

Mechanical and thermal properties of crab chitin reinforced carboxylated SBR composites

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Abstract. The addition of small amounts (up to 9 wt%) of chitin microsized particles, originating from shellfish waste, to carboxylated styrene-butadiene rubber (XSBR) matrix (as received and annealed to 100°C) has been studied. In particular, this study concentrated on their mechanical (creep investigation by nanoindentation and dynamical-mechanical analysis), thermal (differential scanning calorimetry and thermogravimetry) and swelling behaviour (toluene absorption) and was completed by morphological characterisation by scanning electron microscopy and atomic force microscopy.

The results show that annealing has a limited effect on materials properties, effects which are further reduced by the addition of growing amounts of crab chitin. It should be noted that the limited filler content used in the study does not substantially modify the linear creep behaviour of XSBR for sufficiently long loading times. The thermal stability of the system does also appear to be preserved even with the maximum chitin content added, while it serves sufficiently as an effective barrier against aromatic solvent absorption.

Keywords: rubber, nanoindentation, crab chitin, thermal properties, solvent absorption

1. Introduction

Chitin is a high molecular weight polymer, mainly with linear structure, based on a polysaccharide compound containing an acetamide group, specifically β -(1 to 4) (N-acetyl -D- glucosamine). It is widely present in plants and animals, being the second most abundant biopolymer in nature after cellulose and therefore biodegradable: in addition to being biodegradable, chitin is highly crystalline and depending on its origin it occurs in three forms identified as α , β , and χ chitin [1]. Other positive qualities include non-toxicity, non-allergenicity, anti-microbial effect, insolubility in water and resistance to acids, alkalis, and many organic solvents, ver-

satile biological activity and excellent biocompatibility [2]. The above characteristics make chitin suitable for applications in a number of areas other than food industry, such as e.g., in biosensors, and in medical and pharmaceutical applications as wound-dressing material and device for controlled drug release [3].

Chitin can easily be isolated from crab shell, when it is found to be highly thixotropic and liquid crystalline [4]. When isolating the crystalline regions of chitin, referred to as whiskers, from the crab shells and squid pens by hydrochloric acid hydrolysis, it was found that these microfibrillar arrangements have quite uniform properties [5]. In the specific

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case of chitin whiskers extracted from crab shells, the distribution in length has been found to range from 100 to 500 nm, while diameter was between 10 and 80 nm, which implied that the average aspect ratio (length/diameter), was 10 ± 5 [6].

The introduction of these natural polymers as nanofillers in a rubber matrix has been suggested, to improve specific properties in some applications. In particular, they are likely to reduce the amount of swelling due to absorption in membranes [7], and can allow SBR to compete with vulcanised rubber, in that their reinforcing capability, depending on the aspect ratio of the chitin, can be comparable to the traditional inorganic nanofillers e.g., clay [8]. In addition, the compatibilization efficiency of styrene-butadiene matrices generally depends on the conditions of blend preparation and processing [9]. In particular, thermal annealing of rubber blends results often in a substantial hardening of the material, which is capable of providing a stronger interface for the possible introduction of reinforcement in the rubbery matrix [10].

If suitable conditions for compatibility are achieved, the active surface of natural nanofillers facilitates chemical derivation and grafting, and forms strong physical interaction with polymer matrix. This was explained by the fact that the whiskers take the appearance of a rigid network, which results from strong interactions between them, in particular from hydrogen bonds: the network is possibly governed by a percolation mechanism only at high temperature [11]. Unmodified chitin whiskers, obtained from squid pen [12] and crab shells [5] have been tested as the reinforcing elements in polymer matrices, such as polycaprolactone [13], acrylic resins [14] and natural rubber [4–6]. Modification of chitin whiskers by different chemical agents, in particular succinic anhydride, and different types of isocyanates, has also been attempted, with no substantial improvement for the introduction into a natural rubber matrix [15]. It has been suggested that this loss of performance is due to the partial destruction of the aforementioned three-dimensional network of chitin whiskers assumed to be present in the unmodified composites [16].

This work concentrates on the study of the mechanical and thermal properties of composites with crab chitin introduced into an XSBR latex: a number of studies of these properties for the pure unvulcan-

ized matrix are available, in particular [9, 17–20]. This study does also include the degradation scenario of these composites, in particular measuring their dynamical properties, their creep profile, their temperature degradation and their swelling by toluene absorption.

2. Materials and methods

2.1. Materials

2.1.1. Base materials

The XSBR latex used in this study was supplied by Apar Industries Ltd., Bombay, Maharashtra, India. Table 1 reports the most important features of this latex. α -Chitin powder was supplied by Marine Chemicals, Cochin, Kerala, India. All the chemical products needed for the chitin treatments, namely 3N-hydrochloric acid (HCl), potassium hydroxide (KOH – 5% solution), sodium hypochlorite (NaClO₂) (solution for bleaching) and 3N-sodium acetate buffer, were purchased by Indian chemical suppliers. In order to obtain nano-sized chitin whiskers, a process consisting in several steps was carried out.

Table 1. Properties of carboxylated styrene butadiene rubber latex

Dry rubber content (DRC)	47%
Total solid content (TSC)	50.7%
Styrene content	59%
pH	8.60
Mechanical stability	Good

2.1.2. Chitin deproteinisation

The first part of the process consists in the deproteinisation of the chitin. Firstly, the chitin powder was stirred and boiled with 5 wt% aqueous KOH solution for 6 h. Then it was rinsed with distilled water and filtered. Lamarque *et al.* [21] reported that the sodium hydroxide concentration influences the nanostructure of chitin whiskers. After this treatment, chitin was bleached with 17 g of NaClO₂ in 1 L of distilled water mixed with 27 g of NaOH in 75 mL of acetic acid completed with 925 mL of distilled water. The suspension was stirred at 80°C for 2 h. This procedure was repeated three times.

