.5	n/a	n/a	9.66±0.44	203.48±8.06
	crosslinked in room 240 h	101.3±8.7	n/a	n/a	12.55±0.51	294.04±6.92
	aged 90°C/240h	99.5±0.9	n/a	n/a	10.23±0.32	193.48±5.33
	aged 135°C/240h	61.0±0.4	n/a	n/a	10.70±0.39	208.38±4.23

Evolution of tensile properties of DEX1 and DEX2 copolymers crosslinked in water bath is given in Fig. 6.18. Similarly as in the case of Visico, the ageing above melting temperature leads to dramatic drop of modulus. Due to higher crystallinity, DEX1 has higher initial modulus than DEX2. On the other hand, the drop of modulus associated with ageing at 135 °C is much more significant, what is other evidence of the relevance of crystalline arrangement in EVTMS copolymers in terms of tensile properties, since the morphology has the strong influence on the toughness.

Both DEX copolymers have composition enabling faster crosslinking. Thus, the changes of stress and strain at break during crosslinking and ageing are more pronounced. Decrease of drawability in time is evident and is caused by crosslinking. On the other hand, while stress at break of DEX2 increases in time, DEX1 exhibits the decrease. There is a question, if this decrease is somehow connected with the morphology evolution, since increasing of strength during crosslinking should be rather expected.

Fig. 6.18: Evolution of tensile mechanical properties during ageing of DEX polymers crosslinked in water bath. First symbol represents non-crosslinked sample and second symbol crosslinked sample with no ageing: DEX1 aged at 90 °C (——); DEX1 aged at 135 °C (— —); DEX2 aged at 90 °C (——); DEX2 aged at 135 °C (— —).

Tensile properties of DEX1 and DEX2 crosslinked at room conditions and aged in the oven are shown in Fig. 6.19. It should be emphasized that slow crosslinking, opposite to fast crosslinking in water bath, shows gradual evolution of tensile properties in time.

It can be expected that the modulus remains constant, since no morphological improvement occur at room temperature. As can be seen, changes during ageing are not as clear as in Fig. 6.17. Decrease of modulus at the beginning of ageing is in both cases could be connected with already mentioned orientation caused by extrusion. However as can be expected, decrease of modulus at 135 °C is more pronounced than at 90 °C.

During crosslinking, strain at break exhibits slow decline and this trend continues also during ageing. This is not surprising, because both polymers have better crosslinking capability, thus evolution of tensile properties, especially associated with the breaking point, should be more influenced by crosslinks density. Furthermore, stress at break clearly increases in crosslinking time, although development during ageing is unclear and rather constant. The changes of characteristics at the beginning of ageing could relate to the temperature induce crosslinking, since higher temperature can cause additional chemical reaction. From this point of view, it seems that crosslinking of DEX copolymers in water bath is more intense and faster and there are some differences depending whether crosslinking proceeds in water bath at 90 °C or at room temperature.
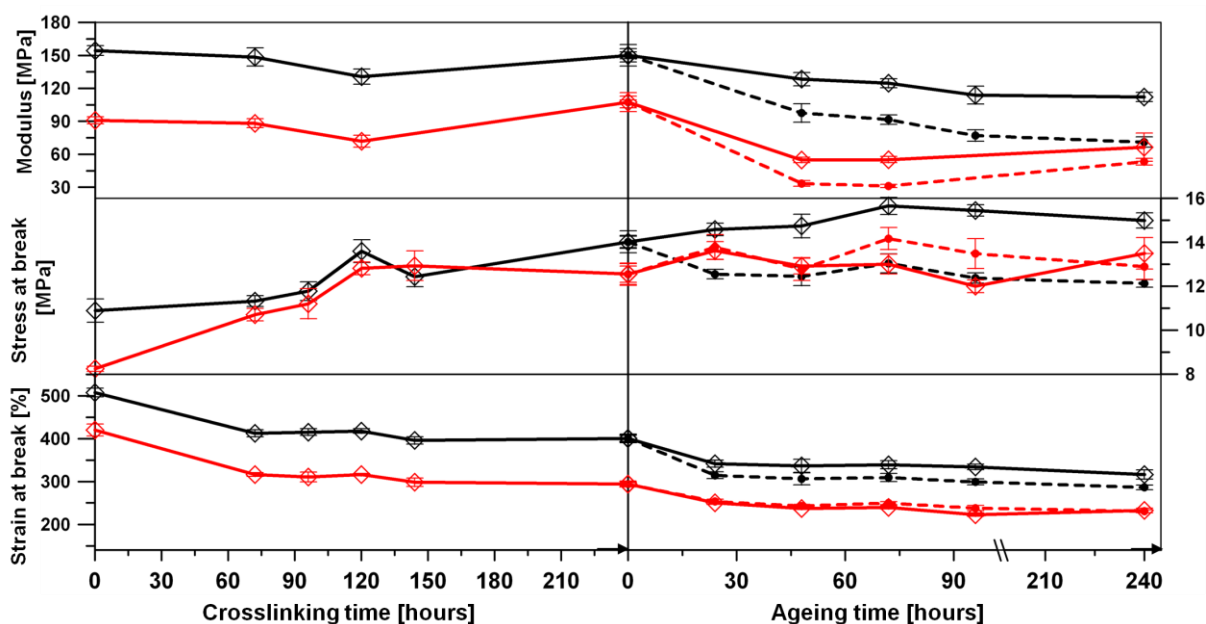
Fig. 6.19: Evolution of tensile mechanical properties during ageing of DEX polymers crosslinked at room conditions (left part) and subsequently aged (right part); DEX1 (——), DEX2 (——); ageing at 90 °C (solid), ageing at 135 °C (dashed).

