

# The Rheological Behavior of Wheat Starch Particulates Filled Uncured Styrene-Butadiene Rubber

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**ABSTRACT:** *This study treats one important aspect of starch-filled rubber compounds which is their rheological behavior. Starch-based SBR<sub>1712</sub> masterbatches resulting from various formulations were prepared using a mini two roll mill and an internal mixer (Plastograph Brabender). The content in starch was varied from 0 to 50 phr. The effect of starch content on the rheological behavior was evaluated through the flow characteristics in the temperature range (130-160 °C) which matches that used in the vulcanization process. Four experimental techniques were considered to assess the mixing and the flow behavior of the materials: 1) Brabender mixer, 2) melt flow index, 3) capillary rheometer and finally 4) dynamic rheological properties through strain sweep experiments using a plate-plate rheometer. It came out that the four techniques used in the assessment of the rheological behavior of such materials are appropriate, complementary and successful. The melt flow index, and viscosity measurements indicate a resistant flow for the rubber and its starch composites. Even high temperatures do not seem to reduce the viscosity considerably. Nevertheless, small amounts of starch incorporated in the gum will ease the flow to some extent. The materials showed a pseudoplastic behavior, and storage made a slight change in their melt flow index. Morphological studies showed that the particles of starch were not destructed during the mixing and their interaction with the rubbery matrix is very poor.*

**KEYWORDS:** *Rheological properties; Styrene-butadiene Rubber; Starch; Filler; Composites.*

## INTRODUCTION

In the world of manufacture of rubber products, around ten millions of tons of the styrene-butadiene copolymer (SBR) are consumed each year. This cheap synthetic material has interesting specific properties such as elasticity, deformability, good adherence and high capacity to absorb the irregularities of the ground and the shocks when used

in tire [1-3]. For the time being, and from the rubber consumption point of view, this material is the leader but it could not have been so if it was not reinforced by the use of particulate fillers. And in general, in the rubber industry, carbon black and silica are unquestionably the most widely used reinforcing fillers for this material [4-9].

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1021-9986/2017/1/159

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In the last few decades and mainly for ecological reasons, starch has become a very strategic material for the polymer industry. Its use in the field of the development of ThermoPlastic Starch (TPS) after its gelatinization is well instituted for the production of biodegradable plastics. It has been used also as an additive to polyethylene in order to enhance its biodegradation [10,11].

In the rubber technology, starch has received a considerable attention as a particulate filler to substitute carbon black and silica. The valorization of this abundant, renewable, biodegradable, and cheap raw material has palliated its use in the rubber industry and more particularly in the tire compounds, not only for ecological reasons, but in order to lower the rolling resistance and simultaneously reduce the energy consumption as well. The use of starch as a filler faced two major problems which are, its large particle size and its hydrophilicity which makes its dispersion difficult in the rubber matrix [12-14]. Many attempts were undertaken to reduce the filler particle size and to improve the interfacial interactions between rubber and the hydrophilic particle surface of the filler considering different modification methods for starch [15-25]. In recent years, research has been emphasizing on the development of new type of filler derived from starch called Bio-TRED which has been creatively and successfully used in the tire compounds [26-29].

In the rubber technology, an adequate dispersion state of formulation ingredients and among them the filler must be achieved before the material is shaped and vulcanized in order to fabricate parts with appropriate properties and performance. So, for this, the mixing of the filler and its dispersion in the rubbery matrix is an important step in the compounding operation. We have to keep in mind that the prepared compound is going to be heated to the vulcanization temperature at which it is going to be at the melt state and so, fluid enough to flow and fill the mold prior to vulcanization. So the rheological behavior of rubber compounds in the melt state is also considered to be one of the most important and fundamental factors in determining the properties of the final product. Usually filled rubber compounds are complex polymer systems that exhibit a number of singular flow properties markedly different from those of unfilled, molten polymers. The flow properties are

strongly affected by the presence and the content of the filler and eventually on the resulting interactions which may develop between the rubber and the filler. Studies on the rheological behavior of starch filled rubbers are not encountered and most studies in this field are focused on the use of carbon blacks and silica. Actually when studying the effect of carbon black on the flow properties of rubber Leblanc reported an increase in the viscosity of the uncured compounds [5]. He assigned this to the strong interactions arising between the elastomer and the surface of the filler which gave rise to what is known as the bound rubber. *Choi et al.* explained the sudden increase of the Mooney viscosity with increasing the silica content in the rubber compound and then its decrease at a certain point during the measurement by the strong filler-filler interaction of silica [30]. Demirhan and col. found that the properties of carbon black such as surface area and structure beside its loading have an important role in changing the rheological properties of SBR<sub>1512</sub> and SBR<sub>1502</sub> compounds [31,32]. It is clearly seen that as the carbon black loading ratio increases the values of both elastic and the viscous moduli also increase proportionally till 60 phr then decrease the loading ratio for all types. While the value of tangent delta ( $\tan \delta$ ) decreases in all compounds. In another study of the rheological behavior of the synthesized Natural Rubber Latex (NRL) Multi-Walled Carbon Nanotubes (MWCNT) nanocomposites in the presence of surfactants showing an enhancement in the storage modulus which indicates better dispersion of the nanotubes in latex [33].

The main objective of the present work was to investigate the morphological structure and to assess in detail the mixing operation and the rheological behavior of unvulcanized elastomeric formulations prepared from SBR<sub>1712</sub> filled with various contents of wheat starch. And in order to fulfill this, four rheological characterization methods were used: Brabender autograph, melt flow indexer, capillary rheometer, and parallel plate rheometer. For a better outlook on the rheological behavior of this type of materials, various contents of starch (0, 5, 7.5, 10, 15, 20, 35 and 50 phr) and different temperatures (130, 140, 150 and 160 °C) were used. The morphology and the storage time effect on the rheological behavior will be partially investigated as well.

## EXPERIMENTAL SECTION

### Materials

Synthetic rubber SBR used in this study is of the type SBR<sub>1712</sub> (Chemische, WERKE HÜLLS, Germany). It is an oil extended general purpose grade, obtained by cold emulsion polymerization. This copolymer has 23.5% of styrene units and the gum contains 37.5 phr of naphthenic oil. Its Mooney viscosity MI (1+4) at 100 °C is 55 units. The native wheat starch was obtained from Roquette Frères (France). Its amylose and amylopectin contents are 23 and 77 %, respectively. Its specific gravity is 1.482g/cm<sup>3</sup> and its mean of the granule size distribution is 16 μm [34].

### Preparation of the formulations

Various formulations were prepared and the starch content incorporated is given in phr. The composition of these formulations and their appropriate designations are given in Table 1. The preparation of these formulations was done using two techniques:

The Brabender elastography was used to evaluate the mastication and the mixing properties of SBR with starch and to find the optimal conditions for the best dispersion for starch. In this case, a volume of 24 cm<sup>3</sup> of each formulation was introduced into the mixing chamber of the Brabender elastography (model: PL3S), treated for 10 min at 40 rpm and at 40 °C. The torque corresponding to the shear resistance developed during the mastication and the mixing was recorded with time for each formulation.

The compounds which have been used to measure the rheological properties were prepared on a mini two roll mill (Polymix type) having 80 mm in diameter. A mass of 100 g of the gum was introduced between the cylinders of the mixer with a gap of 1 mm and after three minutes of mastication (except for the first formulation: five minutes) the material becomes flexible, and then the filler according to the various formulations was added. And then the mixing was extended to further 5 min.

