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INVESTIGATION ON THE DISPERSION OF CARBON NANOTUBES IN NITRILE BUTADIENE RUBBER: ROLE OF POLYMER-TO-FILLER GRAFTING REACTION

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ABSTRACT

This contribution reports on the dispersion by simple melt blending of tiny amounts of carbon nanotubes (CNT) in Nitrile Butadiene Rubbers (NBR). Acrylonitrile (ACN) units of NBR are known to generate free radicals upon heating and/or shearing. This paper highlights elements evidencing a possibility for NBR polymer chains to react by a free-radical mechanism and to graft onto CNT surface all along the process of mechanical blending of NBR with CNTs. More precisely and since the formation of the free-radicals takes place on the ACN units, the influence of the ACN relative content in NBR on the grafted CNT amount has been studied. It comes out that the polymer grafting rate onto the CNT surface increases with the ACN content in NBR. Interestingly, the nanotubes proved more finely dispersed in NBR containing higher relative ACN content as evidenced by morphological observations as well as electrical measurements.

KEYWORDS: A. Carbon nanotubes, A. Nitrile butadiene rubber, A. Nano composites, E. Reactive processing, E. Grafting reaction

INTRODUCTION

Carbon nanotubes (CNTs) are fillers of choice for the conception of composites due to their exceptional thermal, mechanical and electrical properties [1]. Even if their physical properties are impressive, it appears difficult to obtain the expected reinforcement by their incorporation within polymeric matrices. Indeed the load transfer of the properties is highly dependent on the extent of both the distribution and the dispersion of these anisotropic nanofillers, which are rarely achieved. To improve the dispersion of CNTs in polymer matrices, different experiment methods have been investigated and mainly they both rely upon two strategies involving either the formation of covalent bonds or the establishment of non-covalent interactions between the polymer chains and nanotubes surface [2]. Melt blending, solution stirring, and coagulation methods commonly lead to “non-covalent” driven dispersion of CNTs. Surface and extremity functionalization but also *in-situ* polymerization most of the time enhance the quality of the nanotubes dispersion using these physical methods. The so-called “grafting to” and “grafting from” approaches involving (functionalized) CNTs are also known to lead to good nanofillers dispersion with the formation of covalent bonds between the nanotubes and polymer chains [2-5].

During melt blending, and depending on their chemical composition, polymers can be more or less altered due to thermo-oxidation and/or thermo-mechanical degradations. Such degradations generally involve the formation of free-radicals [6-8]. For instance, Zhang *et al.* have reported that free-radicals are generated on polystyrene

during its melt mixing [9]. As carbon nanotubes are known to readily react with free-radicals [10, 11], grafting of polymer chains onto the CNT surface could take place [12].

Nitrile Butadiene Rubber (NBR) is a random copolymer of butadiene and acrylonitrile. After vulcanization, it is used for the conception of tires, wires, joints,… Undoubtedly it represents a good candidate for the conception of CNT-filled/grafted NBR nanocomposites for several mean reasons:

- NBR degradation during the melt mixing process [13] leads to the formation of free-radicals on the polymer chains [14-16];
- high affinity between acrylonitrile groups (ACN) and CNT [17];
- no significant poisoning effect by CNTs on vulcanization process [18].

Accordingly, various NBR samples characterized by increasing content in ACN have been chosen for the production of conducting elastomer nanocomposites filled with multiwall CNTs surface-grafted by NBR chains. Firstly, we will highlight that the thermo-oxidative and/or thermo-mechanical degradation of the polymer taking place during the melt-blending process leads to the covalent grafting of elastomer chains onto the nanotube surface. Then we will show that the content in surface-grafted CNTs increases with the ACN relative content spread along the NBR chains. Finally, transmission electron miscroscopy (TEM) and electrical measurements will be approached for highlighting the effect of the ACN content on the extent of dissociation of the native nanotube bundles and the quality of the nanofillers distribution and dispersion throughout the NBR matrix.

EXPERIMENTAL PART

MATERIALS

The Nitrile Butadiene Rubbers (NBR) used in this study were kindly supplied by Lanxess, Germany. Three different grades were employed: Perbunan 1846, Perbunan 3445 and Perbunan 4456 containing different acrylonitrile contents, respectively, 18, 34 and 44 wt%. They were used without any purification or pre-treatment.