6.3.2 Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis is a sensitive method invented for the measurement of thermo-mechanical behavior of viscoelastic properties. The main characteristics of analysis is the development of the storage modulus E' representing elastic properties, the loss modulus E'' representing viscous behavior and tan δ referred to the loss tangent. Loss tangent is ratio of E''/E', and the occurrence of local maxima of loss tangent is connected with significant changes of mechanical properties, related to relaxation transitions occurring at characteristic temperatures such as glass transition temperature (T_g) and melting temperature (T_m). The measurements of branched polyethylene at lower frequencies show loss maxima at approx. 70 °C, -20 °C and -120 °C labeled as α, β and γ transitions, respectively. The γ transition is believed to be primary relaxation, i.e. T_g, occurring in the range of -150 to -100 °C and is attributed solely to the amorphous fraction of polymer. The β transition is attributed rather to the relaxation of chain branches. The α transition is, on the other hand, assigned to crystalline relaxation [98].

It is well known that chemical crosslinks reduce the free volume due to packing of chains close together what leads to the increase of T_g. Furthermore, T_g increases as the crystallinity increases, since γ transitions is connected with the amorphous content of polymer. Thus, crosslinking of semi-crystalline polyethylene is a combination of both effects [99, 100].

Dynamical mechanical properties of selected Visico samples are given in Fig. 6.20. As can be seen, there is not visible clear glass transition temperature (T_g). This is because the curves start from -130 °C showing shoulder of peak, thus we could expect that T_g of Visico is below this temperature. It can be expected that T_g of EVTMS copolymer should be lower than T_g of linear PE due to presence of irregularities in chemical constitution caused by statistical copolymerization with vinyl trimethoxysilane. The first peak of tan δ is attributed to temperature about -15 °C and second at about 70 °C (Tab. 6.5).

There are not any significant differences between Visico without Ambicat and with 5% Ambicat annealed below T_m. Some differences are visible at temperature higher than α loss tangent peak, i.e. 70 °C. Above this temperature, the changes of morphology occur and Visico without Ambicat exhibits the highest changes due to absence of crosslinked structure, thus the viscous behavior, i.e. flow, become dominant process. Furthermore, annealing and crosslinking of Visico with 5% of Ambicat lead to slightly higher E', what can be effect of recrystallization as well as crosslinking.

On the other side, Visico (5% Amb) aged at 135 °C exhibits distinct thermal behavior, mainly above -18 °C. It is interesting that both peaks of loss tangent are shifted, and storage as well as loss modulus decreases more than modulus of samples aged at 90 °C. This is probably the effect of remelting of initial morphology and subsequent creating of completely new morphology with lower T_m and X_c, which has an influence on position of transition maxima. *Khonakdar*

