



1. Introduction and objectives

Friction is the resistance that one body encounters when sliding over another. In many daily activities and in most industrial processes friction plays a key role. Without friction, it would not be possible to walk, grip objects and drive a car, just to mention some of the several common tasks performed every day. On the other hand, in some cases like moving machine parts, bearings, seals etc., reduced friction is desired in order to minimize the energy loss and the consequential heating up that, in the worst case, could even lead to machinery breakdown. In his 1966 report, the father of tribology P. Jost, analysed the role of friction in modern society considering its impact on the economy. He estimated the loss due to tribology ignorance to be about 6% of the USA gross national product. It is clear then that, if high efficiency and quality are to be achieved, friction interactions need to be carefully studied and optimized according to the specific application.

Despite its importance, the prediction of frictional behavior is a far from easy task because of the wide range of variables related to contact mechanics and tribology that involve the disciplines of physics, mechanics and material science. Therefore, friction was a matter of interest already for the ancient civilizations, like the Egyptian, who figured out that the pulling force to drag a heavy slab stone on sand could be dramatically reduced by adding a certain amount of water just in front of the progressing edge. The first documented scientific study concerning friction was done thousands of years later by Leonardo Da Vinci (1452-1519). He measured the force required to move a body on a plane depending on its shape and nature. Experimentally, he found that the friction coefficient, defined as the ratio between the force parallel to the moving direction needed to start the sliding of the body and the normal load acting on it, was independent of the material and always equal to a constant value. Since then, many other scientists and researchers have investigated the friction interaction and demonstrated that, in opposition to Da Vinci's finding, the friction coefficient may strongly vary according to material properties, temperature, nominal contact pressure, sliding velocity, presence of a third medium in the contact, surface roughness and morphology.

Friction is generally classified into the following categories [1] [2] [3]:

- *Dry friction* when contact takes place between two solid surfaces



- *Lubricated friction* is when a lubricant is present between two solid surfaces
- *Fluid (or hydrodynamic) friction* describes the interaction between layers of fluids moving relative to each other
- *Skin friction* is the drag caused by the friction of fluid when a body is moving through it
- *Internal (or hysteresis) friction* is the force resisting the motion between the elements making up a solid material while it undergoes deformation.

Due to the complexity of a system involving all these contributions a general predictive formulation of friction forces does not yet exist and, in many cases, empirical formulations and trial and error testing are still used to estimate friction behavior. The trend in recent years has been to develop models based on more or less sophisticated physical formulations, capable to estimate the friction coefficient for a specific case which can be used by engineers as a guideline during the design phase of new machines and devices. In this way, laborious trial and error procedures as well as rigorous expensive "on site" testing can be minimized.

Of course a detailed understanding of the basic phenomena taking place during the sliding of bodies is required. The aim of the present work is to investigate the fundamental contact mechanics in case of dry and wet friction between a rubber body and a rigid substrate with specific emphasis on the effects of both substrate morphology and compound properties. The friction interaction was investigated using innovative experimental techniques, analytical physical approach and computational modeling.

The thesis is structured as follows:

In chapter 1, an overview of rubber properties is provided, with a special focus on mechanical behavior and viscoelasticity, since they are a prerequisite to understand friction mechanisms. The main features of the polymers used for the investigation will be also briefly described.

The state of the art for rubber friction is introduced in chapter 2, with an overview of the most acknowledged friction theories. The mechanisms involved in rubber friction will be presented and a particular interest is given on hysteresis and adhesion.



In chapter 3 an introduction to continuum mechanics with respect to finite elements analysis is reported. The constitutive material models used for the investigation will be then described together with the numerical implementation of viscoelasticity. The contact mechanic algorithms used to calculate friction interactions is given in the same section.

In chapter 4, the materials and methods used for the experimental investigation will be presented, with a particular interest in optical analysis and finite elements modeling.

Chapter 5 deals with the results and their discussion. The first part will concentrate more on the mechanical characterization of the compounds and friction measurements in case of sinusoidal model substrates. In the second part, a deep analysis of hysteresis friction for both sinusoidal and rough model substrates by use of finite element analysis will be presented. The simulations will be finally compared with experimental measurements.