The carbon nanotubes (CNTs) (grade NC7000) are kindly supplied by Nanocyl, Belgium. They are non-purified Multiwall Carbon Nanotubes (MWNTs) used as received without any further purification.

Sulfur, stearic acid and zinc oxide (GoodYear, Germany) were used as vulcanization agents (see hereunder).

PROCESSING CONDITIONS

NBR/CNT composites were prepared using a two-step process. The components (*i.e.* NBR, CNTs and vulcanization agents, if any) were mixed simultaneously in a Brabender internal mixer. Typical compositions of the studied compounds are reported in Table 1. Except when indicated, all the compounds were prepared at 50°C for 10 minutes at 60rpm and were then vulcanized at 190°C under 50 bars for 15 min.

<Insert table 1>

CHARACTERIZATIONS

Thermogravimetric analyses (TGA) were carried out under He with a Hi-Res TGA 2950 device from TA Instruments with a heating rate of 20°C/min from room temperature to 800°C. The percentage of residual ashes (CNTs + carbonized NBR) was taken as the value reported at 530°C.

For "bound rubber" tests, each blend (typically 0.5g mixed with 10 wt% CNTs) was introduced in a glass tube containing a magnetic stirring bar. Approximately 30g of an equivolumic solution of $CHCl_3$/toluene were added to the blend sample, so that the NBR concentration was the same in every experiment. The mixture was placed under stirring at a controlled temperature (25°C) for 24 h. The tube was centrifuged (4000 rpm, 40 min), and the insoluble products (CNTs + adsorbed/grafted NBR) were filtered off and dried under vacuum at 70°C until mass stabilization. Then Q_{ads}, the mass of adsorbed polymer per gram of nanofiller was calculated. The experiment was performed 3 times for each compounds.

For swelling tests, each compound was introduced in at least 50g of toluene at ambient temperature. They were weighted after mass stabilization, typically after 48 hours.

TEM analyses were performed with a Philips CM100 apparatus using an acceleration voltage of 100 kV. Ultrathin sections of the composites (ca. 80 nm thick) were cut at −100 °C from 3 mm thick hot-pressed plates using a LEICA ultra-cryomicrotome equipped with a diamond knife.

Electrical measurements were performed in collaboration with Nanocyl using a Keithley 2700 multimeter. Samples are 8cm long, 1cm large and 3mm thick. Silver paint was used to provide good electrical contacts between the samples and the tips.

RESULTS AND DISCUSSION

I. COVALENT GRAFTING OF NBR TO CARBON NANOTUBES

I.1. Solubilization tests.

A way to appreciate basically if carbon nanotubes (CNT) are grafted by polymer chains is to perform preliminary solubilization tests on the polymer/CNT composites. Figure 1 represents two solubilization tests. The picture on the left (Figure 1(a)) corresponds to the reference, i.e., neat NBR is solubilized in $CHCl_3$ and CNT are incorporated in the solution, after a previous dispersion by sonication in chloroform. After magnetic stirring and centrifugation of the resulting solution, it appears that CNTs are non-solubilized and settle down in the glass tube, the supernatant being colorless. The same process is performed on a NBR/CNT composite prepared by melt blending as described in the experimental part. After centrifugation, the supernatant remains dark brown (Figure 1(b)). Most of the CNTs settle down again in the glass tube, but the intensive coloration of the supernatant reveals that part of them remains solubilized in chloroform, more likely as a result of polymer chain grafting/adsorption.

<Insert figure 1>

I.2. Thermogravimetric analyses (TGA) of the supernatants.

A way to estimate the quantity of CNTs effectively solubilized in choroform is to characterize the supernatants by TGA. For sake of comparison, unfilled NBR was first analysed under He flow. The degradation of NBR occurs around 500°C. Above this temperature, a residue, issued from the NBR carbonization under inert atmosphere, of 4.5% in weight of the initial mass (for a NBR sample containing 44 wt% ACN units) is

found. If CNTs are present in the analyzed compounds, an increase of the mass of the residue will occur (CNT do not degrade at this temperature range under He), which corresponds directly to the percentage in weight of (grafted) CNT (%CNT). Accordingly, TGA analyses have been performed on the dried supernatants and the resulting curve is reported on Figure 2. The increase of the residue mass (%CNT) is equal to 1.4 wt%, meaning that approximatively 45% of the initial mass of the CNTs are grafted to the elastomer phase.

