

Elastomeric matrix composites: effect of processing conditions on the physical, mechanical and viscoelastic properties

D. Zaimova^{a,b}, E. Bayraktar^{b,*}, D. Katundi^b, N. Dishovsky^a

^a University of Chemical Technology and Metallurgy,
8 Kliment Ohridski blvd., Sofia 1756, Bulgaria

^b Supmeca/LISMMA-Paris, School of Mechanical and Manufacturing Engineering, France

* Corresponding e-mail address: bayraktar@supmeca.fr

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Properties

ABSTRACT

Purpose: The aim of this study is to investigate the influence of accelerator-vulcanizing agent system and the vulcanization temperature on the properties of vulcanizates based on Natural rubber/Polybutadiene rubber (NR/BR) compounds. This preliminary study will allow optimizing the composition for improving the mechanical properties and understanding the damage behaviour.

Design/methodology/approach: NR/BR based composites with different vulcanization temperatures and curing systems were characterized in respect of their curing characteristics (for 140°C and 160°C) and mechanical properties. The cure characteristics of the rubber compounds were studied by using the Monsanto MDR 2000 rheometer. The mechanical properties were investigated- tensile strength, elongation at break, tensile modulus at 100% (M100) and at 300% (M300) deformation. The hardness (Shore A) and molecular mass of the samples were also determined. Scanning electron microscopy was used to study the microstructure of the fracture surfaces.

Findings: The processing, physical, mechanical and viscoelastic properties and chemical structure of the mixture of Natural rubber/Polybutadiene rubber (NR/BR) compounds have been evaluated in detail for the compounds of D1 and D2 (140/160).

Research limitations/implications: limitations/implications: Some critical point, control of the temperature during vulcanization in press, can introduce some restrictions; these measurements can play on the final vulcanizates and in the course of processing.

Practical implications: In practical way, mechanical test results (tensile and shore A) give very useful information about the damage behaviour of the elastomeric matrix composites.

Originality/value: Natural rubber/Polybutadiene rubber (NR/BR) compounds were mixed by additions of some certain elements to improve physical, mechanical and viscoelastic properties and damage behaviours of these compounds produced under certain conditions.

Keywords: Vulcanization; Elastomeric composites; Optimization methods; Curing; Damage behaviour; Swelling test; Crosslink density

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1. Introduction

Elastomers are one of the oldest and largely used materials in different application of manufacturing engineering. During the vulcanization process of elastomeric compounds and also in other processing stages different chemicals are used that are called accelerators. It is important to choose these accelerators for vulcanization because they determine the type of network structure and naturally the specific material properties [1-8].

The formulations of elastomers are built up to assemble some specific requirements. Thus, each one of the various components taking part in a particular formulation has an important role as to give its contribution to the final properties [8-15]. However, even with the wide choice of ingredients available, the whole set of characteristics may still not be reached and many times a combination of two or more rubbers has to be used in the preparation of compounds for special properties. So, generally speaking, elastomeric materials are blended for properties improvement, better processing or lower cost [2,4-7].

Natural rubber (NR) is the adequate choice when good tensile and tear strengths are demanded, since these characteristics can be developed due to the capability this rubber has to crystallize under stress [8-13]. Polybutadiene rubber (BR) is characterized by its superior abrasion resistance, so that blends of NR and BR that combine the excellent processing and physical properties of the former with the superior abrasion resistance of the latter are largely used in the industry in the production of tyre treads and conveyor belts [1-6,14].

As the rubbers mixtures are usually multiphase systems, according to the used compounding mode, different distributions of the additives in each rubber phase can be achieved, depending on the degree of affinity that each additive has towards each rubber. In general, competitive vulcanization occurs due to different rates of vulcanization and/or rates of diffusion of the additives (including sulfur, accelerator and other compounds) in each of the elastomeric phases [15-17]. When two or more rubbers are blended, one of the problems one must be concerned with is the difference in vulcanization rate each rubber presents towards the particular vulcanizing system used. NR is known to have a strong tendency to undergo reversion as the result of thermo oxidative degradation brought about by long heating times [18-24].

Upon thermo oxidative degradation, with normally occurs via scission or depolymerization of the polymer molecules, NR gradually becomes softer and sticky and as a consequence, the maximum torque, which is the parameter related to the number of crosslinks, decreases. One of the reasons to blend BR to other elastomers is the difficulty this rubber presents concerning processability. By blending these two rubbers, BR and NR, the properties obtained were inferior to those for NR but, in comparison to BR, there have been improvements in performance as well as in processability. The lower price of NR is also a positive factor in favour of these blends.

Vulcanization temperature has a significant effect on crosslink structure. Optimum properties are when curing is done at the lowest possible temperature. However, to increase productivity, higher temperatures are frequently used.