In chapter 6, the results will be summarized in conclusion of the work.



1.1. Elastomers and general properties

Rubber is a generally soft material characterized by a remarkable elasticity, namely the ability to recover its original shape and dimensions after being substantially deformed. Rubber is not only elastic, but also resilient, resistant to tearing, waterproof and a good electrical and thermal insulator. All these properties make rubber a very interesting material capable of fulfilling a huge number of engineering requirements. Rubber materials are polymers, which are high molecular weight compounds consisting of long chains of one or more types of molecules, the monomers. Consequently, the name elastomer (elastic polymer) is commonly used as a synonym for rubber.

One should point out that all the above mentioned characteristics are related to rubber at room temperature, which is the most common environmental condition. In case the material is cooled down below a certain temperature, rubber becomes harder and brittle, like glass. For this reason such a temperature, which for rubber is typically below zero degree, is called glass transition temperature, or in short T_g . This transition is something that only happens to polymers and makes them unique materials.

Nowadays there are several types of rubber available, each of them showing different features. The type of rubber with the longest history of use is polyisoprene, the constituent of natural rubber (NR), which is the concentrated and purified form of latex extracted from a tree, most usually the *Hevea Brasiliensis*, cultivated in tropical regions, mostly South East Asia. In the 1940s several synthetic rubbers were developed to provide an alternative to natural rubber. The ones used most are styrene-butadiene rubber (SBR) and polybutadiene rubber (BR), which are derived from the synthesis of petroleum and natural gas products. The process of synthesis often consists in a free radical emulsion polymerization, whereby a vinyl monomer is polymerized by itself or combined with another monomer to create a high molecular weight polymer. In recent years, the anionic polymerization in solution with use of alkyl lithium catalysts has become very important to manufacture SBR, which in this case is known as S-SBR, and is widely used in the tire industry.

Although historically natural latex has always enjoyed a cost benefit advantage over synthetic versions, the great advantage of synthetic rubbers is the possibility to obtain products with specifically tailored properties. Hence, a clear comprehension of rubber molecular structure is essential for an understanding of its physical properties.

1.1.1. Natural rubber (NR)

The rubber hydrocarbon component of NR consists of over 99.99% of linear cis-1,4 polyisoprene (Fig. 1.1) and its average molecular weight ranges from 200,000 to 400,000 with a relatively broad molecular weight distribution [4]. As a result NR has a peculiar processing behavior.

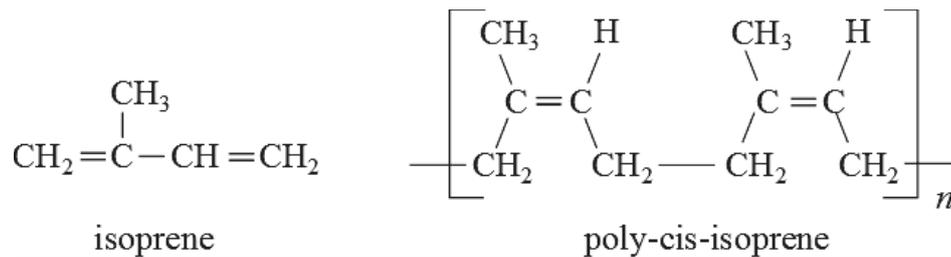


Fig. 1.1: Chemical structure of isoprene and poly-cis-isoprene which is the main constituent of natural rubber.

The double bonds present in the isoprene unit are reactive group for vulcanization reactions with sulphur, but double bonds can also react readily with oxidizing agents, like oxygen and ozone, thus making NR very sensitive to oxidations processes which can significantly degrade its properties (aging). In order to obtain a good aging resistance it is necessary to use protective agents in the compound, and use thiazol accelerators in short cure cycles with not too high temperatures. Nevertheless, even under optimum conditions, the aging and heat resistance of NR vulcanizates does not reach that of most SBR and BR vulcanizates.