et al. [99] observed similar results: peroxide crosslinked PE shows lower T_g opposite to non-crosslinked PE due to homogenizing of network structure and drop of crystallinity caused by crosslinking above T_m. It is obvious that a change in morphology is the dominant process opposite to creation of network structure with low density, since the decrease of α transition occurs. On the other hand, the β transition seems to be virtually shifted to higher temperature (although there is not a maximum of loss tangent) which can relate to contribution of crosslinks to the amorphous fraction. As can be further seen, E'' decreases more than E' above 50°C, thus sample exhibit more elastic behavior probably due to homogenizing of network structure at remelting process. Therefore a new morphology seems to be more effective in terms of elastic behavior, but the same process causes a deterioration of toughness.
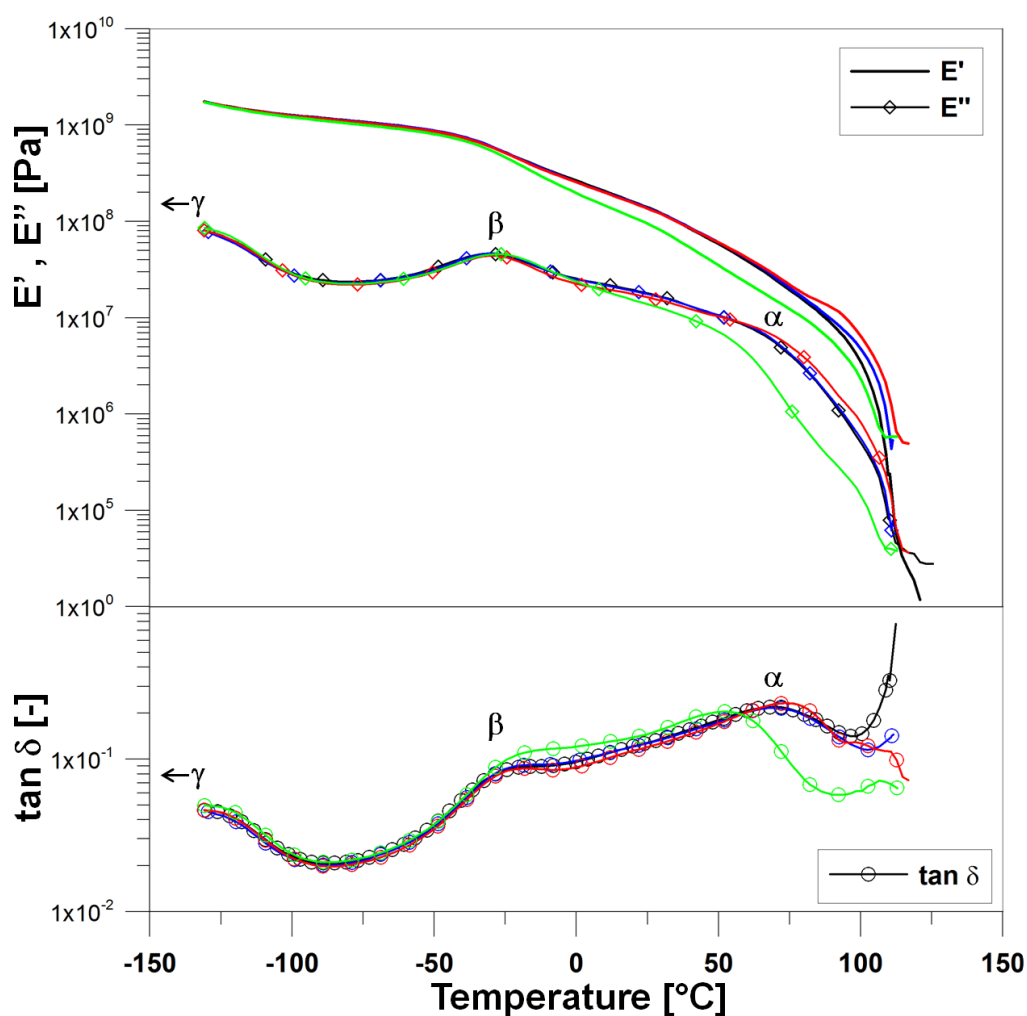
Fig. 6.20: Dynamic mechanical thermal properties of selected Visico samples. E' – storage modulus, E'' – loss modulus, tan δ - loss tangent. Visico (0% Amb) non-crosslinked (━━━);Visico (5% Amb) non-crosslinked (━━━);Visico (5% Amb) aged at 90 °C, 240 h (━━━);Visico (5% Amb) aged at 135 °C, 240 h (━━━).