2.1.3. Preparation of nanochitin whiskers

The chitin whisker suspensions were prepared by hydrolyzing the purified chitin with 3N HCl at the boiling point for 1.5 h while stirred. After acid

hydrolysis the suspensions were dialyzed for 2 h in distilled water and then overnight in running water. An additional dialysis by dialysis bag for 12 h by changing the distilled water every 2 h was performed until a pH = 6 was reached. The dispersion of whiskers was completed by three successive ultrasonic treatments for 2 minutes each. The concentration of the chitin particles suspension was 2.88 g over the 40 mL batches, which means 7.2 wt%, then it was progressively diluted to obtain the other concentrations.

2.1.4. Preparation of composites

In order to obtain the blends, the XSBR latex and the chitin suspension were mixed together and stirred for 2 hours, then cast in Petri dishes. The solid nanocomposite films were obtained drying the solution in an oven at 40°C, allowing the water to evaporate.

In all the prepared composites, the XSBR latex volume fraction was kept constant, whereas the volume fraction of chitin whiskers suspension was tuned from 30 to 70 vol%, which correspond to a weight between 2.16 and 5.04 grams of chitin in 100 mL total XSBR latex. Throughout the present paper, the compositions of the composites are expressed in terms of volume percentages, for convenience. The pure XSBR matrix is also prepared and used as the control. To observe the effect of an annealing treatment on the produced materials, the neat XSBR and all the nanocomposite blends were heated to 100°C for 90 minutes, then tested and compared with the non-annealed ('as received') materials. This procedure has the aim of showing the effect of exposure to a temperature slightly exceeding the maximum service temperature, in particular showing the effect of high temperature washing (vapour vacuum cleaning) on the material, thinking of the below mentioned application of it in the textile field.

The annealing treatment can be supposed to yield an accelerated drying of the composites, also from

water collected by chitin, given that lower temperatures, usually 40 or 60°C, have been applied for that purpose in literature [22–23] and also harden the rubber matrix by removing the water content of the latex. Heating at this temperature is also likely to promote filler flocculation, as proposed in [24], to modify their geometry and evaluate the effect of this treatment on the mechanical properties. The flocculation effect for the filler has been revealed for equivalent systems in [9], demonstrating that even the addition of a few weight percent of synthesized clays, up to 2.5% of unmodified fluorohectorite, produces a slight but perceivable decrease of the viscosity.

Table 2 summarized all the studied materials with their composition.

2.2. Methods

2.2.1. DMA analysis

Dynamical mechanical analysis has been often performed on filled systems based on including unvulcanised rubber to determine the viscoelastic properties of the system [5, 17, 25, 26]. In this work, DMA was performed by using a Rheometric Scientific (Piscataway, NJ, USA) -ARES N2 rheometer. The sample size was 10 mm in width, 30 mm in length, and about 1.5 mm in thickness. The measurements were carried out in the dynamic time sweep test starting from $T = -40$ up to 80°C (heating rate = 5°C/min) and frequency fixed at 1 Hz and shear strain at 0.15%. The storage modulus, loss modulus and loss factor ($\tan\delta$) of the samples were measured.

2.2.2. SEM analysis

An assessment on the morphological aspects of the produced material was carried out with a field emission scanning electron microscope (FESEM) ZEISS (Carl Zeiss s.p.a., Arese, Italy) model Supra 25.

2.2.3. AFM examination

The chitin whiskers, as well as the nanocomposites, were also characterized using a Veeco (Plainview,

Table 2. Composition of the different samples used

XSBR latex [mL]	Chitin solution [mL]	Chitin content [g]	Chitin wt%	Samples
100	0	0	0	XSBR, XSBR-A
100	30	2.16	4.1	CW30, CW30-A
100	50	3.60	6.6	CW50, CW50-A
100	70	5.04	9.0	CW70, CW70-A

Samples marked with A have been annealed at 100°C

NY, USA) MultiMode scanning probe microscope with a Nanoscope V controller. For the analysis of chitin, a droplet of the aqueous whisker suspension (0.5% by weight) was dried on a mica surface prior to AFM examination. The nanocomposite films were microtomed using a diamond knife after embedding in epoxy resin and were analyzed directly. The images for the whiskers and the nanocomposites were collected using a tapping mode etched silicon tip, with a nominal spring constant of 5 N/m and a nominal frequency of 270 kHz.

2.2.4. Thermogravimetric analysis (TGA)

The thermal stability of the produced materials was investigated by means of thermogravimetric analysis (TGA). The measurements were performed with a thermogravimetric analyzer Seiko (Seiko Instruments, Inc., Chiba, Japan) model Exstar 6300 in nitrogen atmosphere, and consisted in dynamic scans at the heating rate of 20°C/min from 30 to 900°C. Bulk samples of about (10±1) mg were tested.

2.2.5. Differential scanning calorimetry (DSC)

Differential scanning calorimetry was performed using a differential scanning calorimeter MDSC TA (TA Instruments, Vimodrone, Italy) model Q200. The temperature range analyzed was –90 to 200°C.

2.2.6. Swelling experiments

Toluene absorption tests on as-received and annealed samples have also been carried out, with the idea of considering the durability of the matrix and its envisaged application, which was discussed above.

The kinetics of toluene absorption was determined for XSBR based composites. The specimens used were square shaped samples with 2 mm side and around 1–1.5 mm thick. The thickness, $2L$, of the film was therefore supposed to be thin enough so that the molecular diffusion was considered to be one-dimensional. After weighing, the samples were immersed in toluene. The samples were removed at specific intervals (t) and weighed (M_t) up to an equilibrium value (M_∞). The swelling rate of the samples was calculated by dividing the gain in weight ($M_t - M_0$) by the initial weight (M_0). Since these swelling experiments were more difficult to perform for unvulcanized materials (part of the sample could dissolve in toluene), the following analysis was also performed for these samples. Thin square shaped samples were first weighed (M_0) and then immersed in toluene for 48 h. They were subsequently dried for 12 h at 55–60°C and weighed again (M_0'). The 'sol' fraction (M_0'/M_0) and relative weight loss (RWL) $[M_0 - M_0']/M_0$ were then determined. This allowed estimating the fraction of XSBR bonded to the filler and the fraction of XSBR dissolved in toluene.