Increases in sulfur and accelerator concentrations give higher crosslink densities and, therefore, higher moduli, stiffness,

hardness, etc. However, as the ratio of the concentration of accelerator to the concentration of sulfur increases, the proportion of monosulfidic crosslinks increases in natural rubber stocks (also called rubber compounds). Greater amounts of accelerator (with respect to sulfur) also give an abundance of pendent groups of the type, -Sx-Ac, which are attached to and "dangle" from the rubber molecular chains. Higher ratios of sulfur concentration to accelerator concentration give both more polysulfide crosslinks and more sulfur combined with the rubber chains to form sulfur-containing six-membered heterocyclic rings along the rubber molecular chains. In addition, conjugated olefinic double bonds appear along the polymer backbone chain. Such changes in the vulcanizate network structure, no doubt, are responsible for changes which occur in vulcanizate properties as a result of changes made in the curing-system recipe [19-24].

The complexity of the vulcanization reactions, the types and relative concentration of crosslinks formed, and the nature and extend of main chain modification vary considerably depending on the curing system itself and the conditions of vulcanization [12-25].

Conventional system (CV): These systems contain high sulfur levels, e.g. 1.5 to 3.5 phr and low level accelerator, e.g. 0.5 to 1 phr (S/A ratio from 1.5 to 70). At optimum cure the vulcanizate contains mostly polysulfidic crosslinks with relatively high level of chain modification. The higher the sulfur content, the more polysulfidic crosslinks. The kind of crosslinks gives little resistance to reversion and oxidative aging and proper long-term flex life [9]. Otherwise, these vulcanizates show good tensile and tear strengths, resistance to fatigue and good low temperature properties.

Efficient systems (EV): These systems contain low sulfur levels, e.g. 2.5 to 5 phr (S/A ratio from 0.05 to 0.3). They will form mainly mono- and disulfidic crosslinks and much less chain modification. Monosulfidic crosslinks are more stable than polysulfidic crosslinks. Short crosslinks provide poor fatigue life and compression set [26-36]; but improve resistance to reversion and oxidative aging. However the drawbacks include lower tear strength, fatigue resistance and abrasion resistance. These kind of systems are appropriate for thick rubber items.

Gonzalez et al [27] has studied the tensile strength and other physical properties of different conventional and efficient systems increasing the crosslink density. They concluded that physical properties are superior for conventional cure system at similar crosslink values, according with the results of Mullins [28]. They explained these results by difference in the vulcanization mechanism of the two cure systems. The conventional cure system produces a homogeneous network while the efficient cure system produces a significant polymerization of double bonds of adjacent chains. This leads to a network of unevenly distributed crosslinks and results in impediment to NR crystallization and stress concentration that anticipates the compound failure. In other words, efficient system includes high crosslink areas, overcrosslinked domains, which inhibit the correct stress distribution, accumulating higher stress areas where micro-crack can be formed and crack propagation is increased.

For this reason the aim of this study is to investigate the influence of accelerator-vulcanizing agent system and the vulcanization temperature on the properties of vulcanizates based on Natural rubber/Polybutadiene rubber (NR/BR) compounds. This preliminary study will allow optimizing the composition for

improving the mechanical properties and understanding the damage behavior.

NR/BR based composites with different vulcanization temperatures and curing systems were characterized in respect of their curing characteristics (for 140°C and 160°C) and mechanical properties. The cure characteristics of the rubber compounds were studied by using the Monsanto MDR 2000 rheometer. The mechanical properties were investigated - tensile strength, elongation at break, tensile modulus at 100% (M_{100}) and at 300% (M_{300}) deformation. The hardness (Shore A) and molecular mass of the samples were also determined. Scanning electron microscopy was used to study the microstructure of the fracture surfaces.

2. Experimental procedures

First of all, the two basic compounds (D1 and D2) were mixed in laboratory using two rolling mixer. The moulding conditions were determined from torque data using moving die rheometer MDR 2000 (Alpha Technologies) for temperatures 140°C and 160°C. At the end, four compounds (D1-140/160 and D2-140/160) based on sulphur vulcanized Natural rubber/Polybutadiene rubber blends were prepared containing certain fillers and/or reinforcements in order to investigate their deformation behaviours.

The exact composition of the blends is kept in reserve because of the confidentiality matters. The results discussed in the present paper give partial results carried out in the frame of the applied project supported by French - Bulgarian research cooperation

Cured sheets were prepared by compression moulding by using a special hot press. The moulding took place at 140°C and 160°C and pressure 100 kg/cm².

The behaviour of these compounds in detrimental environmental conditions were tested by means of swelling experiments that all of the swelling tests were carried out with the molded samples by putting them in excess of toluene at room temperature. After these tests, the crosslink densities for each compound were calculated according to the molecular mass between two crosslinks. All of the crosslink densities were calculated according to Fory-Rehner relation [29]:

$$\frac{1}{2M_c} = \frac{1}{2\rho V_0} \left[\frac{\ln(1 - V_r) + V_r + \mu V_r^2}{V_r^{1/3} - \frac{1}{2} V_r} \right] \quad (1)$$

and

$$v = \frac{1}{2M_c} \quad (2)$$

where: M_c – molecular mass between crosslinks; ρ – Density of the rubber; V_0 – molar volume of the solvent; V_r – volume fraction of the swollen rubber; μ – interaction parameter between the rubber sample and the solvent; v – Crosslink density.