Tab. 6.5: Dynamic storage modulus at 23 °C and loss tangent peak temperatures of samples from Fig. 6.19.

Sample	tanδ peaks [°C]		E' at 23 °C [MPa]
	β	α	
Visico (0% Amb) non-crosslinked	-15.6	69.9	148
Visico (5% Amb) non-crosslinked	-14.5	69.3	146
Visico (5% Amb) aged at 90°C, 240 h	-17.9	73.7	144
Visico (5% Amb) aged at 135°C, 240 h	—	50.7	101

7. CONCLUSION

The goal of this work was to investigate relation between the preparation, structure and properties of the final products of crosslinked and thermally aged EVTMS copolymers. Copolymers used herein have properties similar to LDPE and they are often used as an electric insulation for low voltage cables and wires. Compared to radical crosslinked polyethylene, the ethylene-vinyl trimethoxysilan copolymers are crosslinked by moisture giving the possibilities to monitor the characteristic silanol and siloxane bands by FTIR method. As was shown in the work, following of chemical changes in Visico copolymer is relatively simple if given wavenumber region is not affected by other bands. Unfortunately, this is not the case of DEX copolymers due to their chemical composition affecting the intensity of bands and monitoring of chemical reactions become more difficult. However, suitable chemical composition of the mixture allows following the extent of crosslinking reactions in time. Further, FTIR method showed significant influence of the catalyst and antioxidant compounds on the chemical reactions in the copolymer. While the catalyst significantly affects the crosslinking reaction, the antioxidant conversely ensures the stability of the chemical structure during aging, especially above the copolymer melting temperature (135 °C). Ageing without stabilization leads then to the changes of color, morphology and mechanical properties of copolymers. On the other hand, the catalyst can cause premature crosslinking of the copolymers, which occured in both, Visico and DEX copolymers, although the premature crosslinking was more intense in DEX due to their chemical composition. However, the crosslinking in water bath at 90 °C for 4 hours is proper arrangement to ensure sufficient extent of crosslinking reactions for Visico and DEX. Furthermore, the crosslinking of DEX copolymers in water bath seems to be more efficient than crosslinking in the room at ambient conditions for 240 hours. The results further indicate that the crosslinks formed in DEX materials (mainly DEX2) can have different structure in comparison to Visico due to faster crosslinking leading to formation of oligomeric siloxane bonds.

Other chemical changes that occur during ageing are modest what suggests additional crosslinking. The temperature differences (90 °C and 135 °C) do not only affect the reaction kinetics, but in the case of 135 °C, the copolymers are in molten state, and thus it is possible to assume that the loss of the crystalline structure affects the diffusivity of reaction species. Therefore, it is evident that further chemical reactions are more intense at 135 °C.

The difference in the extent of reactions between Visico copolymers with different concentrations of Ambicat (5% to 7%) is minimal, although the chemical changes are logically greater in Visico with 7% of Ambicat. This demonstrates that the composition of the catalyst masterbatch enables effective crosslinking even at low concentrations.

Molecular structure of the EVTMS copolymer significantly affects the morphology. The differences in the melting and crystallization behavior are obvious and they are influenced not only by chemical composition but also by process history, temperature and ageing time. The most crystalline copolymer is Visico without Ambicat, while DEX2 polymer contains the lowest crystalline fraction due to specific chemical composition allowing more intense crosslinking. DSC measurement proved that ageing below melting temperature (90 °C) causes crystalline improvement, while ageing above melting temperature (135 °C) causes the remelting of initial morphology and reduction of the crystalline order quality. Of course, the annealing process at 90 °C affects the recrystallization process of copolymers depending on their melting temperatures. While the morphology is almost unaffected by crosslinking reactions during aging at 90 °C, an ageing at 135 °C, as well as remelting, are strongly influenced by the network structure. It can be seen that with increasing network density, the crystallinity decreases after remelting due to homogenizing of initial morphology and subsequent crystallization, which are strongly influenced by crosslinks. The results of thermal fractionation clearly showed that network structure affects the crystallization in terms of reduction of the crystallization ability and melting temperature due to shortening of segments and introduction of irregularities into the macromolecule structures. Effect of recrystallization at 90 °C and homogenization at 135 °C on the copolymers crystallinity is confirmed by XRD results. DSC results further showed that the unstabilized copolymer (Visico without Ambicat) loses its regular arrangement at 135 °C resulting in drastic decrease of crystallinity related to the poor mechanical properties.