<Insert figure 2>

As discussed in the Introduction, NBR is known to degrade during the melt blending step, leading to the generation of free-radicals on the polymer chains. Similarly to other polymers [9], we can assume that these free-radicals could lead to the grafting of NBR chains onto the CNT surface. Assuming this, three composites have been prepared following different processing conditions. The processing time and the rotation speed in the Bradender internal mixer are the parameters that could affect the degradation of the NBR. So they have been varied in order to tune the NBR degradation. These compounds have then been solubilized in $CHCl_3$ and after centrifugation, the supernatants were dried and analyzed by TGA. The corresponding curves are also reported on Figure 2.

For each compound, the percentage of CNTs is increased. For 3wt% CNT-filled rubber, the ashes mass rises by ca. 17 and 38 wt% with the increase of the rotation speed (from 60 to 100 rpm) and the blending time (from 10 to 20 min), respectively. As expected, the relative amount in grafted-CNTs is highly affected by the process

conditions and therefore the extent of both thermo-oxidative and thermo-mechanical degradations, i.e., the formation of free-radicals within the rubber phase.

I. 3. Influence of vulcanization agents on the amount of grafted-CNT.

The vulcanization of rubbers is a free-radical reaction. Sulfur decomposes in radical species, which mostly react in allylic position of the butadiene units of NBR. As NBR chains seem to graft onto CNTs via a free-radical mechanism, the (surface-grafted) CNTs could also take part to some pre-vulcanization occurring during the initial blending process. However, Raman analyses have shown that the vulcanization of natural rubbers is not or only slightly affected by the presence of Single wall CNTs [18]. Even though the authors did not report any significant effect of the nanotubes on the vulcanization rate of the elastomer matrix, this does not mean that further CNT grafting could be triggered by the presence of the vulcanization agents. To shed some light on the occurrence of those grafting reactions, TGA has been performed on the dried supernatant in chloroform of NBR/CNT composites melt processed in the presence of vulcanization additives but recorded before the final vulcanization step (Figure 3). The weight loss recorded at 530°C increases from 4.5 to 10.0 wt%. This increase might be attributed to the presence of the vulcanization agents but also to polymer-grafting onto CNTs. The vulcanization agents correspond to maximum 3.9 wt% of the mass of the compounds, meaning that a minimum of 1.6 wt% of CNTs could be considered as surface-grafted and solubilized in chloroform, i.e., embarked in the supernatant fraction. In the same experimental conditions, but without any vulcanization additives, the percentage of CNTs is at best equal to 1.4 wt%. In conclusion, it comes out that the presence of vulcanization additives does not impede

the grafting reactions onto CNT-surface and even seems to favor these free-radical reactions during the initial melt blending step.

<Insert figure 3>

I.4. Swelling tests.

The implication of CNTs during the vulcanization step can also be checked by swelling tests in toluene. Indeed, the polymer-grafting onto the nanotube surface is expected to affect the crosslinking density of the vulcanized nanocomposite materials. The number-average molar mass between the crosslinking nodes, noted $\overline{Mc}$, was calculated using the Flory-Rehner equation [19]:

$$\overline{Mc} = \frac{V_{mol}.(\mu/2 - \mu^{1/3})}{\ln(1-\mu) + \mu + \chi_{NBR/toluène}.\mu^2}$$

where V_{mol} is the molar volume of toluene and $\chi_{NBR/toluene}$ the interaction parameter between toluene and NBR (equals to 0.435 according to [20]). μ corresponds to the inverse of the swelling ratio, calculated from the following equation:

$$\mu = 1/(1 + d_{NBR}/d_{solvent}.(m_{swollen} - m_0)/m_0)$$

where d_{NBR} and $d_{solvent}$ correspond, respectively, to the density of NBR and toluene, and m_0 and $m_{swollen}$ correspond, respectively, to the initial mass and the swollen mass of the vulcanized samples.

<Insert figure 4>

Figure 4 displays the evolution of $\overline{Mc}$ values with the CNT content from 0 to 3 wt%. The increase of the filler content leads to a significant decrease of $\overline{Mc}$ attesting for the implication of the nanotubes in the crosslinking process. As schematized on Figure 5, it results in an increase of the cross-linking density of the vulcanized compounds and an overall decrease of the number-average molar mass between the crosslinking nodes, which can directly involve the nanotubes themselves.