2.2.7. Nanoindentation creep testing

A NanoTest nanoindenter, supplied by MicroMaterials Inc. (Tampa, FL, USA), was employed to study the creep behaviour of the produced materials. This equipment consists of a pendulum-based depth sensing system, with the sample vertically mounted. A Berkovich-type three-sided pyramidal indenter was used. The indentation was load-controlled to 0.05 mN maximum load for 200 s as the holding period. All

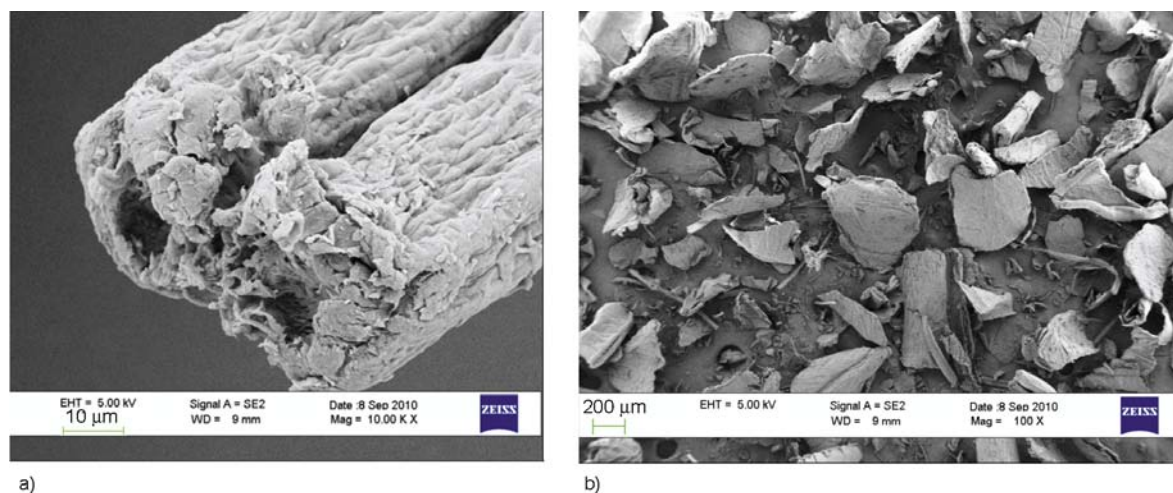


Figure 1. (a) Tip of a chitin whisker, (b) general appearance of chitin powder

the tests were performed at 23°C. Twenty tests were performed on each sample, in order to obtain a good reliability of the results.

3. Results

Commercial chitin from crab shells consists of a mixture of roughly spherical particles with diameter around 0.5–1 mm and ill-defined particles [4]. The treatment followed generated intertwined and spiralling chitin microfibrils, forming whiskers such as the one whose tip is reproduced in Figure 1a. However, the general appearance of chitin powder still includes a wide variability of particle geometries and sizes, as illustrated in Figure 1b.

The discussion of results obtained focused on the two effects of the addition of an increased quantity of crab chitin in the matrix and of XSBR rubber annealing. Crab chitin addition allowed using a waste product originating from seafood industries, while the matrix was annealed to prepare it to the envisaged use of XSBR as back coating for textiles and carpets, for which application an increased resistance to wear and to degradation due e.g., to solvent absorption, is desirable. Previous studies suggested that the addition of limited amounts of chitosan to natural rubber latex decreases benzene diffusivity, an effect which is likely to be observed also in this case for small amounts of chitin [24].

The four-element Burgers model has been used to approximate the creep behaviour in solid-filled rubber [27] and more recently also in natural fibre reinforced polymers [28, 29]. This model is commonly represented by the simultaneous presence of two

Table 3. Constants obtained from the creep model

Samples	K_1 [N/m]	K_2 [N/m]	η_1 [N·s/m]	η_2 [N·s/m]
XSBR	48.664	80.901	1279.90	23 104
XSBR-A	38.028	64.658	925.33	16 152
CW30	40.979	65.195	773.15	20 113
CW30-A	31.537	70.305	1154.00	22 019
CW50	31.279	60.763	985.45	19 678
CW50-A	53.239	103.150	1535.60	24 940
CW70	35.733	58.925	857.38	16 083
CW70-A	78.949	188.090	1981.00	41 791

elastic constants (springs): elastic recovery (K_1) and rubbery elasticity (K_2), and two viscous constants (dashpots): molecular ‘slip’ (η_1) and delayed elasticity (η_2). Respective values are reported in Table 3.

The model appears to closely match the experimental results of creep tests by nano-indentation (Figure 2), giving a representation as the function $H(t) = A \cdot \ln(B \cdot t + 1)$. Comparing the creep results between the as-received and annealed samples, annealing results in a highly increased resistance to indentation for the samples with higher chitin content (CW50 and CW70), an effect which is not observed for the pure XSBR and the CW30 sample. This is a perceivable trend, although the bulk values provided by nanoindentation are not directly comparable with the calculation of elastic modulus. This is due to the fact that it provides information on hardness and surface profile of modulus, surface-based information whose application to the material in general can be affected by the non uniformity of the matrix and further aggravated by the presence of the filler. As a general point, it can be suggested that filler flocculation is amongst the