As in the previous case, it is possible to say that the results of the tensile testing and initial mechanical properties are given by composition and morphology of the copolymers. With the loss of crystallinity and an increase of network density, tensile stress-strain curve changes from polyethylene-like (exhibits the yield point) to the rubber-like material. These differences can be seen especially in comparison of copolymer Visico without Ambicat and DEX2 with 5% of Ambicat. Based on these results, it is possible to conclude that two competing processes occur upon crosslinking and all ageing conditions: (I) improvement of crystalline order, (II) further crosslinking reactions. Both of these processes affect the mechanical tensile properties in different ways. While changes in morphology significantly affect the modulus and yield point, the properties, such as strength and drawability, are affected by crosslinking. It must be emphasized that the changes in morphology affect tensile and dynamic mechanical properties much more than the crosslinking with low network density. Therefore, the morphology changes are dominant factor in terms of mechanical properties of EVTMS copolymers. Aging temperature thus has significant influence on the mechanical properties, especially if chemical changes together with the restriction of chains mobility occur.

8. CONTRIBUTION TO THE SCIENCE AND PRACTICE

The presented research shows possibilities of the thermal resistance and the applicability of specific types of EVTMS copolymers in terms of safe use as cable and wire insulations. It was clearly demonstrated that the properties of crosslinked semi-crystalline polyethylene or its copolymers can be significantly affected by temperature, particularly if the temperature is close to the melting point. Although crosslinking has positive effect on some properties required for certain applications, significantly reduces flow and ensures dimensional stability of products, morphological changes caused by the introduction of irregularities and restriction of chains mobility could adversely affect the final properties of the products. Since the greatest changes occur after melting and crystallization, application area of EVTMS copolymers should not include applications in which melting of copolymer occurs. Temperature below melting point can have impact on the long-term properties due to the morphological improvement, which slightly affects the mechanical properties. Other disadvantage of EVTMS copolymers is the possibility of continuous crosslinking reaction at certain conditions, as well as a risk of premature crosslinking before processing. Therefore, the catalyst system in the mixture should be sufficient effective to ensure that the most crosslinking reactions occur during controlled process, and thus avoid further crosslinking or even breaking of crosslinks by hydrolysis of the siloxane bonds. Crosslinking at room conditions allows savings in production costs compared to crosslinking in the sauna or hot water but, even in that process, a sufficient crosslinking should be ensured. Another advantage of EVTMS copolymers crosslinked by humidity at room conditions is that no morphological improvement occurs due to low temperature.

Furthermore, morphological and chemical changes may deteriorate dimensional stability, create internal stress and reduce application possibilities and durability. Utilization of additives in these copolymers, such as antioxidants, scorch retardants and others, is necessary for long lifetime without additional changes of structure.

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LIST OF FIGURES

80

LIST OF TABLES

LIST OF SYMBOLS AND ACRONYMS

ΔH_c	crystallization enthalpy
ΔH_m	melthing enthalpy
2θ	diffraction angle two theta
COC	cyclic olefins
DMA	dynamic mechanical analysis
DMTA	dynamic mechanical thermal analysis
DSC	differential scanning calorimetry
E	young's modulus
E'	storage modulus,
E''	loss modulus
EAA	ethylene acrylic acid
EVA	ethylene-vinyl acetate
EVS	ethylene-vinyl silane
EVTMS	etylene-vinyl trimethoxysilane
FTIR	Fourier transform infrared spectroscopy
HDPE	high density polyethylene
IR	infrared
L	lamellar thickness
L_B	strain at break
LDPE	low density polyethylene
LLDPE	linear low density polyethylene
L_Y	strain at yield,
MWD	molecular-weight distribution
n_c	network density
PE	polyethylene
PEX	crosslinked polyethylene
RH	relative humidity
RBI	relative band intensity
$\tan \delta$	loss tangent
T_c	crystallization temperature
T_g	glass transition temperature
T_m	melting temperature
UHMWPE	ultra high molecular weight polyethylene
UV	ultraviolet radiation
wt%	percent by weight, mass fraction
X_c	crystallinity
XLPE	crosslinked polyethylene
XRD	X-ray diffraction
ZN	Ziegler-Natta catalysts
σ_B	stress at break,
σ_e	basal surface free energy
σ_Y	stress at yield,

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