### Rheological characterization

#### Determination of the melt flow index (MFI)

The melt flow indexer measures the melt flow index that informs us about the properties of resistance to the flow of SBR<sub>1712</sub> and will show the effect of the presence of starch on the flow behavior of the compounds. The melt flow index is obtained using a fluid meter, Controlab

model, (according to standard NF T 510/6). The principle of this technique consists in measuring the amount of the substance crossing a die with a diameter 2.09 mm and a length 8 mm under the action of a pressure applied to a piston which was developed with the use of a load of 5 kg for different formulations. The Melt Flow Index (MFI) in mass is obtained in grams for 10 minutes, according to the relation,  $MFI = 600 m/t$ , where  $m$  is the average mass extruded in grams (5 extrudates are taken) and the time interval, in seconds, between two cuts of extrudates. The measurements were carried out at the following temperatures, 130, 140, 150 and 160°C.

#### Rheological properties measurements on the capillary rheometer

The capillary rheometer is widely applied as an experimental tool for measuring the viscosity and the shear-stress shear-rate dependence for polymer melts. The basic idea of the instrument is to relate the pressure drop through a capillary of known dimensions to the volume flow. The measurements were carried out using capillary rheometer type Controlab, model: LO2COPLO. A capillary with length  $L=40$  mm and diameter  $D$  of 1.9 mm, making ( $L/D=21.05$ ), and a piston having a diameter of 20 mm are used, and with these dimensions, the Bagley correction can be neglected when calculating the real shear stress. Before starting the extrusion, and to ensure the homogeneity, the material is heated for 25 minutes inside the capillary under a pressure of 300 kg/cm<sup>2</sup>. Then linear rates were applied to the piston and varied from 20 to 60 mm/min. The apparent values of shear stress shear rate and shear viscosity were calculated using the derivation of Poiseuille law for capillary flow [35].

Apparent shear stress (Pa):

$$\tau = \frac{R_c \times \Delta P}{2L_c} \quad (1)$$

Apparent shear rate (s<sup>-1</sup>):

$$\dot{\gamma}_a = \frac{4Q}{\pi R_c^3} \quad (2)$$

Apparent shear viscosity (Pa/s):

$$\eta_a = \frac{\tau}{\dot{\gamma}_a} \quad (3)$$

Table 1: Compositions of the prepared formulations.

Formulation	1	2	3	4	5	6	7	8
SBR (phr)	100	100	100	100	100	100	100	100
Starch (phr)	0	5	7.5	10	15	20	35	50

Where  $R_C$  is the capillary radius (m),  $\Delta P$  is the pressure applied (Pa),  $L_C$  is the length of the capillary (m) and  $Q$  is the volumetric flow rate ( $m^3/s$ ).

A power law equation proposed by Oswald 33, was also applied to the relationship between apparent shear stress and shear rate according to [36]:

$$\tau = K\dot{\gamma}^n \quad (4)$$

Where  $K$  the consistency or viscosity coefficient index (Pa s) and  $n$  is the power law index or flow behavior index.

#### Dynamic rheological measurements

The parallel plates rheometer permits to determine the dynamic rheological properties such as storage modulus ( $G'$ ), loss modulus ( $G''$ ), loss factor ( $\tan \delta$ ) and complex viscosity  $\mu^*$ . Dynamic rheological measurements were carried out in a controlled-stress HaakeRheoWin322 rheometer, using a serrated plate-and-plate geometry (35 mm diameter). The measurements were taken with a gap of 1.0 mm at 150 °C which is the temperature used in the vulcanization of this compound. For this, 1g of the rubber compound which was obtained on the two rolls mill was placed between the two plates and pressed until a gap of 1 mm in height was reached. The dynamic viscoelastic properties were determined with frequencies ranging from 62.83 to 0.428 rad/s. A stress sweep from 161 to 1181 Pa was performed to define the region of linear viscoelasticity.

#### Transmission Electron Microscopy (TEM)

Specimens from compounds obtained on mixing with two the rolls mill were sheeted 3mm in thickness and fractured after freezing in liquid nitrogen. The exposed surfaces were observed using a Philips XL30 Transmission Electron Microscope. An accelerating potential of 1 kV was used for the analysis. The micrographs of the samples were taken at magnification  $\times 500$ .

## RESULTS AND DISCUSSION

### Mastication and mixing using the Brabender plastograph

The characteristics of the mastication and the mixing of the rubber with the filler were obtained through the use of the Brabender plastograph which is considered as an internal type mixer. By measuring torque, one can find some characteristics of rheological properties. The plot of the torque versus mixing time will give the so-called power curve. This will be an indication of the shear developed to bring up the mastication and the dispersion of the filler in the matrix and shows at the same time the different stages through which this operation is taking place. The apparent stability of the system can be seen through the non-variation of the torque at prolonged times where usually a plateau is observed.

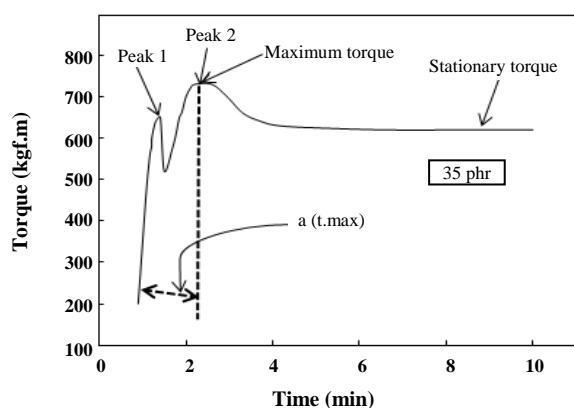
The rheogrammes recording the change of torque of SBR containing various starch contents with time were obtained and their forms are close for all the considered formulations.

A typical rheogramme curve obtained for the formulation containing 35 phr of starch is shown in Fig. 1 where it can be seen that the compounding operation is made of three stages.

The first stage, where the torque increases quickly after the loading of the ingredients in the viscometer chamber, then reaches a maximum rapidly. This has been attributed to the high shear resistance imposed by the rubber during mastication phase. After this first increase in torque, this later decreases slightly and it looks like that when the rubber has started to lose some of its consistency and is becoming softer, the torque will start a second rise, reaches a maximum of 730 kgf.m, which is the highest value seen with this formulation. This represents the mechanical performance needed for the dispersion of the starch particles inside the matrix. After this observed maximum torque, the power curve exhibited an exponential decay to some limiting value seen as a stationary torque followed by a slow gradual decrease in the torque until a quasi-constant state which

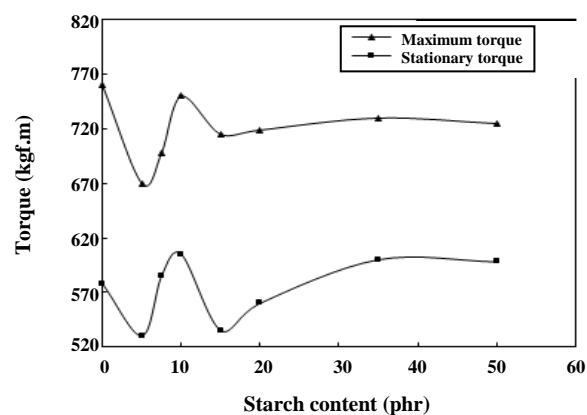
**Table 2: Values of maximum torque, stationary torque, and the time to reach second peak maximum for each formulation.**

Starch content (phr)	Maximum torque (kgf.m)	Stationary torque (kgf.m)	$a_{(t.max.)}$ (min)
0	760	578	1.5
5	670	530	2.5
7.5	698	585	2.0
10	750	605	2.3
15	715	535	2.2
20	719	560	2.0
35	730	620	2.2
50	725	598	2.1

**Fig. 1: A typical torque-time curve as obtained with a Brabender plastograph (formulation with 35 phr of starch).**

appears after 5 minutes of time of mixing. We have to recall that this time of 5 min is very important because it is going to be used during the preparation of the compounds on the two roll mill, even though, the shear developed in this type of mixer is weaker than that encountered in the Brabender plastograph.