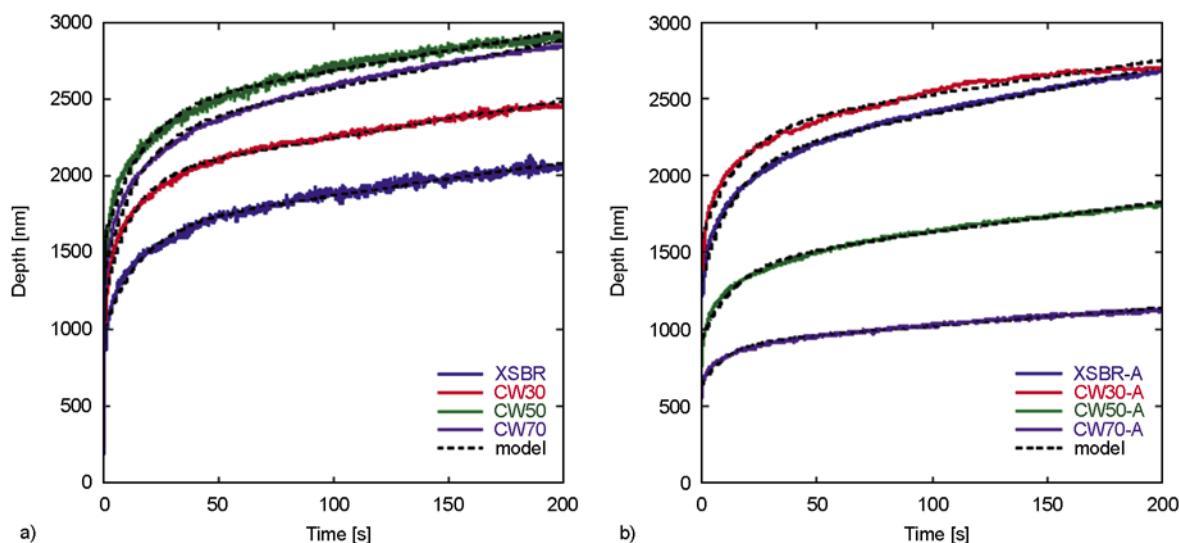


Figure 2. Nano-indentation curves for normal (a) and annealed samples (b)

Table 4. Comparison of the rigidity of normal and annealed samples

Compared samples	Depth difference after			
	50 s [nm]	100 s [nm]	150 s [nm]	200 s [nm]
XSBR-A vs. XSBR	580	650	630	640
CW30-A vs. CW30	270	250	320	230
CW50-A vs. CW50	-980	-1100	-1120	-1080
CW70-A vs. CW70	-1450	-1480	-1690	-1770

Table 5. DMA variables for the different samples

Material	T_{peak} [°C]	$\tan \delta$	$\Delta T_{0.5\text{peak}}$ [°C]
XSBR	-6.32	1.15	17.48
XSBR-30CW	-5.63	0.78	25.07
XSBR-50CW	-9.26	0.81	19.54
XSBR-70CW	-7.96	0.97	18.44
XSBR-A	-8.26	1.20	16.24
XSBR-30CWA	-7.57	0.95	19.09
XSBR-50CWA	-9.07	1.08	17.81
XSBR-70CWA	-8.21	0.78	20.45

Table 6. Storage and loss moduli for the different samples at 25°C

Material	G' [Pa] at 25°C	G'' [Pa] at 25°C
XSBR	$1.3905 \cdot 10^6$	$1.8260 \cdot 10^5$
XSBR-A	$1.4405 \cdot 10^6$	$1.4695 \cdot 10^5$
XSBR-CW30	$3.9459 \cdot 10^6$	$1.0366 \cdot 10^6$
XSBR-CW30A	$3.9459 \cdot 10^6$	$7.0493 \cdot 10^5$
XSBR-CW50	$8.8983 \cdot 10^6$	$3.0748 \cdot 10^6$
XSBR-CW50A	$6.2482 \cdot 10^6$	$1.1311 \cdot 10^6$
XSBR-CW70	$1.7701 \cdot 10^7$	$1.6984 \cdot 10^6$
XSBR-CW70A	$2.5251 \cdot 10^7$	$3.9928 \cdot 10^6$

Table 7. Values of glass transition temperature for the different samples

Material	T_g [°C] of XSBR from DSC analysis
XSBR	10.0
XSBR_A	13.8
CW30	14.2
CW30_A	13.3
CW50	12.2
CW50_A	14.6
CW70	16.0
CW70_A	16.7

causes of increased resistance to indentation provided by the annealed, therefore temperature-aged, samples [30].

By subtracting the depth of nano-indentation at times between 50 and 200 seconds between the as-received and the corresponding annealed sample,

the results reported in Table 4 are obtained, which further clarify the trend observed above. In particular, the rubber matrix does not appear to depart from linearity for high times of loading, as it would have probably be the case for higher filler contents [31]. In addition, annealing at temperatures exceeding the XSBR critical temperature (glass transition of the styrene phase) does result in an easier cracking of the matrix after annealing (Figure 3), an effect which appears mitigated nevertheless by the introduction of progressively growing amounts of crab chitin.

The DMA results (reported in Figure 4 and Table 5) confirm that, as expected, the increasing content of filler in the polymeric matrix has the effect of rising the G' modulus in the entire temperature range. The $\tan \delta$ values for the different systems are almost the same, confirming the calorimetric observations. The amplitude in terms of ΔT of the $\tan \delta$ peak at the half of the maximum value, indicated as $\Delta T_{0.5}$ (reported in the last column of Table 5) slightly grows, even with the introduction of the lowest quantity of chitin.

The annealing treatment has a weak effect on the loss modulus profile, in the sense that only a small increase of the G'' values is obtained in the entire temperature range due to the resulting stiffening. For comparison, the storage and loss modulus values measured at $T = 25^\circ\text{C}$ are reported in Table 6.

DSC results, reported in Table 7, demonstrate that glass transition temperature T_g has a slight growth with increasing chitin content, and some less perceivable increase is also observed as an effect of annealing, which was justified by matrix stiffening. The calorimetric results suggest that the annealing at 100°C maintained for 90 minutes does only slightly modify the mobility of the polymer chains, even in presence of chitin nanoparticles.