<Insert figure 5>

I. 5. Intermediate conclusion.

During the melt blending of NBR with CNTs, the grafting reaction of some polymer chains onto the nanotubes surface has been evidenced. This grafting more likely results from the formation of free-radicals along the polymer chains as generated by thermo-oxidation and/or thermo-mechanical degradation mechanisms. Interestingly the vulcanization, i.e., a free-radical reaction, involves the CNTs reducing the number-average molar mass between the crosslinking nodes at higher nanotubes content. Since it is well accepted that both thermo-oxidative and thermo-mechanical degradations of

NBR chains take place on ACN units [14-16], it has been decided to study the effect of ACN relative content of NBR on the polymer-grafting rate in NBR/CNT blends.

II. Influence of ACN content on amount of grafted-CNTs.

II.1. "Bound rubber" tests.

Acrylonitrile groups and carbon nanotubes are known for their inherent affinity [17]. In that context, it can be assumed that during the blending process of CNTs with NBR, the ACN units spread along the elastomer chains tend to organize and localize preferentially around the nanotubes surface. Such a conformation should later facilitate the grafting reaction of the free-radicals generated preferentially on the ACN units of NBR.

"Bound rubber" tests are often used to check whether physical interactions are established between an elastomer polymer and a selected filler. This test relies upon the determination of the quantity of polymer adsorbed ($Q_{ads)}$ on the filler surface. Q_{ads} is calculated by using the following equation:

$$Qads = \frac{m_{driedresidue} - m_{NTC}}{m_{NTC}}$$

where m_{CNT} correspond to the initial CNT mass, and $m_{driedresidue}$ is the mass obtained after drying of the centrifuged residue (see experimental). Table 2 summarizes the results gathered for the three studied NBR, thus differing in their ACN relative content. Interestingly enough, a substantially higher quantity of polymer chains remains bound/adsorbed on the CNT surface when the ACN relative content in NBR is increased. For instance, Q_{ads} values of 1.7 and 3.3 are determined for NBR matrices containing 18 and 44 wt% ACN units, respectively.

<Insert table 2>

A larger quantity of CNTs appears thus bound to NBR containing higher ACN units, attesting for the expected interactions between the ACN units and CNTs. Moreover, these interactions stress the fact that ACN units are localized in the neighborhood of CNTs. Since ACN groups are highly prone to generate free-radicals by hydrogen atom abstraction, it can be assumed that their promiscuity to CNTs works in favor to the polymer-grafting onto the nanotubes surface.

II.2. TGA analyses

Solubilization tests have been again performed in chloroform starting from the three NBR-based composites containing 3 wt% CNT and differing by their ACN relative content. After centrifugation of the solution, the supernatants were dried before TGA analyses. TGA curves are reported on Figure 6. Figures 6(a) and 6(b) correspond, respectively, to the NBR matrices containing 18 and 44 wt% ACN units, filled or not with CNTs (3 wt%).

<Insert figure 6>

For each compound, there is an increase of the mass of the residue corresponding to the content of polymer-grafted CNT, thus solubilized in chloroform and embarked in the supernatant fraction (Table 3). Reducing the ACN relative content in NBR also leads to a decrease of the percentage of surface-grafted CNTs, shifting from 1.4 to 0.2%, respectively, for rubbers containing 44 and 18 wt% ACN units. In

conclusion, the more the NBR elastomer contains ACN groups, the more the CNTs in the NBR/CNT blends are surface-grafted. Such an observation might be explained by the relatively higher amount of free-radicals thus generated on the ACN groups and the affinity between the acrylonitrile functions and the nanotubes.

<Insert table 3>

III. Influence of the ACN relative content on CNT dispersion.

III.1. Morphological analyses by TEM

Cassagnau *et al.* [2] have previously reported that the grafting of polymer chains on CNTs leads to a better dispersion of CNTs within the corresponding polymer matrix. In NBR, the CNT grafting is monitored by thermo-oxidative/thermo-mechanical degradation of the elastomer chains and by the presence of vulcanization additives. Furthermore a larger quantity of CNTs is surface-grafted by NBR chains at higher ACN relative content. Accordingly, the ACN content might also affect the dispersion ability of the nanotubes into the NBR elastomer matrix.