Concerning its compounding, NR is too hard to be directly processed and therefore it has to be masticated first. The mastication process consists of high shear mixing under the influence of small amounts of oxygen. In this way a scission of polymer chains takes place and the molecular weight is broken down to facilitate the processing of the material [5]. NR vulcanizates show very interesting mechanical properties [6]. In particular, when NR is stretched more than 80 % of its original length, crystallization occurs due to the orientation of the polymer chains (strain crystallization). As a consequence a high tensile strength is observed along the axis of deformation, about 20 MPa or more, contrary to most



types of synthetic rubbers [7] [8]. The ultimate elongation is generally about 500 to 1000 %.

NR is suitable for dynamic applications since it is characterized by low heat build-up and high elasticity. Moreover, tear resistance is also influenced by strain crystallization and is therefore very good, as well as the dynamic fatigue resistance [9] [10].

Being non-polar, NR can be easily blended with a great number of other non-polar rubbers. Blends with SBR and BR are intensively exploited. In this case a product which exhibits both high performance of NR and synthetic rubbers can be obtained [11]. Because of this and the all above mentioned properties NR results to be indispensable in several applications, despite the availability of a great number of synthetic rubbers.

1.1.2. Butadiene rubber (BR)

Butadiene Rubber (BR) is composed of butadiene units which can have joined linearly by 1.4, as well as by 1.2-addition, see Fig. 1.2. The average molecular weight of commercial BR is in the range of 250,000 to 300,000. The microstructure can be strongly influenced by the catalysts using during the polymerization. More specifically, the higher is the cis-1.4 content of BR, the lower is its glass transition temperature, T_g . The T_g raises linearly as the concentration of 1.2 structure (vynil content) increases (see Fig. 1.4) [12]. The ratio between 1.2 and 1.4 content determines also the material performances in terms of abrasion resistance, wet grip and tensile strength. In particular, as 1.2 content increases the abrasion resistance becomes poorer while wet traction improves. Hence, a compromise needs to be found based on the specific case.

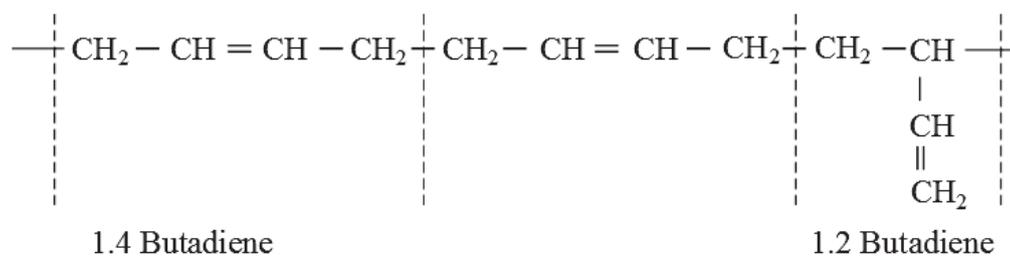


Fig. 1.2: Chemical structure of BR.

The tensile strength of vulcanizates from BR with high cis-1.4 is considerably lower than that of comparative SBR and NR vulcanizates. However, in blends with them BR can satisfy technically demanding properties for high quality products.

1.1.3. Styrene-Butadiene rubber (SBR)

SBR is a general purpose synthetic rubber, produced from the copolymerization of styrene and butadiene, as illustrated in Fig. 1.3. The styrene content ranges usually from about 20 to 40 %.

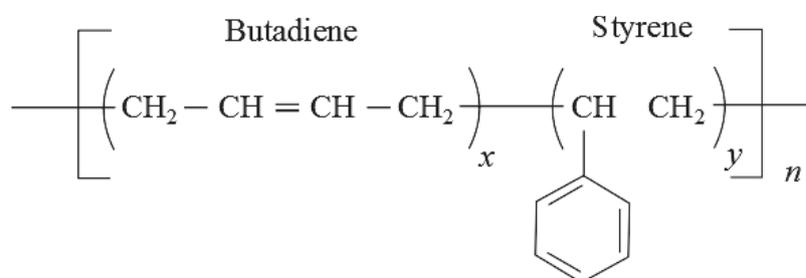


Fig. 1.3: Chemical structure of SBR.