The thickness of the sheets was arranged as 2 mm. The measurements of physic-mechanical properties were carried out in

accordance with ASTM D 412a^{e2} (2010). The samples were cut from the moulded sheets in dumbbell shape. The sample length and thickness were measured. Tensile tests were performed on an Instron (model 4507). A minimum of 3 specimens was tested for each compound. Testing was done at room temperature with a cross head speed of 500 mm/min⁻¹.

Hardness values (Shore A) were measured according to the standard - ASTM D 2240-05 (2010).

Dynamic Mechanical Thermal Analysis (DMTA) was carried out on the Dynamic Mechanical Analyzer MK III system (Rheometric Scientific). As a mode of deformation, single cantilever bending was used at a heating rate of 2°C/min, a frequency of 5 Hz and deformation 64 μ m in temperature range from - 80 to 80°C.

Fracture surface and surface under the fracture of tensile specimens after the tests were observed by means of Scanning Electron Microscopy (SEM).

3. Results and discussion

The rheometric characteristics of the studied for the four compounds are given in Table 1.

Table 1.
Rheometric characteristics of the compounds

Characteristic	Blend №			
	D1-140	D1-160	D2-140	D2-160
ML, dNm	2.67	2.46	2.72	2.45
MH, dNm	35.97	32.70	33.20	30.77
$\Delta M = (MH - ML)$	33.3	30.24	30.48	28.32
T ₉₀ , min:s	16:46	4:26	16:04	4:46
T _{s2} , min:s	5:55	1:29	8:12	2:25
V, %min	9.0	34.0	13	52

The minimum torque (M_L) in a rheograph measures the viscosity of the vulcanizates, and the maximum torque (M_H) is generally correlated with the stiffness and crosslink density.

It is well known that the difference between maximum (M_H) and minimum (M_L) torque is a rough measure of the crosslink density of the samples and usually known as ΔM . From the table it is noticed that the highest value of ΔM is for compound D1-140. Hence the crosslink density is maximal for compound D1-140 comparing with the other three compounds. This is also confirmed by the results for the crosslink density obtained by the equilibrium swelling (Figure 1). The highest crosslink density is registered for compound D1-140. The scorch time (T_{s2}) is the time required for the minimum torque value to increase by two units and measures the premature vulcanization of the material. What makes an impression is that the CV system exhibited shorter T_{s2} values than the EV therefore; more crosslinks are formed in shorter time.

These results are unusual because the greater quantity of the accelerator (in compounds D2-140 and D2-160) should provide superior values for T_{s2} . It is possible this anomaly to be due to the nature of sulphenamide class accelerators (delayed action in the

beginning of vulcanization) and on the other hand the higher content of sulfur in compound D1. But the overall rate (V) of vulcanization is in favour of the compound cured with EV.

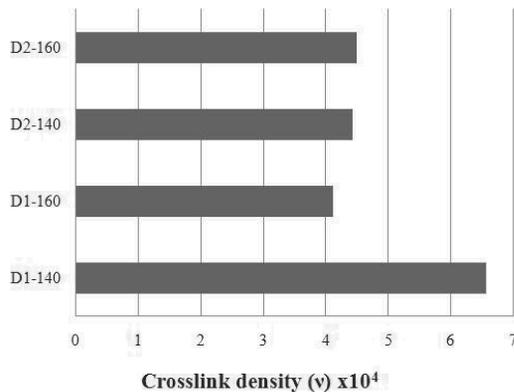


Fig. 1. Crosslink density determined by swelling test

Figures 2 to 5 present the mechanical properties for all of the four compounds studies in the frame of the common research project.

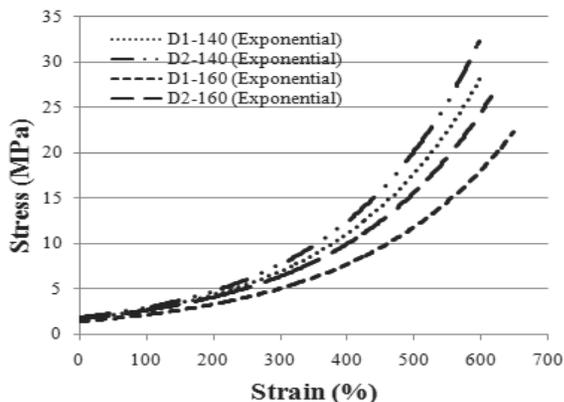


Fig. 2. Stress-strain curve for NR/BR with different ratio of sulfur-accelerator system and vulcanization temperature

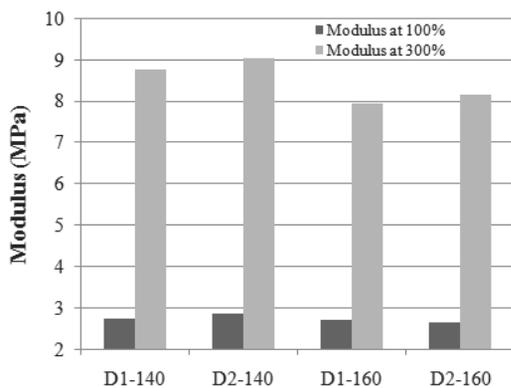


Fig. 3. Comparison of M₁₀₀ and M₃₀₀ for NR/BR with different ratio of sulfur-accelerator and vulcanization temperature