<Insert figure 7>

TEM micrographs reported on Figure 7 correspond to the three studied NBR-based composites differing by their acrylonitrile content and filled with 3 wt% CNTs. Figures 7a, 7b and 7c display, respectively, the matrices containing 18, 34 and 44 wt% ACN units. It is worth pointing out that these three composites were prepared by melt-blending without any vulcanization additives.

As far as the NBR matrix containing the lowest ACN content (18 wt%) are concerned, it appears that the CNT are still agglomerated under the form of bundles heterogenoulsy distributed throughout the matrix. Increasing the relative content in ACN units leads to better desagglomeration of the nanotubes, which start to form percolation ways in the elastomeric matrix. It is noteworthy that the Mooney viscosity of each compound remains very close to each other and can not be taken into account to explain the improvement of the dispersion of the nanotubes. According to the supplier, the Mooney viscosities are equal to 45, 45 and 55 ±5 Mooney respectively for the NBR matrices containing 18, 34 and 44 wt% ACN. TEM pictures (not all shown here) prompted us to conclude that CNTs are more finely distributed and dispersed within the elastomer matrix when the NBR chains are enriched in ACN.

The presence of the vulcanization agents (S, ZnO and stearic acid) does not seem to reduce the dispersion ability of the surface-grafted CNTs (Figure 7(d)). On the contrary and even if it is quite difficult to quantify from the TEM picture, one can even assume a better dispersion of the individualized nanotubes.

III. 2. Electrical properties

Larger disaggregation of CNT bundles and more intensive nanotube dispersion in NBR matrices with higher ACN relative content should favor the formation of a percolation network and likely reduce the electrical percolation threshold. Electrical measurements have thus been performed in order to check the evolution of the electronic conductivity of the vulcanized (nano)composites, in function of both their ACN and CNT contents. The evolution of the electrical conductivity for each composite is presented in Figure 8. There is a clear trend of a percolation threshold increase when

NBR with lower ACN content are used, in agreement with the morphological analysis reported above.

<Insert figure 8>

CONCLUSIONS

Vulcanized NBR/CNT-based nanocomposites have been readily produced by a two-step process involving a first melt blending step in a Brabender internal mixer and then sulfur-curing. It was shown that during the blending process, the polymer chains are grafted onto the CNT surface via a free-radical mechanism. Indeed, NBR generates free-radicals from its ACN units upon heating and/or shearing. As a result of the high inherent affinity between the CNTs and ACN units, and due to the formation of ACN-based free-radicals leading to NBR-grafting on CNTs, increasing the ACN relative content along NBR chains triggers higher polymer grafting on the nanotube surface. As a result, it has been shown by both electrical measurements and morphological analyses that the CNT bundles are more intensively disrupted and the individualized nanotubes more finely dispersed in NBR at higher ACN relative content.

As the process conditions monitor the polymer grafted rates, they also affect the properties of the materials. In a forthcoming paper, the effect of experimental conditions on the properties of the NBR elastomeric matrices filled with (surface-grafted) nanotubes and the possibility to tune them up will be reported.

Acknowledgments

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Captions for Figures and Tables

Figure 1. Pictures of (a) CNTs and NBR mixed in $CHCl_3$ and (b) a NBR/CNT composites prepared by melt blending and then solubilized in $CHCl_3$.

Figure 2. TGA curves of the supernatants in $CHCl_3$ of different melt processed NBR/CNT composites (as recovered before the consecutive vulcanization step).

Figure 3. TGA curves of the supernatants in $CHCl_3$ of NBR/CNT composites prepared by melt blending with or without vulcanization additives (as recovered before the consecutive vulcanization step).

Figure 4. Number-average molar mass between the crosslinking nodes ($\overline{Mc}$) of NBR/CNT vulcanized composites in function of the CNT content.

Figure 5. Schematic representation of the CNT implication in NBR crosslinking process.

Figure 6. TGA curves of the supernatants in $CHCl_3$ of NBR/CNT composites differing by their ACN content.

Figure 7. (a) to (c) TEM pictures of NBR/CNT composites in function of their acrylonitrile content. (d) TEM pictures of a 44% NBR based vulcanized composites.

Figure 8. Electrical properties of NBR/CNT composites in function both of their acrylonitrile and CNT contents.

Table 1. Summary of the %CNT grafted to NBR in function of the melt blending experimental conditions.

Table 2. Bound rubber tests performed on three NBR, differing by their ACN content.