The torque at its steady state indicates that at this time the filler was wetted by the polymer and we can assume that the particulate filler is dispersed in the rubber matrix but just in the form of agglomerates which are large in diameter. As the time of mixing is extended, the mixture is under shear forces which will reduce the viscosity of the stock by molecular scission of the rubber and the reduction of agglomerates in aggregates and probably ever into single particles. The effect of the amount of the filler used was assessed through three characteristics extracted from the rheogrammes obtained when varying the amount of starch. These are the maximum torque,

**Fig. 2: Variation of torque values (the maximum and the stationary) vs. starch content.**

the torque in the stationary state as well as the time  $a_{(t.max.)}$  needed to reach the maximum of the second power peak of the power curve. In Table 2 are gathered these values, and in Fig. 2 the maximum and the steady state values of the torque are represented.

The results obtained on the effect of starch on the mastication and its mixing with styrene-butadiene rubber on the Brabender Plastograph where compared to those of carbon black. In fact, when assessing the effect of this later as filler in oil extended butadiene rubber, Cotten obtained the usual two peaks power curve [37]. On the contrary, the form of the power curve is different when compared to that obtained with wheat starch (Fig. 1). With carbon black, we observe a broader second peak, no stationary torque but a continuous and lengthy decay in the torque when the mixing time is extended considerably. The author justified this by the difficulties in wetting the carbon black by the polymer and the time

for reduction of agglomerates in aggregates. In the case of starch, the maximum state of mixing is rapid and a stationary torque is reached in the only 5min of mixing time which indicates that starch is relatively easier to disperse when compared to carbon black. This ease of the dispersion of starch can partly be associated with the size of its particles when compared to the finer carbon black ones.

According to the results, the highest maximum value of torque is observed with the formulation which does not contain starch where a value of 760kgf.m is reached indicating a very elevated viscosity for the material. But it can be seen that the introduction of just a small quantity of starch in the rubber provokes a quick fall of both the maximum and the stationary torque values and so an ease in the mixing as far as the amount of starch does exceed 5phr. This was interpreted by the fact that starch which is known for its lubricating properties [38,39] will facilitate the flow by mainly increasing the wall slippage effects in rubber compounds. In a certain critical range of filler content, rubber compounds may exhibit slippage at the wall of laboratory or processing equipment, obviously further enhanced when lubricating ingredients are present in the formulation. Beyond the minimum torque values, further increase in starch contents will lead to higher torque values which indicates that the consistency of the material is increased due to the usual hydrodynamic (or volume fraction) effect of the filler, reaches a maximum at around 10 phr starch after which further increase in the starch content will lower both torque values to get to invariable ones even if when the amount of starch is exaggerated. This discrepancy can, therefore, be accounted for relating on the nature of the dispersion i.e. for small quantities of starch, the particles tend to exist in individual state, but on the other hand when the concentrations are high; this leads to the formation of agglomerates whose contribution to the rheological behavior is not going to be the same as that of individual particles. After the observed maximum torque, the power curve exhibited an exponential decay to some limiting value seen as a stationary torque. As far as the kinetics of the mixing are concerned, it is well established that filler particles dispersion is obviously initiated in the early stage of the mixing but it is not instantaneous and has a kinematical character and may depend on the amount of the filler. From the values of  $a_{(t,max)}$  in Table 2, we observe

nearly the same values for the formulations containing starch except for the one with 5 phr where the process is slower and this probably is associated to its lower viscosity.

#### **Melt Flow Index (MFI) measurements**

The melt flow index measurements were carried out on mixtures prepared on the two roll mill as indicated in the experimental part. To evaluate the effect of various starch levels in the range of 0-50 phr used as filler on the Melt Flow Index (MFI) of the SBR based compounds, three temperatures (140,150 and 160°C) were used. It is noted that these values of selected temperatures are corresponding to those which are commonly used in the vulcanization of the SBR and where the easy flow is desired in such compounds.

Fig. 3 represents the variations of melt flow index expressed in g/10min according to the composition of starch at different temperatures.

The curves obtained for the three temperatures show that the values of the melt flow index of the SBR used as well as those of the mixtures are low (in general between 0.1 and 0.3). This can be justified by the viscoelastic nature of the rubber as well as its high molecular weight effect. We note that the effect of temperature changing is mainly pronounced for the pure elastomer where the melt flow index is seen to increase importantly when rising the temperature and so it is obvious that the thermal effect will reduce the viscosity of the material thus making the flow easier and consequently a higher melt flow index. But once starch is introduced in the rubber, the effect of the temperature does seem to have a noticeable effect mainly when the starch content is lower than 10phr where the curves tend to be very close. At higher starch contents small changes are observed with an exception made for the formulation containing 15 phr when treated at 140°C, where the curve presents only one maximum. Concerning the influence of starch content on the melt flow index, the outcome is quite surprising. Usually, in rubbers, high filler loading leads to the higher viscosity of the compound, hence a higher resistance to flow and lower melt flow index is observed. This was not the case with starch filled Styrene-butadiene compounds where the effect of starch content was not well pronounced. The results show small decreases in melt flow index mainly in the starch content range 20-50 phr. This could be explained by

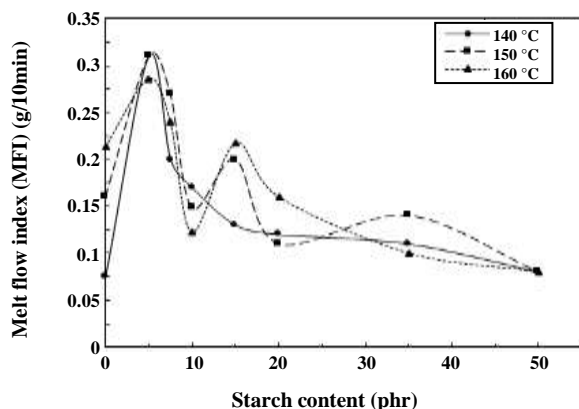


Fig. 3: Variation of melt flow index (MFI) vs. starch content at different temperatures.

the fact that the consistency developed by starch in the compound, which will make the flow difficult is counterbalanced by its lubricating action.

The most striking result of this study about the influence of starch as a filler on the flow properties is the existence of a relationship between the results obtained on the Brabender rheometer (Fig. 2) and those of the melt flow indexer (Fig. 3). It can be seen that the melt flow index values, whatever the temperature used, over all the starch content range, go in an inverse way relatively to those of the stationary and the maximum torques, which means that the formulation which showed the least resistance during the mixing operation will have the highest values for the melt flow index. And the most outstanding observation is especially with the formulation containing 5 phr of starch, where a value of a melt flow index multiplied by a factor of four is attained when compared to that of SBR alone. This was interpreted by the same fact as above where it has been suggested that starch is able to act as an agent of lubrication by reducing the friction existing in the interface between the substance and the walls of the melt flow indexer thus making the flow easier. In rubber this phenomenon is well known, and graphite was often useful for this objective. In certain circumstances, disulphide molybdenum is able also to achieve this result [40].