TGA and DTG measurements (Figures 5 and 6) demonstrate that chitin addition does not substantially change the thermal stability of XSBR matrix: in other words, the annealing process does not have a large influence on the maximum weight loss rate. The presence of the degradation peak of the chitin is visible in the DTG profile as a shoulder of the main peak at $360\text{--}375^\circ\text{C}$ (depending on the filler content), while the peak due to the matrix degradation remains virtually unchanged. These results confirmed that the thermal stability of the system is

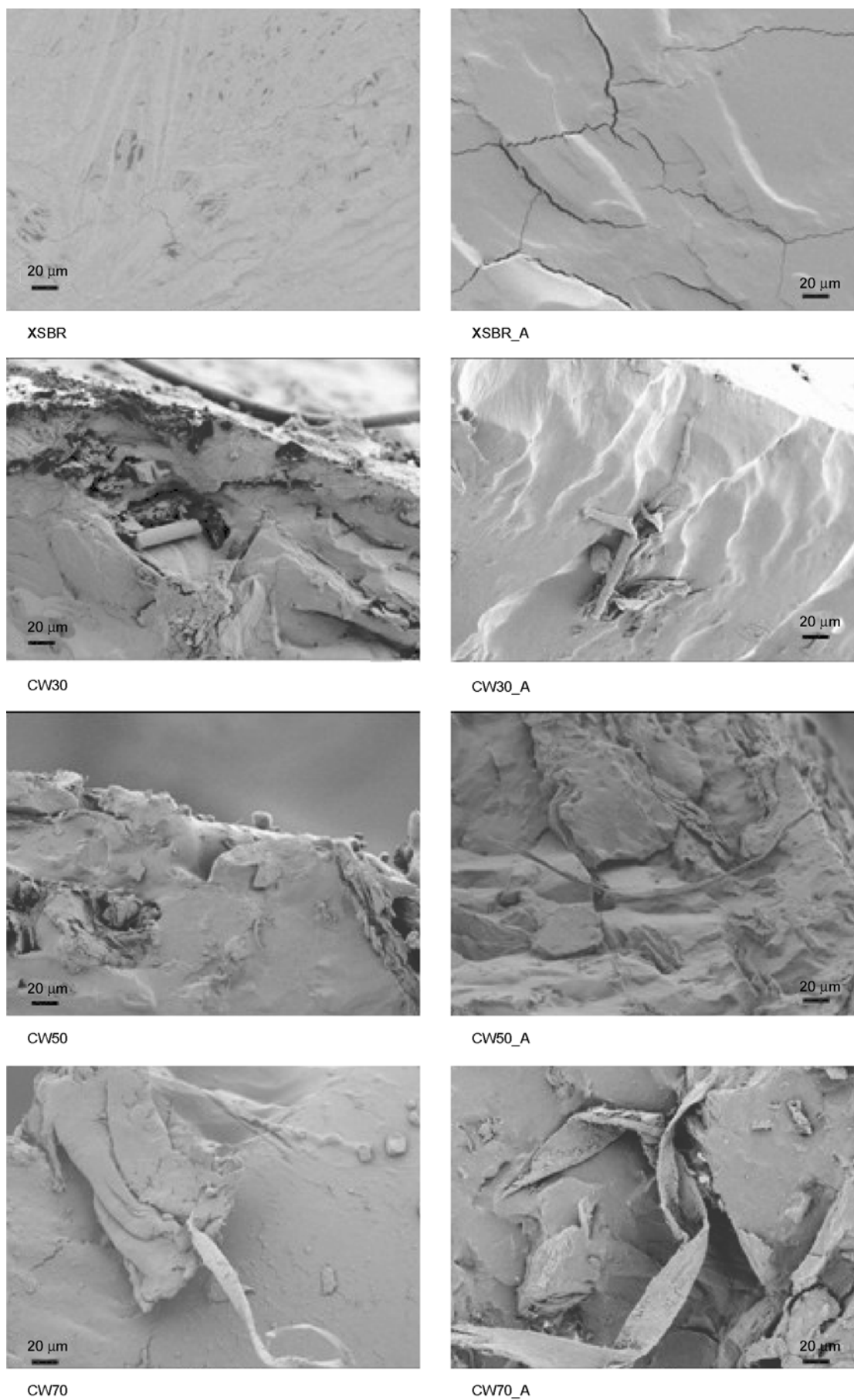


Figure 3. Comparison between as received (left) and annealed (right) SBR nanocomposites

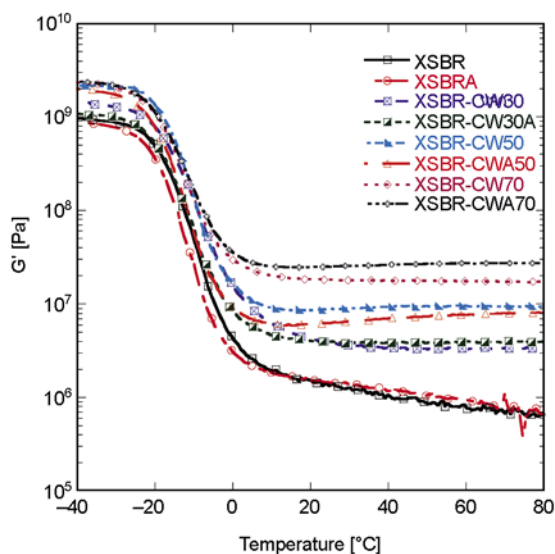


Figure 4. Storage modulus of the different samples

preserved, also with variable amounts of natural filler with thermally unstable behaviour. This can be considered as a positive outcome, since it demonstrated that the introduction of a natural filler, which is inherently thermally unstable, does not cause at these concentrations any change in the thermal stability of XSBR rubber.

Toluene absorption tests on as-received and annealed samples have also been carried out, with the idea of considering the durability of the matrix and its final application, which was discussed above. The selection of the solvent was done considering the matrix and its final application, not the filler. The sorption tests (Figure 7) demonstrate that the maximum weight gain is obtained for the unfilled XSBR matrix, while the decreasing slope in the curve

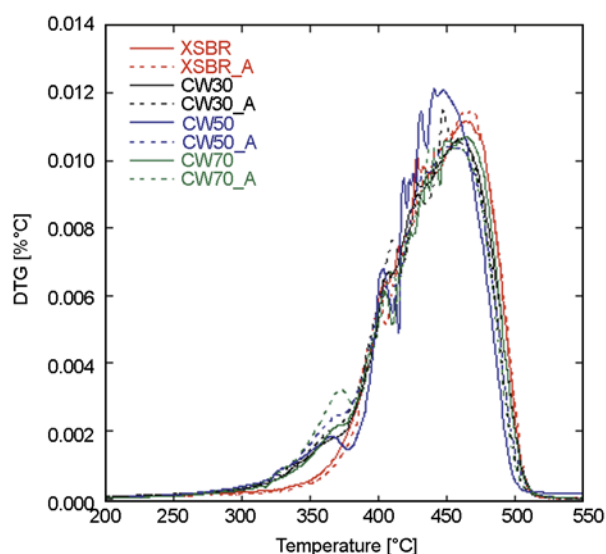


Figure 6. DTG of as-received and annealed samples

(weight gain vs time^{1/2}) is an indication of the effectiveness of the chitin as a barrier to the solvent uptake. In general, it has been shown already as XSBR samples filled with clay or silica micron-sized fillers showed reduced swelling rate owing to the tortuosity of the path [32].