Table 3. Summary of the %CNT grafted to NBR in function of the ACN relative content of the rubbers (initial CNT content in NBR composites: 3 wt%)

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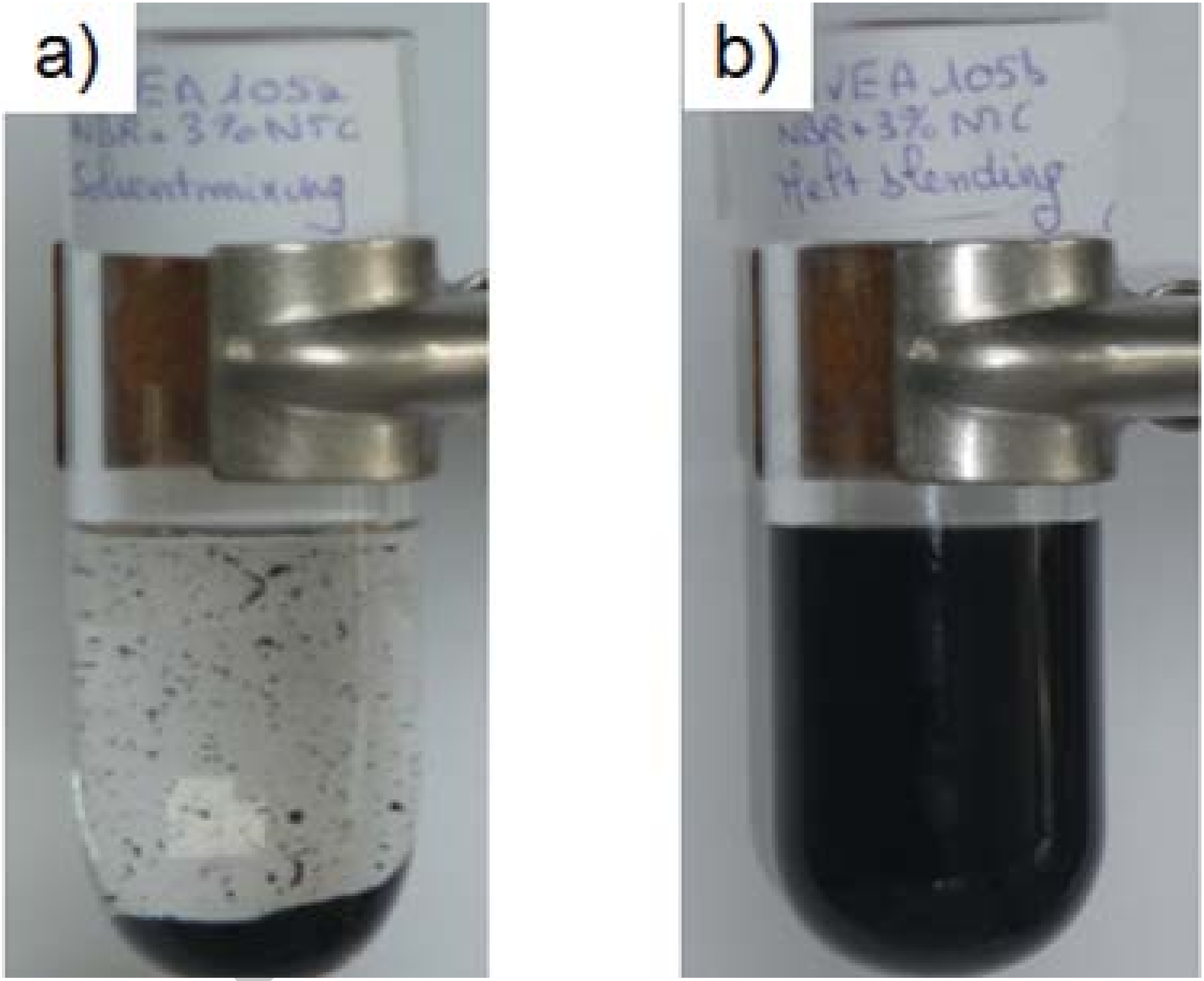
Coumpounds	phr
NBR	100
CNT	3(wt%)
S	2.4
ZnO	3
SA	2