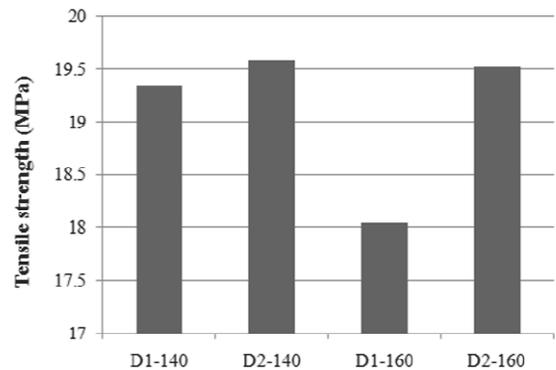


Fig. 4. Tensile strength of NR/BR with different ratio of sulfur-accelerator and vulcanization temperature

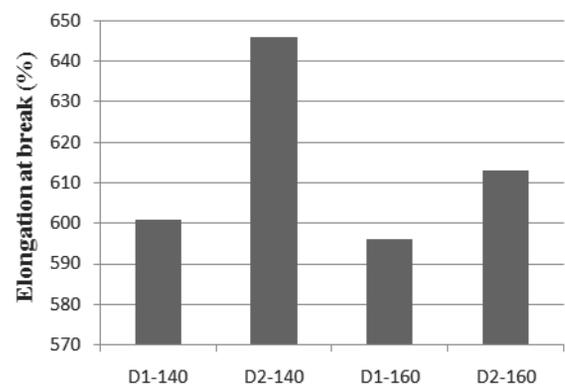


Fig. 5. Elongation at break for NR/BR with different ratio of sulfur-accelerator and vulcanization temperature

Tensile properties are commonly used to measure the degradation (damage) behaviour of elastomers. The modulus is related to the cross-linking density of the rubber vulcanizates. These changes are directly associated with changes in the original crosslink structure, such as main chain scission and crosslink modifications [30,31]. There is a slight difference in the values obtained for M₁₀₀ and M₃₀₀ (Figure 3) in favour of compound D2 (EV). This result is not in accordance with the literature [8,10].

Concerning the temperature of vulcanization 140°C the values for all mechanical properties - modulus M₁₀₀ and M₃₀₀, tensile strength and elongation at break are a little bit higher than for temperature of vulcanization 160°C. This result could be due to forming of better structure because of the lower temperature of vulcanization and degradation of NR under the influence of the higher vulcanization temperature.

The results for M₁₀₀ and M₃₀₀ are confirmed from the results obtained for the tensile strength values (Figure 4). Tensile strength is higher for D2 compounds than those of D1. The same dependence is observed for the elongation at break-final tearing as given in Figure 5.

The Shore (A) Hardness values (Figure 6) is increasing with increasing of the vulcanization temperature. According to the literature, the hardness should increase with increasing of the crosslink density [20-32] however the compound "D1-140" has the lowest hardness although it has the highest crosslink density.

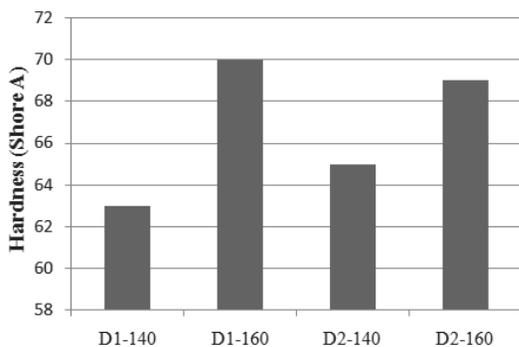


Fig. 6. Hardness “Shore A” values measured for each compound

It seems that the compound cured with conventional vulcanization system (D1) comparing with efficient vulcanization system (D2) gives lower values for Tan Delta as will be seen here.

It is known from literature [7] that overcure also affects Tan Delta since the higher the degree of vulcanization, the lower will be the magnitude of Tan Delta. This can explain the results obtained for the physic-mechanical properties because over-cured compounds give worse results due to the degradation of the rubber after the optimum time. Although the difference between T_{90} for both D1 and D2 is minimal probably the vulcanization mechanism plays role for the degree of curing.

The dependences of storage modulus (E') and dynamic mechanical loss angle tangent (Tan Delta) on the temperature of vulcanization and vulcanization system were studied in the temperature interval from -80°C to $+80^{\circ}\text{C}$.

As shown in Figure 7, in the range of -80°C to -40°C there are any considerable changes occurred in the storage modulus (E'). The decrease of storage modulus (E') with the increasing temperature, in other word, the transition from the glass to the high elastic state occurs at about -40°C .