The same result can be observed in experiment limited at 48 hours, point at which the systems start to lose their shape and going into solution due to the unvulcanized state of the rubber: the scattering of the different curves in Figure 7a is due to this condition. In particular, toluene absorption is decreased with growing chitin content in rubber. The larger effect is observed for the addition of the first 30%. The effect of annealing on this property appears to be not very consistent, apart from 70% samples,

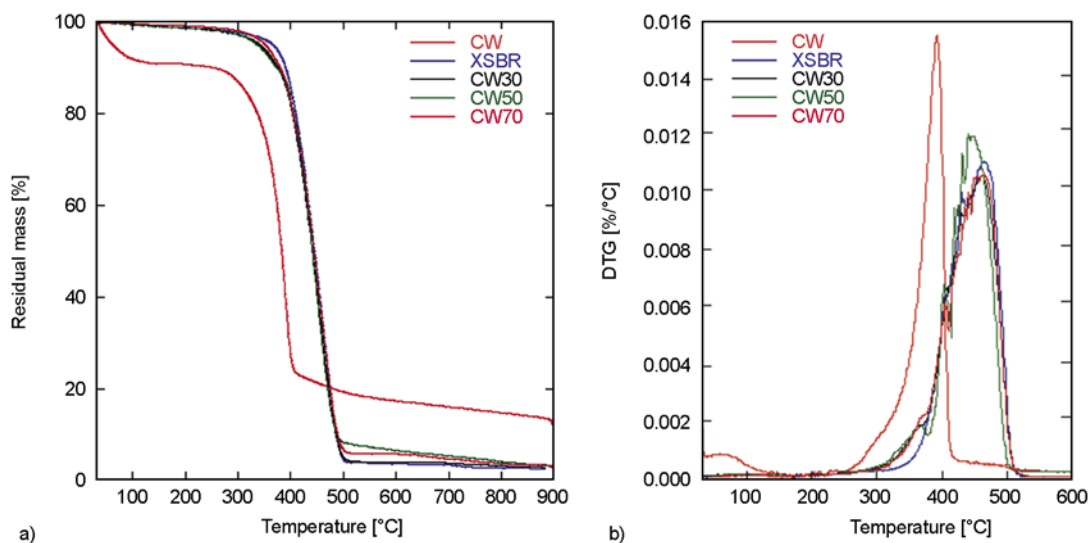


Figure 5. TGA and DTG results of as-received samples, compared with results from pure chitin (CW)

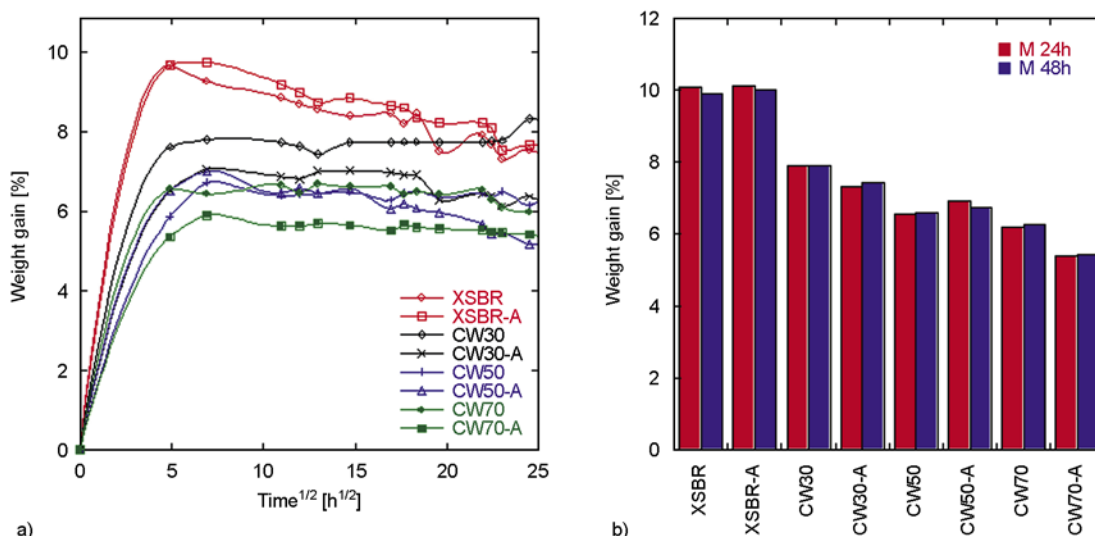


Figure 7. Weight gain during toluene absorption for 600 hours (a) and details of the comparison of 24 and 48 hours (b)

















Measurement time	M0	M48	Measurement time	M0	M48
XSBR57			XSBR_A		
CW30			CW30_A		
CW50			CW50_A		
CW70			CW70_A		

Figure 8. Aspect of samples before and after toluene absorption for 48 hours

where it may be due to reduced mobility of chitin filler, which does not allow allocating more solvent in the material. It is also noteworthy that the annealing does not ease geometry preservation during degradation due to toluene absorption (Figure 8). The morphological investigation of the samples by SEM (Figures 9 and 10) highlighted that the solvent absorption gives rise to an exfoliation of the rubber matrix, showing the weak interface between the XSBR and aggregates of chitin nanowhiskers, which have micrometric dimensions. This effect is not substantially worsened by the annealing treat-

ment (Figure 10), a finding that suggests once again that exposure to 100°C temperature for limited amounts of time does not significantly modify the properties of the material.