#### Storage effect on Melt Flow Index (MFI)

Storage effect, usually known as storage maturation effect, is an important factor aspect in rubber mixtures preparation where usually large rubber masterbatches are prepared, stored and the stocks are consumed with time.

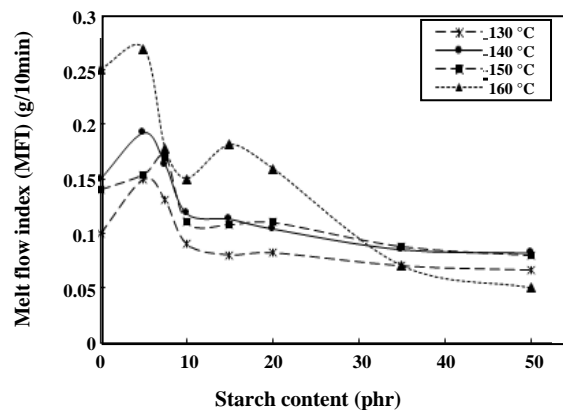


Fig. 4: Variations of melt flow index (MFI) vs. starch content at different temperatures after one-month storage.

At dump, a rubber compound is far from equilibrium in terms of rubber-filler interactions, not only because the theoretical mixing energy level can not realistically be achieved in practical operations, but also because at dump the rubber matrix which has been submitted to such high stresses needs a certain time for relaxation processes to proceed towards an equilibrium state. If this is seen as being essentially a physical process, then it is at best the adsorption-desorption balance of rubber segments and filler particle sites at a given time. As long as equilibrium is not reached, the mechanism of the system is likely to evolve further while the compound is at rest, which may lead to a change of the rheological properties of the material. For this purpose, usually, sulfate or chloralhydrate of hydroxylamine uses at a percentage of 0.15% compared to dry rubber allowed to obtain a rubber with stabilized viscosity.

In order to study the effect of storage the melt flow index of the mixtures was re-measured under the same conditions after one month of storage at dark and at room temperature to estimate the stability of the mixtures, and to see to which extent this phenomenon can be affected by the presence of the starch in rubber, knowing well that SBR<sub>1712</sub> grade contains a great quantity of oil. It is noted that the measurements were made by using four temperatures 130,140,150 and 160°C. The variations of the melt flow index are reported in Fig. 4.

The analysis of Fig. 4 shows that the curves of the melt flow index and the content of starch at different temperatures have almost the same shape as those obtained for the mixtures freshly prepared. We can see

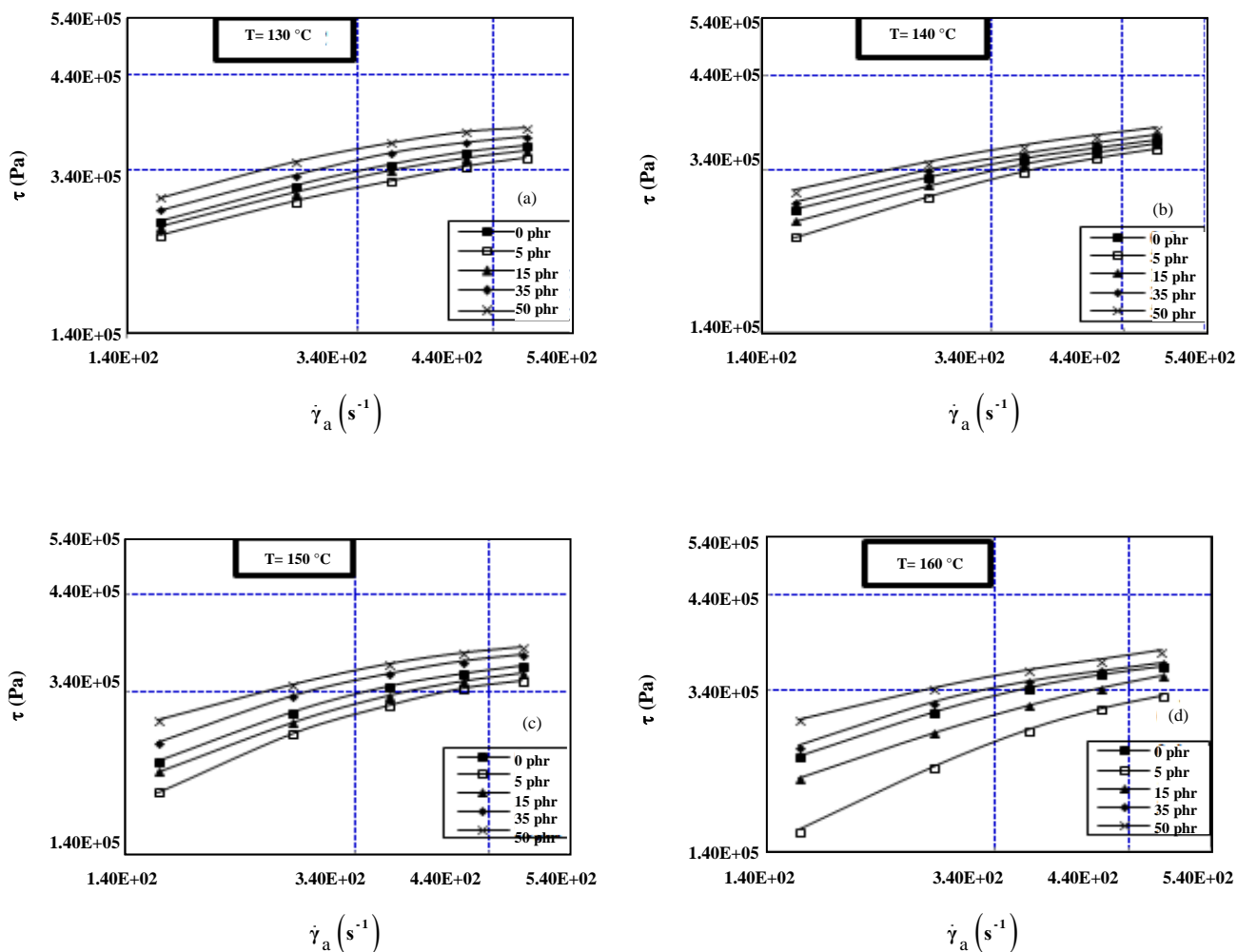


Fig. 5: Graphs showing shear stress vs. apparent shear rate (log/log scale) for different starch contents for different temperatures 130°C (a), 140°C (b), 150°C (c) and 160°C (d).

that 5 phr in starch is going to increase the melt flow index and beyond this content, it will decrease, and from 10 phr except at 160 °C, no noticeable change is observed in the values of the melt flow index even at 50 phr. The effect of temperature is comparable with that observed for the same formulations freshly tested. In general, it was found that the melt flow indices obtained after one month of storage is lower than their homologs obtained just after the operation of mixing. This was interpreted by the fact that some hardening did take place in the formulations containing starch. On the contrary, those which are starch free showed a remarkable increase in their melt flow indices probably due to a better dispersion of the naphthenic oil in the matrix and thus a better plasticization.