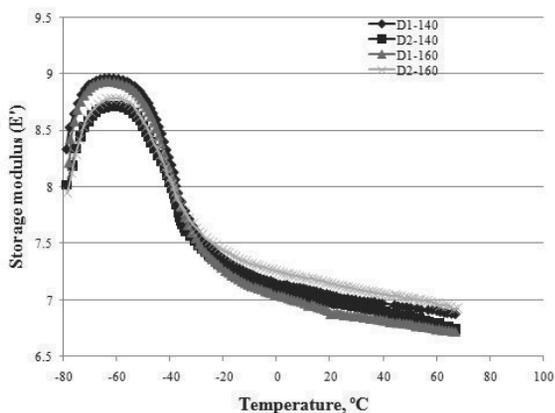


Fig. 7. Storage modulus as a function of temperature

The observation of DMTA curves also gives very useful information on the material homogeneity. From Figure 8, the width of the Tan Delta peaks for the D2 is larger than D1, which means that D2 for both temperatures is less homogeneous than D1. According the test results obtained for the four compounds, the glass transition temperatures are more and less similar for all

of the compounds. In general meaning, the temperature of vulcanization does not play role for the dynamic mechanical properties.

The mechanical loss angle tangent is the ratio between the dynamic loss modulus (E'') and the dynamic storage modulus (E') ($\text{Tan Delta} = E''/E'$). It represents naturally the macromolecules mobility of the chains and polymers phase transitions [7,11-15]. It is accepted that the higher the Tan Delta is the greater the mechanical losses; these losses are related to high energy input required for the motion of the molecular chains of the polymer as the transition is being approached [29,35].

The mechanical losses are greater for compound D1 (the maximum of the peak Tan Delta is higher). It suggests better interaction between the rubber matrix and carbon black. However the reinforcing effect of the filler is better for compound D2 regarding the results obtained from the tensile tests. This could be due to a higher vulcanization quality for compound D2. In this point, some agreements are found in literature as in [15,24,35]. It is well known also that Tan Delta peak corresponds to the glass transition temperature (T_g) of the composite. As this value is indicated in Figure 8, the glass transition temperature (T_g) of the vulcanizates does not show considerable variation under the test conditions studied in the frame of this work (within the limits of $2-3^{\circ}\text{C}$).

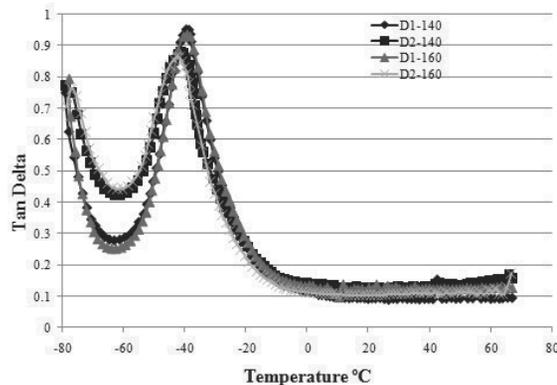


Fig. 8. Tan Delta values as a function of temperature

Fracture surface and surface properties under the fracture were observed by means of Scanning Electron Microscope (SEM) observations as indicated in Figures 9 (A, B, C, D).

Tensile damage surfaces after final tearing and surface under the fracture side indicate different damage behaviours due to the different vulcanizates conditions. Apparently, D2 compounds are more homogenized than D1 compounds. There is no gas bubbles occurred as an internal defect. No cavitations are observed (very weak hydrostatic effect). Secondary cracks are observed on the surfaces just under the fracture surfaces, mainly in the compounds of D1-140/160. Again, very brittle and similar cleavage surfaces are observed on the fracture surfaces of these compounds. A typical damage behaviour called “tongue formation” on the fracture surfaces of the compounds of D2-140/160.

The diameter of particles was about $2-4\mu\text{m}$ and they were homogeneously dispersed at all ranges of volume content (Figures 9C and 9D). Particularly, cavities were appeared in certain specimens, very often in the compounds of D1-140/160, which indicated the relatively weak interaction of particles with matrix.