The observation of the chitin powder with the nanowhiskers was possible under AFM: this showed clearly the typical needle-like structure of the whiskers (Figure 11a) [33], while these are disposed non uniformly across the matrix (Figure 11b), a finding which may explain the aforementioned interface issues.

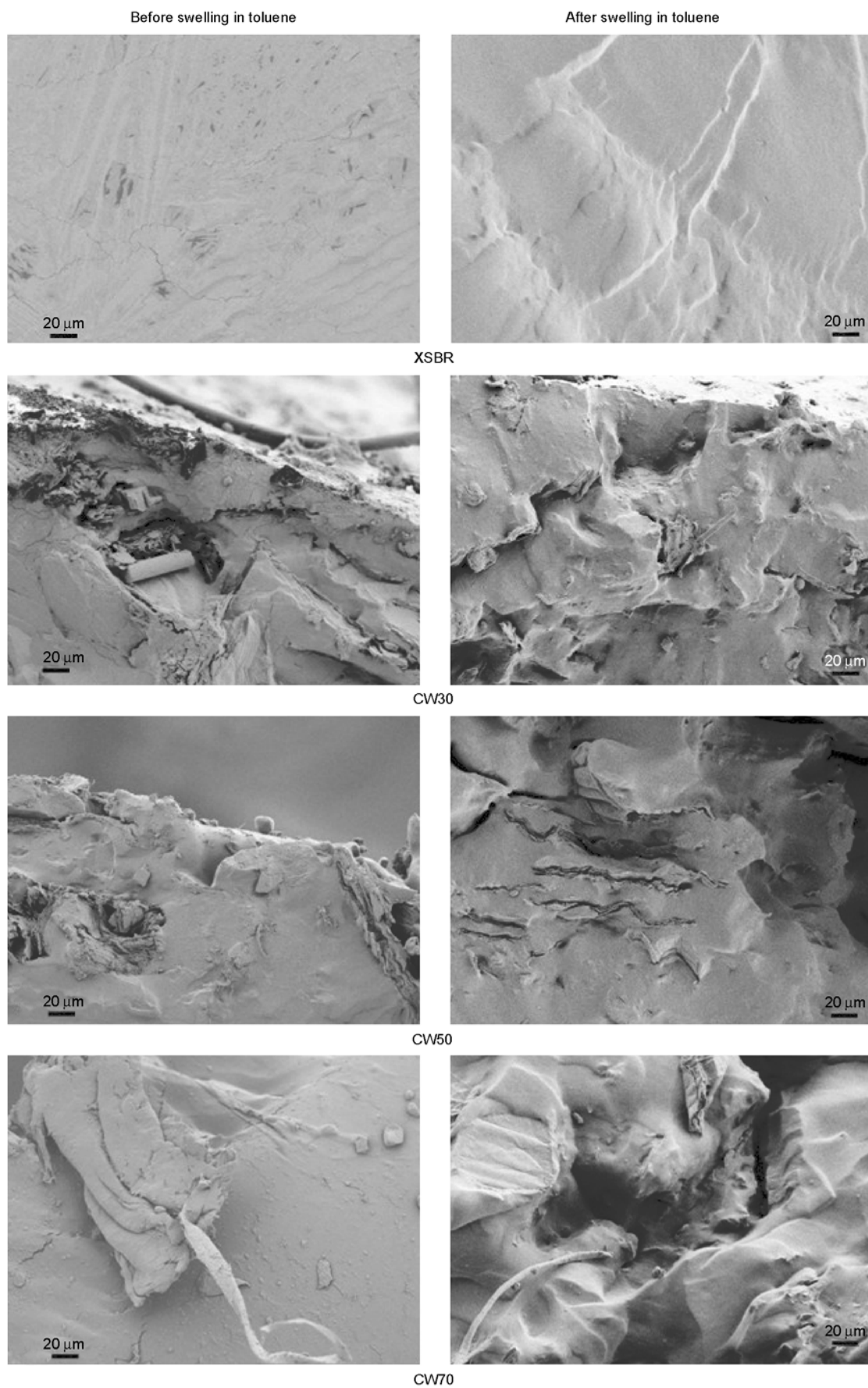


Figure 9. SEM micrographs of samples as received before and after toluene absorption for 48 hours