#### Capillary flow characteristics measurements

The rheological characteristics of the various formulations were measured using a capillary rheometer. For a better control and understanding of the rheological behavior, as well as the determination of some flow parameters, the measurements were realized at the temperatures of 130, 140, 150 and 160 °C. Easy flows at moderate temperatures of transformation are often desirable for practical and economic reasons. In Fig. 5 (a), (b), (c) and (d) were plotted the variations of apparent shear stress as a function of shear rate (Log/log scale) for temperatures used of the various formulations varying in starch content.

The shape of the various curves of  $\text{Log} \tau = f(\text{Log} \dot{\gamma}_a)$  is nearly linear in all the cases. Furthermore, the observed flow



behavior over the range of shear rates employed has been treated by the power law which was represented by Eq. (5), where,  $K$  is the consistency corresponding to the viscosity  $\eta_0$  in the case of Newtonian fluids, and  $n$  the power law index. The obtained values, calculated for all the cases and in general, vary between 0.3 and 0.4, thus testifying for a pseudo plastic behavior for all the formulations under the experimental conditions used.

As a whole and with regard to the values of the shear stress obtained while varying the shear rate, those ones are considered to be high, which can be taken as an obvious result of the difficult flow encountered with these materials. The curves for each temperature are distinguished between them, thus indicating the rheological differences brought by the presence of various starch contents. What is remarkable and is of great importance is the curve of the formulation 0 phr starch. This latter is placed in between those which contain the starch in high content. But that which contains 5 phr of starch is located at bottom of the series for all the temperatures. For the average starch content, the curves are intermediate and they are superimposed upwards by increasing the starch content. There is also an analogy between these results and those obtained from the measurements of the flow index where we can see that flow is made effortless when small amounts of starch are incorporated into the elastomer. When comparing the curves obtained at different temperatures, paradoxically and not surprising when we look back at the effect of temperature on the melt flow index, the effect of the temperature in the stress-strain behavior is marginal. By comparing the values of the apparent shear stress at the same shear rate, we observe that there are weak diminutions by increasing the temperature from 130 to 160°C.

Measurements of the apparent shear stress as a function of shear rate for the various formulations at different temperatures were exploited to extract the values of the apparent viscosity (Eq. (6)) for each case. The values obtained have undergone a correction according to the law of Rabinovitch. In Figs. 6(a), (b), (c) and (d) are represented the variations of apparent viscosity (Log form) versus the apparent shear rate.

It is noted that the decreases are nearly linear. The highest values are those of the formulations highly filled with values comparable to those with the pure SBR.

Although the effect of starch on this property is very apparent, the effect of the temperature remains modest.

An attempt to quantify the effect of temperature on viscosity and to extract energies of activation for the process by considering a law of exponential activation was made and some values of energies of activation of the order 2.8-9.6 kJ/mol were obtained for some formulations. The values cited above are judged low and can be the consequence of the weak differences in viscosity when changing the temperature.

#### **Measurements of dynamic viscoelastic properties**

When an elastomeric material is subjected to a periodic, small sinusoidal amplitude torque (stress) it shows a viscoelastic behavior which is intermediate between an ideally elastic material and a true Newtonian liquid. The study of uncured silica (silane treated)-filled SBR compounds in comparison with carbon black-filled compounds demonstrates significant differences that are believed to reflect the particular nature of the filler. For instance, while 50 phr carbon black-filled SBR does not exhibit a linear viscoelastic domain; the corresponding silica-filled material shows a linear plateau up to a dynamic strain of 1° (14% deformation). The size of the linear-plateau increases as silica level decreases [41].

The dynamic storage modulus ( $G'$ ) is a measure of the energy stored in the material and recovered from it per cycle of sinusoidal deformation. From Fig. 7, it was seen that the values of  $G'$  increase significantly with increasing the amount of starch over the whole range of frequencies.

The loss modulus ( $G''$ ) is defined as a measure of the energy dissipated or lost (as heat) per cycle. As it can be seen, Fig. 8 illustrates that the loss modulus  $G''$  is significantly lower than the storage modulus  $G'$ , clearly reflecting the high elastic nature of this uncured material. For example, both values of  $G'$  and  $G''$  for the unfilled system at 13,54 rad/s were about 33800 and 23970 Pa respectively while they increase to 54940 and 38840 Pa respectively for the formulation containing 50 phr of starch.

Another parameter which is often useful in indicating the physical behavior of a system is the loss tangent ( $\tan \delta$ ). It is the ratio of the energy lost to the energy stored for each cycle of the deformation, i.e.  $\tan \delta = G''/G'$ . It is a useful indicator of the relative contributions of