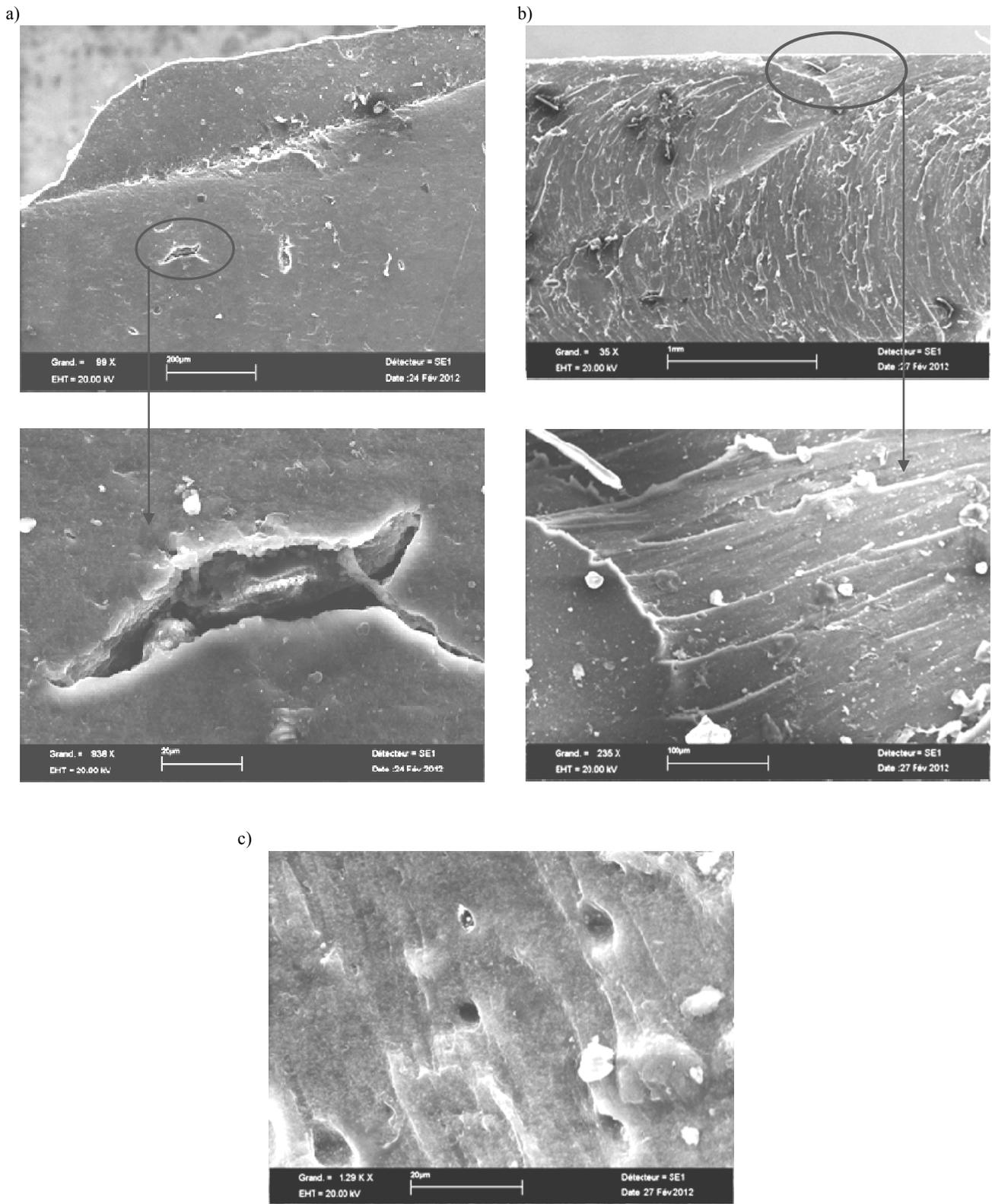


Fig. 9A. Surface appearance under the fracture side a) and detail of fracture surfaces b, c) for the compound D1-140