The largest share by far of SBR is produced in emulsion (E-SBR) using redox initiators, but solution SBR (S-SBR) is steadily gaining in importance [13]. In case of E-SBR the small difference of chemical reactivity between styrene and butadiene implies that the monomers are statistically arranged along the polymer chain. The butadiene unit can be present in different configurations, as in the case of BR, according to the polymerization temperature. As a consequence material properties, like the Tg can be strongly affected by the overall arrangement of the copolymer micro structure. The strongest influence is given by the styrene content. As the styrene content in the SBR increases, the glass transition temperature becomes higher, while abrasion resistance and resilience become smaller (see Fig. 1.4). A similar effect is induced by varying the amount of vinyl groups. Good dynamic properties, aging and heat resistance as well as abrasion resistance make SBR product of high versatility for many technological application.

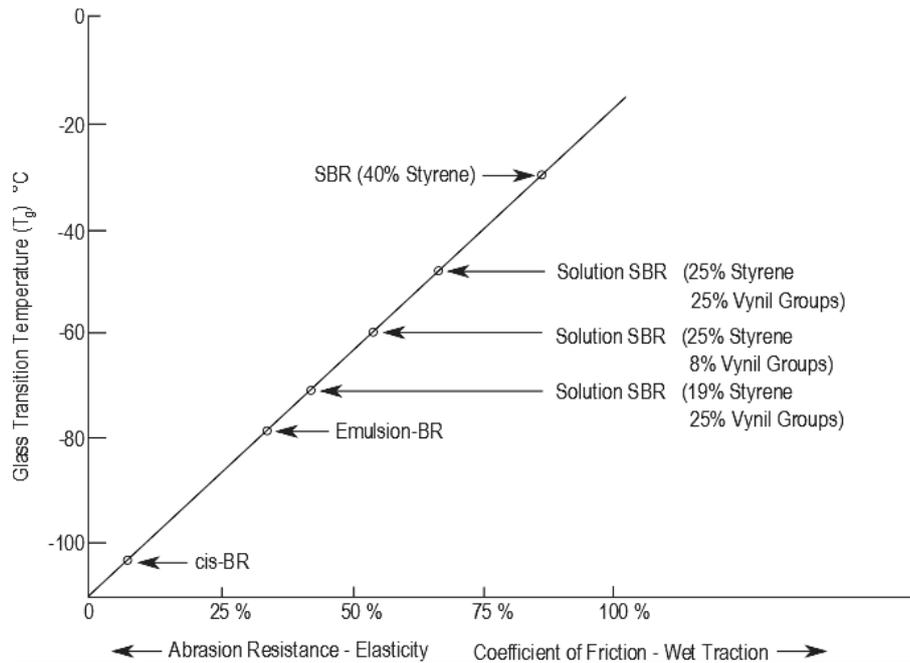


Fig. 1.4: Dependence of the glass transition temperature on the styrene and the 1,2-component of BR. Several cases of synthetic rubbers are reported as example (from [14]).

Compared with E-SBR, S-SBR has the advantage to be produced in stereospecific combinations thanks to catalysts based on organo-metallic compounds. This means that it is possible to obtain a custom-made SBR with a wide range of specific properties by choosing appropriate polymerization systems and conditions. Thus for high performances products S-SBR is usually preferred to E-SBR [15].

1.1.4. Vulcanization and filler reinforcement

In raw state, both natural and synthetic rubber show poor mechanical properties, as they are brittle when cold and become sticky when hot. Therefore crude rubber is not suitable for most applications we know nowadays. Thanks to the so-called vulcanization process, discovered in 1839 by Goodyear, mechanical properties and thermal stability can be improved [16] [17]. During a typical vulcanization process, sulfur together with various chemical additives is added to raw rubber and the mixture is then heated. Sulfur atoms create a series of chemical links between the intricate network of polymer chains [18]. Such cross-links prevent the slippage of the randomly coiled polymeric chains, thus giving the

material increased elasticity and stiffness as well as better resistance to heat, cold, abrasion and oxidation. This process is also called crosslinking or curing.