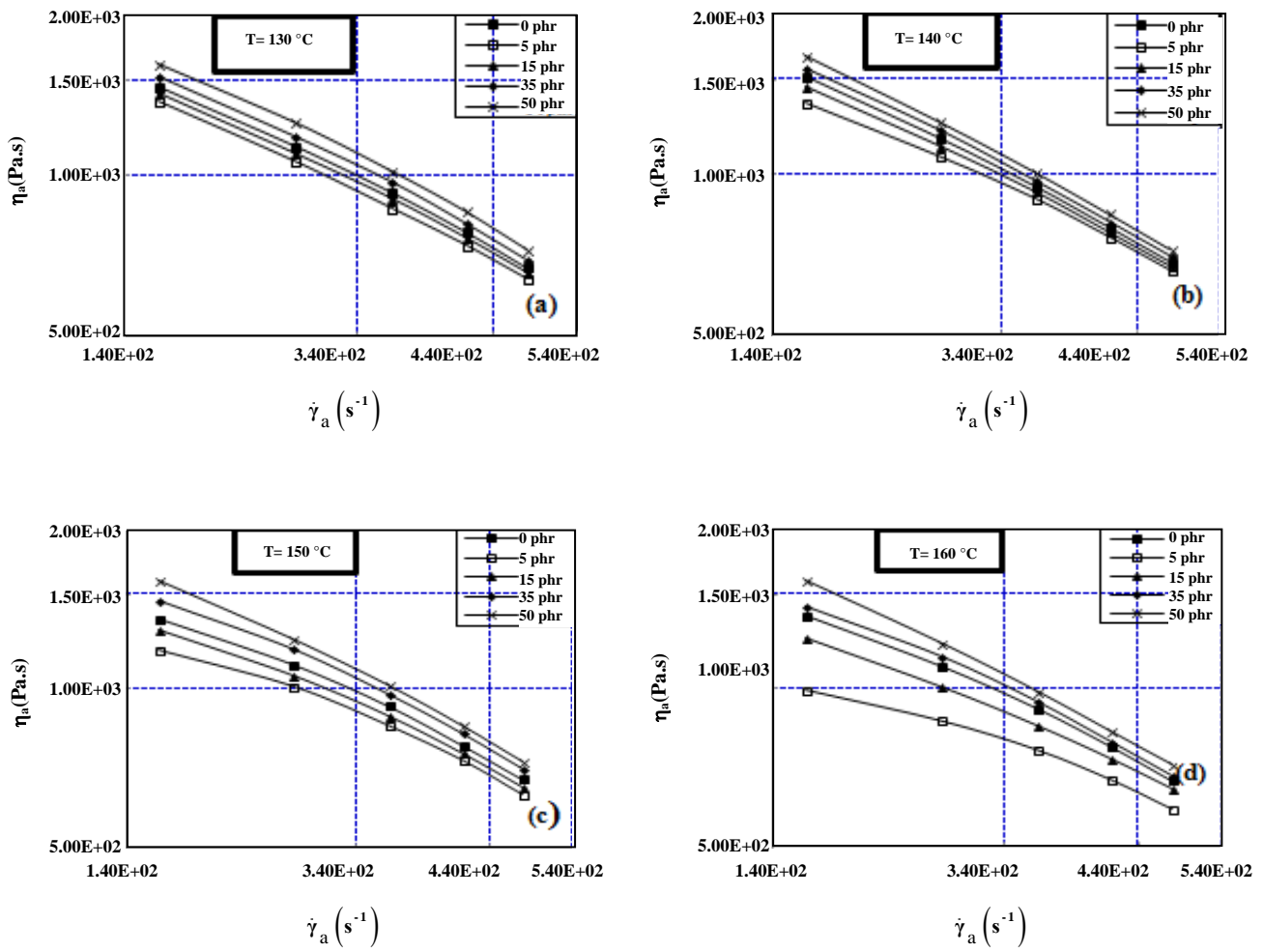


Fig. 6: Graphs showing apparent shear viscosity vs. apparent shear rate (log/log scale) for different starch Contents for different temperatures  $130^\circ C$  (a),  $140^\circ C$  (b),  $150^\circ C$  (c) and  $160^\circ C$  (d).

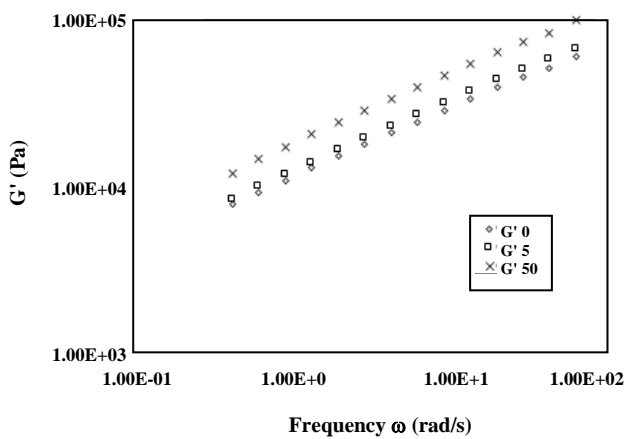


Fig7: Dynamic modulus  $G'$  at  $150^\circ C$  for uncured compounds of SBR 1712 filled with  $\diamond$  0 and  $\blacksquare$  5 and  $\blacktriangle$  50 phr of starch.

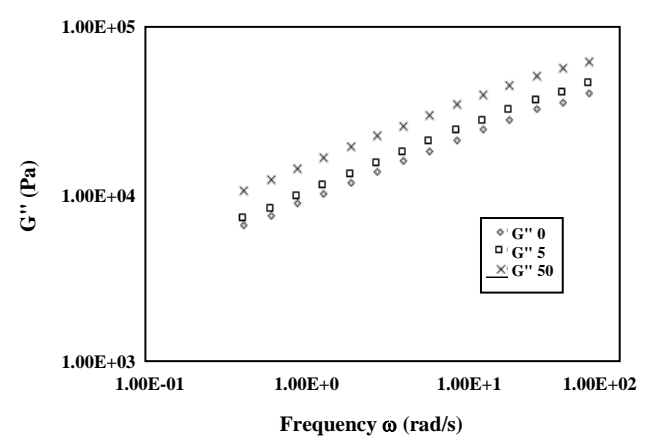


Fig. 8: Loss modulus  $G''$  at  $150^\circ C$  for uncured compounds of SBR 1712 filled with:  $\diamond$  0 and  $\blacksquare$  5 and  $\blacktriangle$  50 phr of starch.

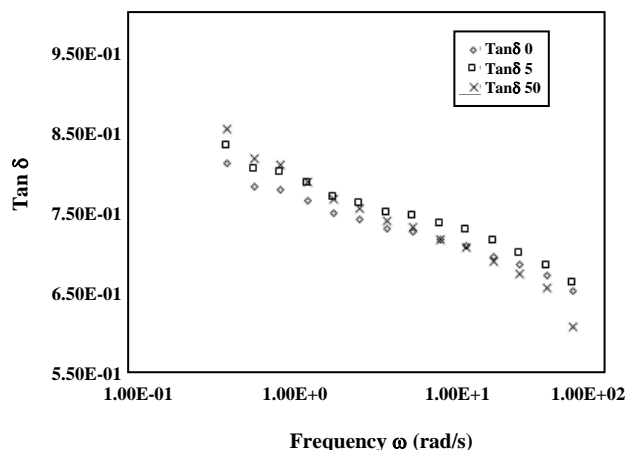


Fig. 9: Variation of  $\tan \delta$  as a function of frequency for uncured compounds of SBR 1712 filled with:  $\diamond$  0,  $\blacksquare$  5 and  $\blacktriangle$  50 phr of starch.

the viscous ( $G''$ ) and elastic ( $G'$ ) components to the viscoelastic properties of a material.

From Fig. 9 it was observed that the effect of filler loading is relatively moderate on  $\tan \delta$ . The loss tangent ( $\tan \delta$ ) of the formulation of 50 phr of starch exhibits slightly higher values than that of pure polymer from 0.428 to 62.83 rad/s due to the restricted movement of the polymer segments and the enhancement in stiffness of the material. Then it takes the same value of 0.717 at 9.222 rad/s and finally, it reveals lower values attributed to the increase in the mobility of the rubber matrix. The more mobile the matrix, the lower are the values of  $\tan \delta$ .

The effect of starch content on complex viscosity is shown in Fig. 10. The complex viscosity ( $\eta^*$ ) of all formulations with 0, 5 and 50 phr of starch follow a power-law behavior and there is no Newtonian plateau for the viscosity curve within the measured region of a frequency range. It was observed that complex viscosity of filled systems is higher than that of the unfilled system. For instance at 13.54 rad/s for all formulations containing 0, 5 and 50 phr of starch  $\eta^*$  increase from 3061 to 3394 and then to 4970 Pas.

### Morphological studies

Morphology of the polymer composites plays an important role in the properties of the final product; especially because their mechanical properties depend on it. The leading idea is that the morphology in rubber compounds arises from specific interactions between the

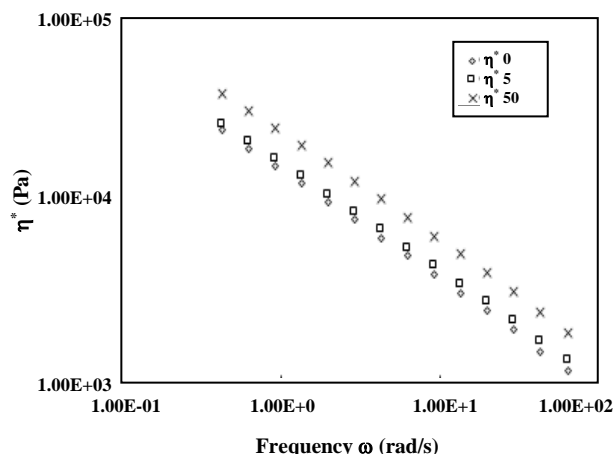


Fig. 10: Variation of complex viscosity as a function of frequency for uncured compounds of SBR 1712 filled with:  $\diamond$  0,  $\blacksquare$  5 and  $\blacktriangle$  50 phr of starch.

elastomer and the filler particles and that the resulting structure affects the flow properties. This morphology is partly decided during the mixing of the filler with the matrix and the flow phase of the compound during the mold filling. In our present study, the TEM analysis performed on compounds lead to the images shown in Fig. 11 (a-b). Morphological studies indicated a relatively uniform dispersion of starch particles in the compounds. Their number increases with the starch content used and at high content aggregates of filler particles are formed. The micrographs showed that the starch particles were not demolished and they kept their original shape. Some of them were removed from the surface of the composite during the fracture of the specimen, leaving behind some cavities on the fracture surface. The smooth surface inside the cavities testifies to the very poor interaction at the interface between the starch particles and the SBR matrix. This is taken as one reason for the poor mechanical properties of the styrene-butadiene rubber/starch composites. The pioneer researchers on rubbers/starch compounds have by many attempts tried to overcome this obstacle considering different approaches and the main ones are, the preparation by mixing using the co-precipitation methods and the chemical modifications of starch in order to improve its compatibility with the rubber [18].