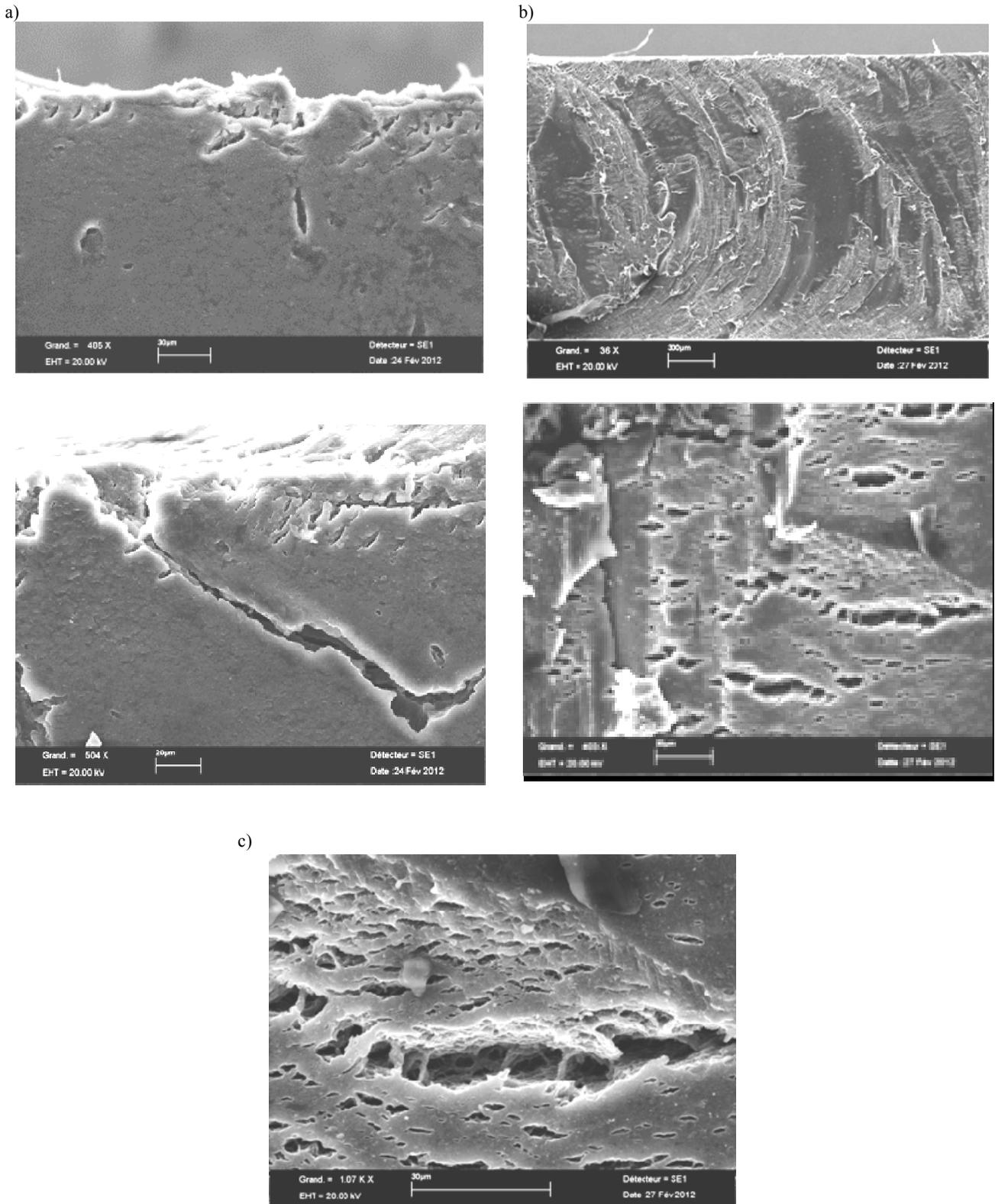


Fig. 9B. Surface appearance under the fracture side a) and detail of fracture surfaces b) for the compound D1-160

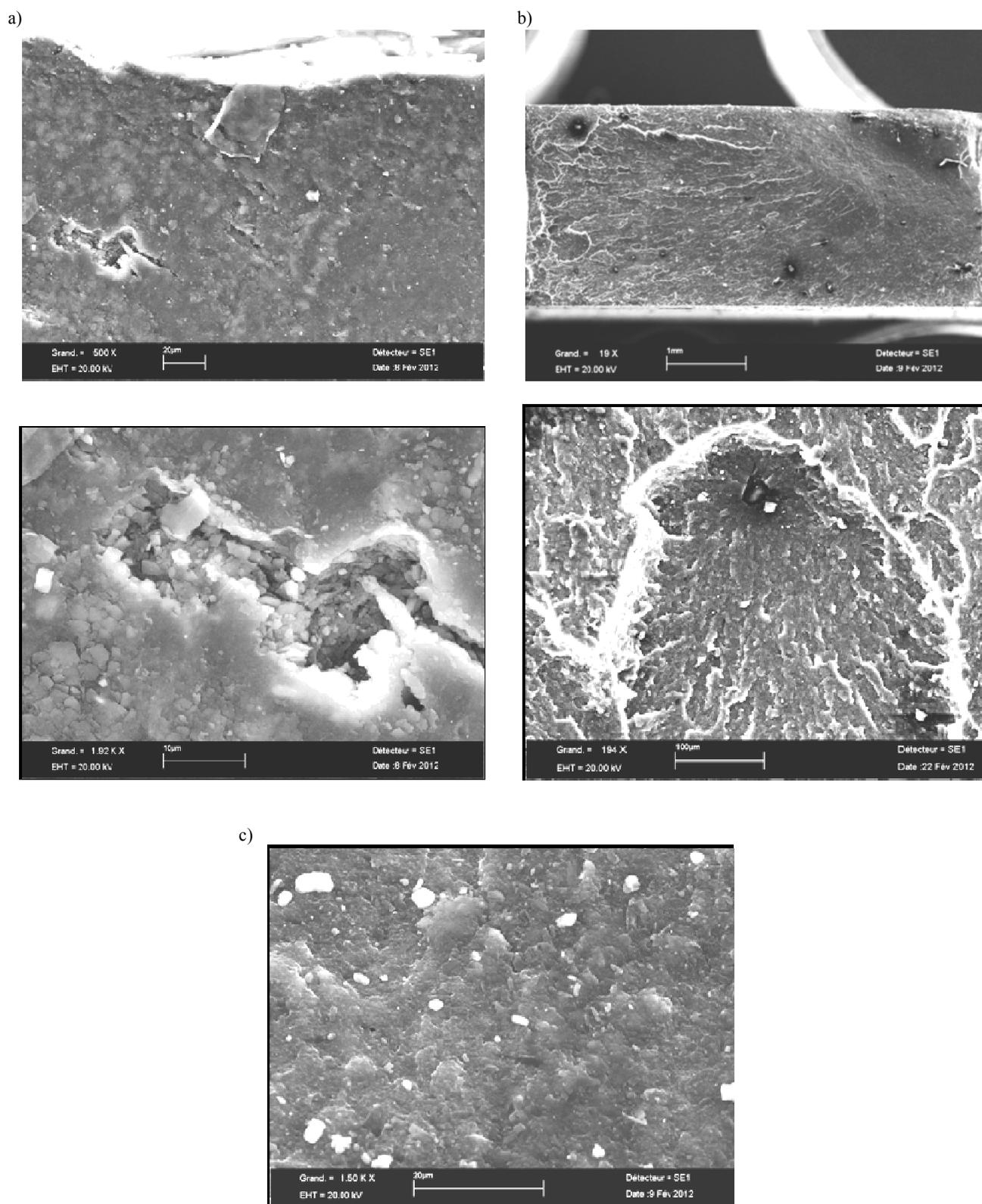


Fig. 9C. Surface appearance under the fracture side a) and detail of fracture surfaces b) for the compound D2-140