The vulcanization reaction is determined in large measure by the type of vulcanizing agents, the temperature and time. The number of crosslinks formed, also referred to as crosslink density or degree of vulcanization, has an influence on the final properties of rubber vulcanizates [19] [20].

For nearly all engineering applications a reinforcing filler, usually carbon-black or silica, is added to give to the rubber compound the desired mechanical properties. Tensile strength, abrasion resistance and tear resistance can be strongly improved by the interaction between rubber and filler [21].

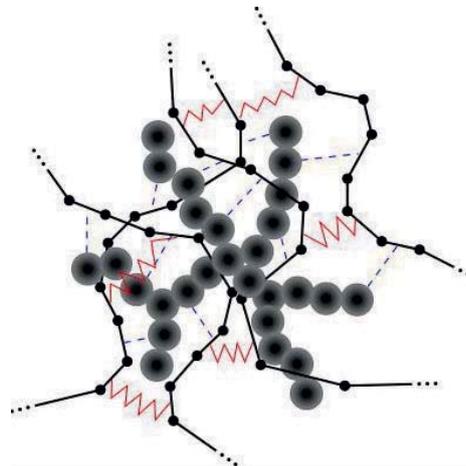


Fig. 1.5: Microstructure for a filled rubber vulcanizate. Grey circles: filler particles. Black lines: polymer chains. Blue dashed lines: Filler-Polymer interaction. Red zigzag lines: crosslinks.

The fine filler particles form a structure within the material leading to both physical and chemical bonds with the polymer chains after vulcanization (see Fig. 1.5.). Such a structure acts like a stiff network which provides increased strength to the rubber compound [22]. Hardly any filler will enhance all mechanical properties at the same time to the same optimal degree. In order to obtain the desired reinforcing effect the filler-rubber interaction and the filler structure must be considered. As an example, the activity of fillers in BR, SBR is often quite more pronounced because of their lack of strain crystallization than in NR [23]. In addition to this the chemical composition and the structure of the filler's surface are of importance as they influence the interaction with the polymer chains [24]. Therefore

the quantity and the type of filler, to be added to the rubber compound, must be carefully selected in order to achieve a product featuring the desired properties.

1.2. Mechanical properties of elastomers

As already mentioned, rubber consists of many polymer molecules interpenetrated with each other, thus, strong limitations of mobility occur, especially for translational motions of molecular center of gravity. Usually, the microstructure of a polymeric material is visualized as a spaghetti coil. The main effect which determines the mechanical behavior of such a system under an external force is the presence of entanglements, which tie the spaghetti together and prevent large movement when loads are applied [25]. In Fig. 1.6 a schematic representation of an entanglement, between two macromolecules with linear chain, is shown.

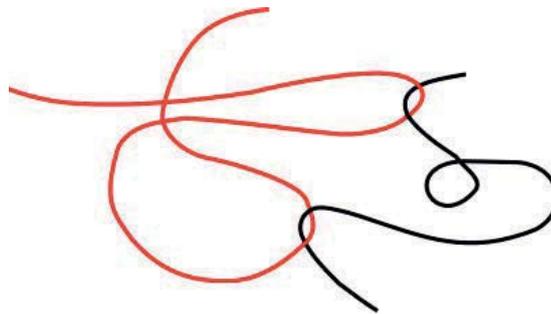


Fig. 1.6: Example of entanglement between molecular chains.

Such bond between chains has nothing to do with the chemical covalent bond. These bonds are merely physical and can reform in other places keeping its effect just from a statistical point of view. The polymer chain result then confined in a tube-like structure by all the entanglements [26] [27]. Based on the time scale any chain can disentangle from its neighbours by slipping along the tube and therefore a macroscopic flow of material is sometimes observed [28].

This special micro-structure is responsible of the particular and complex mechanical behavior of elastomers at macroscopic scale. In the undeformed state the long polymer chains, entangled and, in case of cured rubber, crosslinked with each other, are arranged in a high entropy random coil configuration [29]. When external stresses are applied, the