### CONCLUSIONS

Even though it looks that the full substitution of rubber classical fillers by starch is not imminent, the actual environmental concern and the in-depth focusing

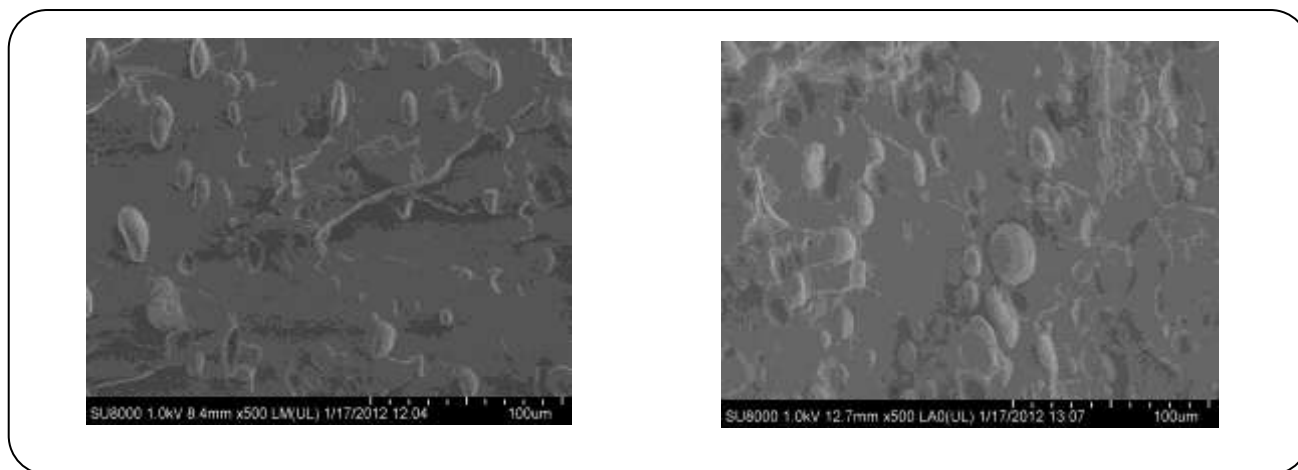


Fig. 11: TEM micrographs of the fracture surface of SBR<sub>1712</sub> compounds filled with starch: (a) 5, (b) 50 phr.

on the subject which is leading to a huge amount of work going on in this field, are good signs for future optimistic results.

As far as this work is concerned where the different rheological aspects of SBR<sub>1712</sub> filled with variable wheat starch content were elaborated, it can be concluded that the different methods and equipment used for the assessment of the effect of starch on the flow behavior of the pure gum and its starch composites are appropriate, complementary and successful. The high torques values recorded on the Brabender plastograph during the transformation, the low melt flow indices for the pure gum as well as its starch composites and their high viscosities witness for the high resistance imposed by these materials to flow. We have to keep in mind that small amounts of starch will help the flow by acting as a lubricating agent and increasing the wall-slippage. The very high starch contents did not increase the viscosity of the compounds to higher values as it is usually observed with other systems. The flow is pseudo plastic in nature in this type of materials characterized by a reduction in the viscosity at high shear rates. The rising of the temperature in order to lower the viscosity and ease the flow does not seem to be very effective. The dynamic rheological properties of materials filled with starch showed comparable results to those compounds reinforced by carbon black and silica. Also values of  $G'$  higher than those of  $G''$  illustrate a high degree of elastic behavior. Storing the materials for one month made a slight reduction the melt flow indices. Morphological studies showed that the particles of starch were not destructed during the mixing and their interaction with the rubbery matrix is very poor.

#### Acknowledgements

Miss Z. Djetoui is indebted to the ministry of higher education and research (Algeria) for the PhD grant, to the University Ferhat Abbas Sétif-1, Faculty of technology, for the laboratory research program, the facilities and the assistance, and to the Instituto de Ciencia y Tecnología de Polímeros, ICTP-CSIC. Juan de la Cierva 3, 28006-Madrid, Spain for the cooperation program.

Received: Jan. 28, 2016 ; Accepted: May 17, 2016

#### REFERENCES

- [1] Thorn A. D., Robinson R. A., "Compound design", In: Bhowmink A. K., Hall. M. M., Benarey. H. A., "Rubber Products Manufacturing Technology" Marcel Dekker, New York (1994).
- [2] Railsback H. E., Howard W. S., Stumpe N. A., Butadiene-Styrene Copolymers, *Rubber Age (RA)*, 46-55 (1974).
- [3] Rouilly A., Rigal L., *Agro-Materials, J. Macromol. Sci.(JMS)*, **42** (4): 441–479 (2002).
- [4] Boonstra B. B., *Role of Particulate Fillers in Elastomer Reinforcement, J. Polym.(JP)*, **20**: 691-704 (1979).
- [5] Leblanc J. L., *Rubber-Filler Interactions and Rheological Properties in Filled Compounds, J. Prog. Polym. Sci.(JPPS)*, **27**: 627-687 (2002).
- [6] Arrighi V., McEwen I. J., Qian H., Serrano Prieto M. B., *The Glass Transition and Interfacial layer in Styrene-Butadiene Rubber Containing Silica Nanofiller, J. Polym.(JP)*, **44**: 6259– 6266 (2003).