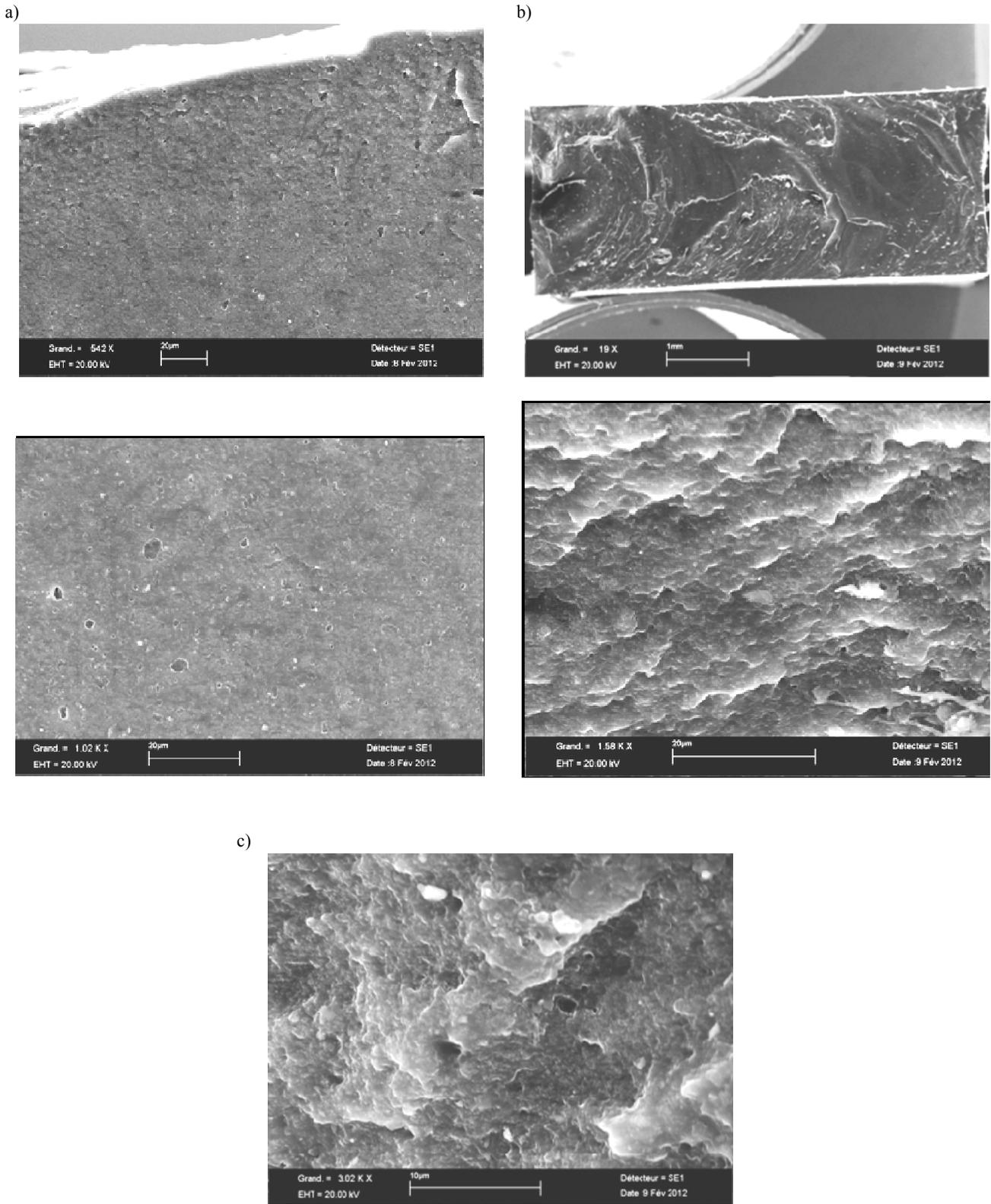


Fig. 9D. Surface appearance under the fracture side a) and detail of fracture surfaces b) for the compound D2-160

4. Conclusions

The processing, physical, mechanical and viscoelastic properties and chemical structure of the mixture of Natural rubber/Polybutadiene rubber (NR/BR) compounds have been evaluated in detail for the compounds of D1 and D2 (140/160).

With changing the vulcanization temperature from 140°C to 160°C is observed decreasing in all mechanical properties (modulus M_{100} and M_{300} , tensile strength and elongation at break). This is probably due to the partial destruction of the crosslinks under the influence of the high temperature (160°C). Hardness is increasing with the increasing of the temperature. The temperature of vulcanization does not play role for the dynamic mechanical properties (storage modulus and Tan Delta).

As for the vulcanization system, modulus M_{100} and M_{300} are increasing with the passage from CV (compound D1) to EV (compound D2). Tensile strength and elongation at brake are also increasing. These results are not in accordance with the literature but can be explained by overcure of compound D1.

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