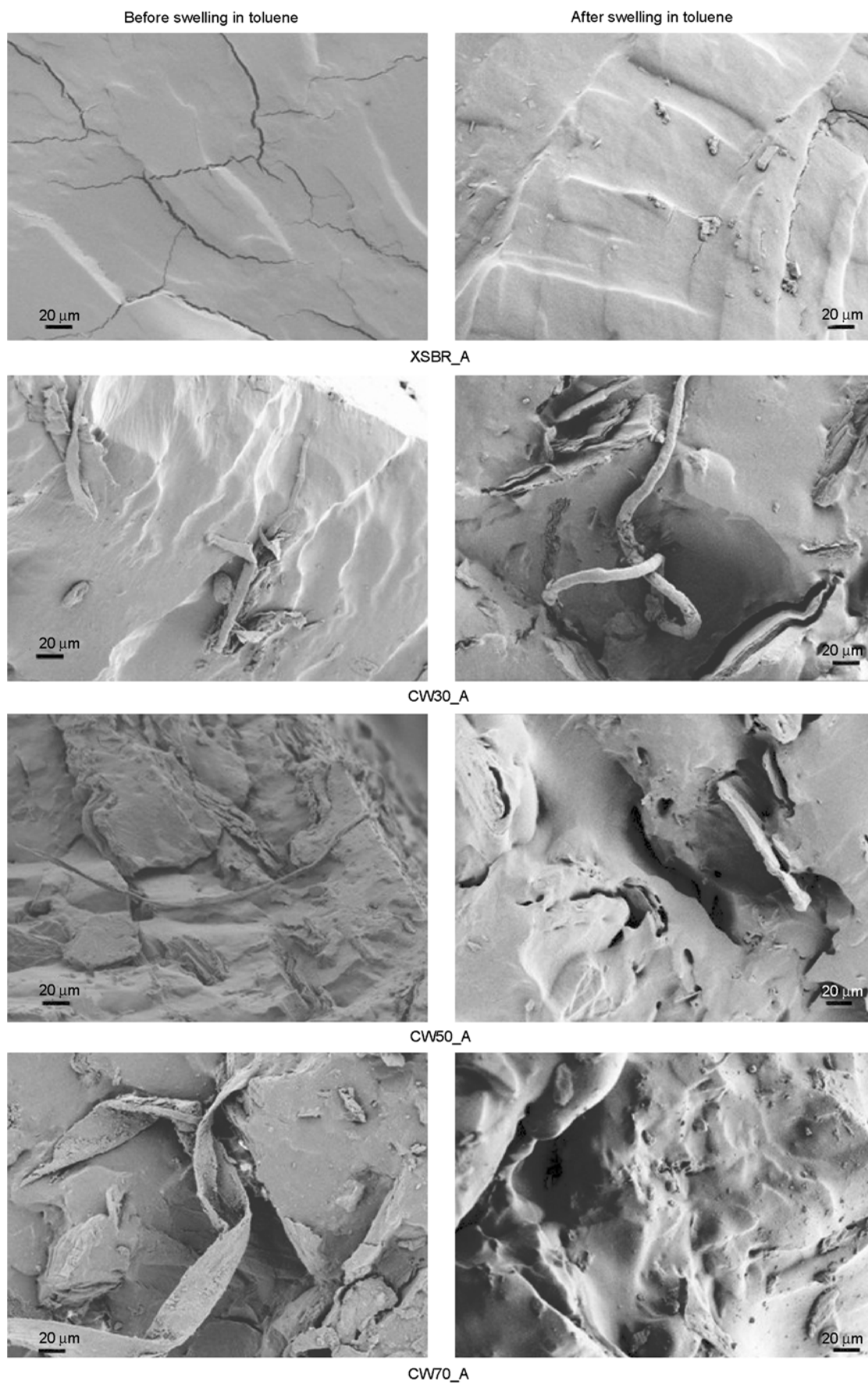


Figure 10. SEM micrographs of annealed samples before and after toluene absorption for 48 hours

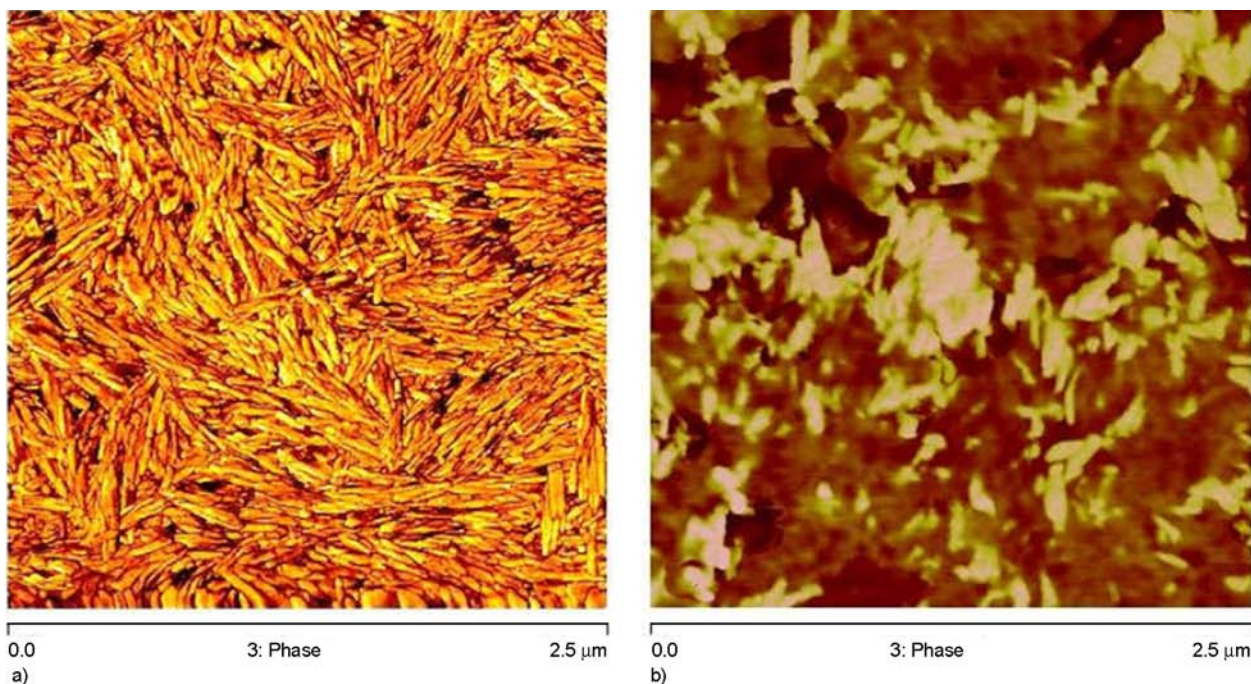


Figure 11. AFM imaging of: (a) a dilute suspension of nanochitin whiskers and (b) XSBR-CW50 (6.6 wt% chitin whisker nanocomposites)

4. Conclusions

This investigation was mainly aimed at evaluating the effect of the addition of small quantities of crab chitin from shellfish waste on the thermal, mechanical and morphological properties and swelling behaviour under toluene absorption of carboxylated styrene-butadiene rubber. A subsequent objective was also measuring the variation of the above properties as a consequence of annealing to 100°C, to give indication of the system resistance to service in the envisaged application (back coating for textiles and carpets).

The results show that crab chitin, also in very low amounts, offers some solvent barrier effect, while on the other side it does not substantially affect the thermal stability and the creep properties of the matrix. In addition, the system does not appear to be substantially modified by the exposure at high temperature for limited amounts of time, compatible with service needs (annealing was applied for 90 minutes).

This study can be suggestive for the investigation of the effect of introduction of different microsized fillers, originating from waste products, in this rubber matrix or in other similar blends.

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