- [7] Anoop A.K., Sunil J.T., Rosamma A., Rani J., Natural Rubber-Carbon Nanotube Composites Through Latex Compounding, *Int. J. Polym. Mater.(IJPM)*, **59**: 33–44 (2010).
- [8] Sengloyluan K., Sahakaro K., Dierkes W. K., Noordermeer J.W.M., Silica Reinforced Tire Tread Compounds Compatibilised by Using Epoxidised Natural Rubber, *Eur. Polym. J.(EPJ)*, **51**: 69–79 (2014).
- [9] Salaeh S., Nakason C., Influence of Modified Natural Rubber and Structure of Carbon Black on Properties of Natural Rubber Compounds, *Polym. Compos. (PC)*, **33**(4): 489–500 (2012).
- [10] Torabi Angaji M., Hagheeghatpadjooh H. R., Preparation of Biodegradable Low-Density Polyethylene by Starch-Urea Composition for Agricultural Applications, *Iran. J. Chem. Chem. Eng. (IJCCE)*, **23**(1): 7-11 (2004).
- [11] Rouba N., Sadoun T., Boutagrabet N., Kerrouche D., Zadi S., Mimi N., Thermo-Oxidation and Biodegradation Study of Low-Density Polyethylene /Starch Films by IR Spectroscopy, *Iran. J. Chem. Chem. Eng. (IJCCE)*, **34**: 69-78 (2015).
- [12] Xie F., Pollet E., Halley P. J., Avérous L., Starch-Based Nano-Biocomposites, *Prog. Polym. Sci.(PPS)*, **38**: 1590-1628 (2013).
- [13] Liu H., Xie F., Yu L., Chen L., Li L., Thermal Processing of Starch-Based Polymers, *Prog. Polym. Sci. (PPS)*, **34**: 1348-1368 (2009).
- [14] Belarbi A., Haye B., Lévêque C., "L'amidon et ses Dérivés, Application Industrielle", Elsevier, Paris (2000).
- [15] Wu Y. P., Ji M. Q., Qi Q., Wang Y. Q., Zhang L.Q. Preparation, Structure, and Properties Starch/Rubber Composites Prepared by co-Coagulating Rubber Latex and Starch Paste, *Macromol. Rapid. Commun.(MRC)*, **25**: 565-570 (2004).
- [16] Tang H., Qi Q., Wu Y., Liang G., Zhang L., Ma J., Reinforcement of Elastomer by Starch, *Macromol. Mater. Eng. (MME)*, **291**: 629-637 (2006).
- [17] Wu Y. P., Qi Q., Liang G. H., Zhang L. Q., A Strategy to Prepare High-Performance Starch/Rubber Composites: In Situ Modification During Latex Compounding Process, *Carbohydr. Polym.(CP)*, **65**: 109-113 (2006).
- [18] Qi Q., Wu Y., Tian M., Liang G., Zhang L., Ma J., Modification of Starch for High-Performance Elastomer, *J. Polym. (JP)*, **47**: 3896-3903 (2006).
- [19] Angellier H., Molina-Boisseau S., Lebrun L., Dufresne A., Processing and Structural Properties of Waxy Maize Starch Nanocrystals Reinforced Natural Rubber, *J. Macromol.(JM)*, **38**: 3783-3792 (2005).
- [20] Buchanan R.A., Kwolek W.F., Katz H.C., Russell C.R., Influence of Starch Type and Concomitant Variables in Reinforcement of Styrene-Butadiene Rubbers, *Die/Stärke (DS)*, **23**: 350-359 (1971).
- [21] Buchanan R. A., Starch Xanthide Styrene-Butadiene Rubbers: Effect of Prolonged Water Immersion, *Die/Stärke (DS)*, **26**: 165-172 (1974).
- [22] Katz H. C., Kwolek W. F., Buchanan R. A., Doane W. M., Russell C. R., Influence of Amylose Content of Starch Upon the Water Resistance of Starch-Reinforced Styrene-Butadiene Rubbers, *Die/Stärke (DS)*, **26**: 201-206 (1974).
- [23] Buchanan R. A., McBrien J., Otey F. H., Russell C. R., Starch Xanthide Styrene-Butadiene Rubbers: Effet of Humidity and Outdoor Weathering, *J. Starch/Stärk (JSS)*, **30**: 91-96 (1978).
- [24] Rajisha K. R., Maria H. J., Pothan L. A.; Ahmad Z., Thomas S., Preparation and Characterization of Potato Starch Nanocrystal Reinforced Natural Rubber Nanocomposites, *Int. J. Biolog. Macromol.(IJBM)*, **67**: 147–153 (2014).
- [25] Déborah L. C., Angellier-Coussy H., Preparation and Application of Starch Nanoparticles for Nanocomposites: A Review, *React. Funct. Polym. (RFP)*, **85**: 97–120 (2014).
- [26] Corvasce F. G., Linster T. D., Thielen G., (Goodyear Co.), Starch Composite Reinforced Rubber Composition and Tire with at Least One Component Thereof: *U.S. Patent 5,672,639*, September 30 (1997).
- [27] Materne T. F. E., Corvasce F. G., (Goodyear Co.), Tire with Tread of Rubber Composition Prepared with Reinforcing Fillers which Include Starch/Plasticizer Composite: *U.S. Patent 6,273,163*, August 14 (2001).
- [28] Sandstrom P.H., (Goodyear Co.), Rubber Containing Starch Reinforcement and Tire Having Component Thereof: *U.S. Patent 6,391,945*, May 21 (2002).
- [29] Pawlikowski J. F., (Bridgestone/Firestone North American Tire, LLC), Vulcanizable Elastomer Compositions Containing Starch/Styrene Butadiene Rubber Copolymer as a Reinforcing Filler: *U.S. Patent 6,548,578*, April 15 (2003).

- [30] Choi S.S., Nah C., Lee S.G., Joo C.W., [Effect of Filler-Filler Interaction on Rheological Behaviour of Natural rubber Compounds Filled with Both Carbon Black and Silica](#), *J. Polym. Int. (JPI)*, **52**: 23-28 (2003).
- [31] Demirhan E., Kandemirli F., Kandemirli M., Kovalishyn V., [Investigation of the Physical and Rheological Properties of SBR-1712 Rubber Compounds by Neural Network Approaches](#), *J. Mater. Des.(JMD)*, **28**: 1737-1741 (2007).
- [32] Demirhan E., Kandemirli F., Kandemirli M., [The Effects of Furnace Carbon Blacks on the Mechanical and the Rheological Properties of SBR1502 Styrene Butadiene Rubber](#), *J. Mater. Des. (JMD)*, **28**: 1326-1329 (2007).
- [33] Ponnamma D., Sung S. H., Hong J.S., Ahn, K.H., Varughese K.T., Thomas S., [Influence of Non-Covalent Functionalization of Carbon Nanotubes on the Rheological Behavior of Natural Rubber Latex Nanocomposites](#), *Eur. Polym. J. (EPJ)*, **53**: 147-159 (2014).
- [34] Colonna P., Doublier J. L., Melcion J. P., de Monredon F., Mercier C., [Extrusion Cooking and Drum Drying of Wheat Starch. I. Physical and Macromolecular Modifications](#), *Cereal Chem.* **61**(6): 538-543 (1984).
- [35] Cogswell F. N., "Polymer Melt Rheology: A Guide for Industrial Practice", Woodhead Publishing House, Cambridge (1981).
- [36] Han C.D., "Rheology in Polymer Processing", Academic Press, New York (1976).
- [37] Cotten G. R., [Mixing of Carbon Black with Rubber: Measurement of Dispersion Rate by Changes in Mixing Torque](#), *J. Rub. Chem. Technol. (JRCT)*, **57**: 118-133 (1984).
- [38] Ceseracciu L., Heredia-Guerrero J.A., Dante S., Athanassiou A., Bayer I.S., [Robust and Biodegradable Elastomers Based on Corn Starch and Polydimethylsiloxane \(PDMS\)](#), *Applied Materials & Interfaces*, **7**(6): 3742-3753 (2015).
- [39] Birsa G., Shogren R., [Friction Properties of Chemically Modified Starch](#), *J. Synthetic Lubrication (JSL)*, **25**: 17-30 (2008).
- [40] Franta I., "Elastomer and Rubber Compounding Materials", Elsevier, New York (1989). ISBN 0-444-42994-8
- [41] Leblanc J. L., Cartault M., [Advanced Torsional Dynamic Methods to Study the Morphology of Uncured Filled Rubber Compounds](#), *J. Appl. Polym. Sci. (JAPS)*, **80**: 2093-2104 (2001).