ACN content (wt%)	18	34	44
$Q_{ads}1$ (g_{NBR}/g_{CNT})	1.9	2.9	3.1
$Q_{ads}2$ (g_{NBR}/g_{CNT})	1.3	3.3	3.4
$Q_{ads}3$ (g_{NBR}/g_{CNT})	1.9	2.3	4.3
$Q_{ads}^{average}$ (g_{NBR}/g_{CNT})	1.7	2.8	3.3
ΔQ_{ads} (g_{NBR}/g_{CNT})	0.3	0.5	0.2

ACN content	18wt%	34wt%	44wt%
CNT grafted wt%	0.22	0.88	1.38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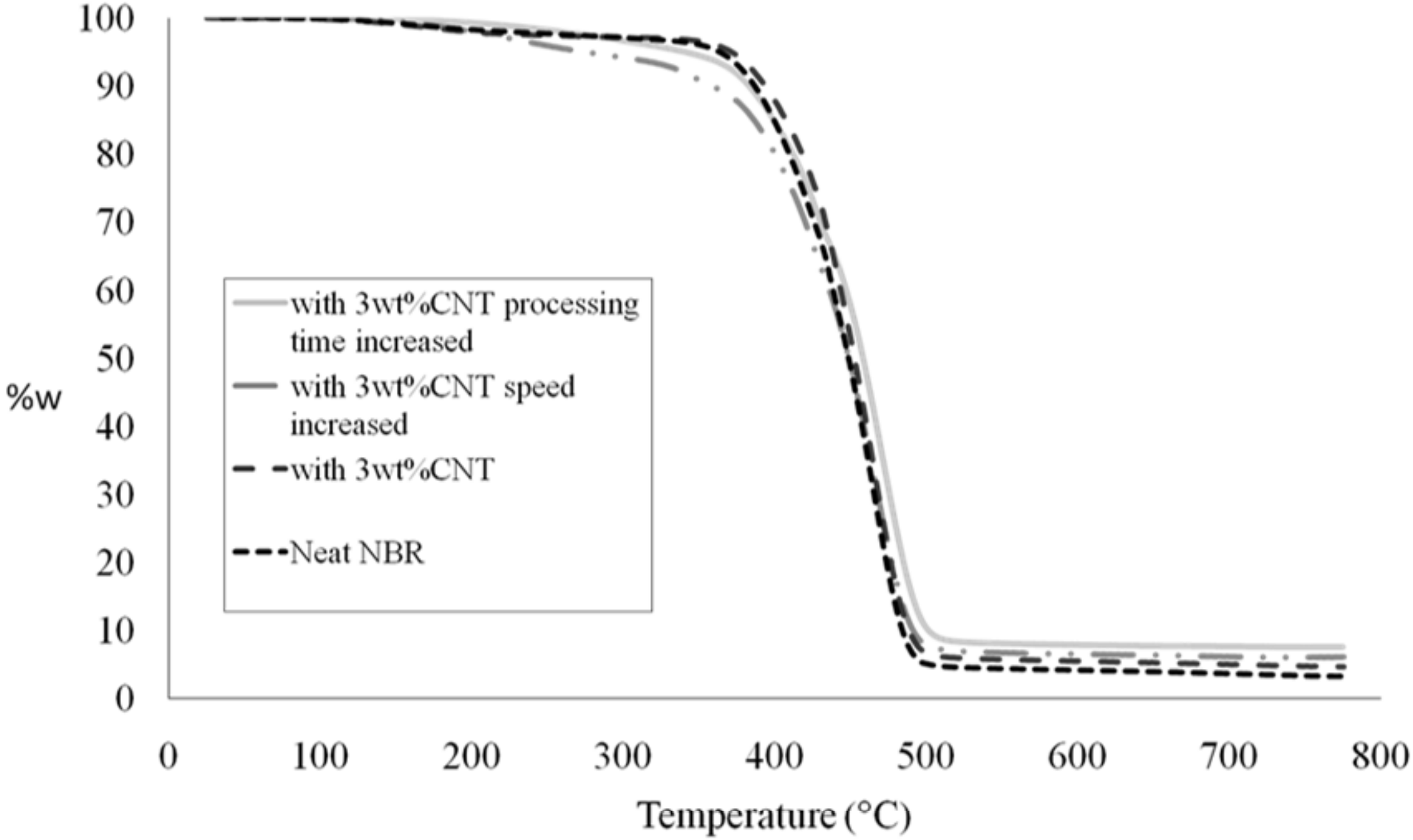

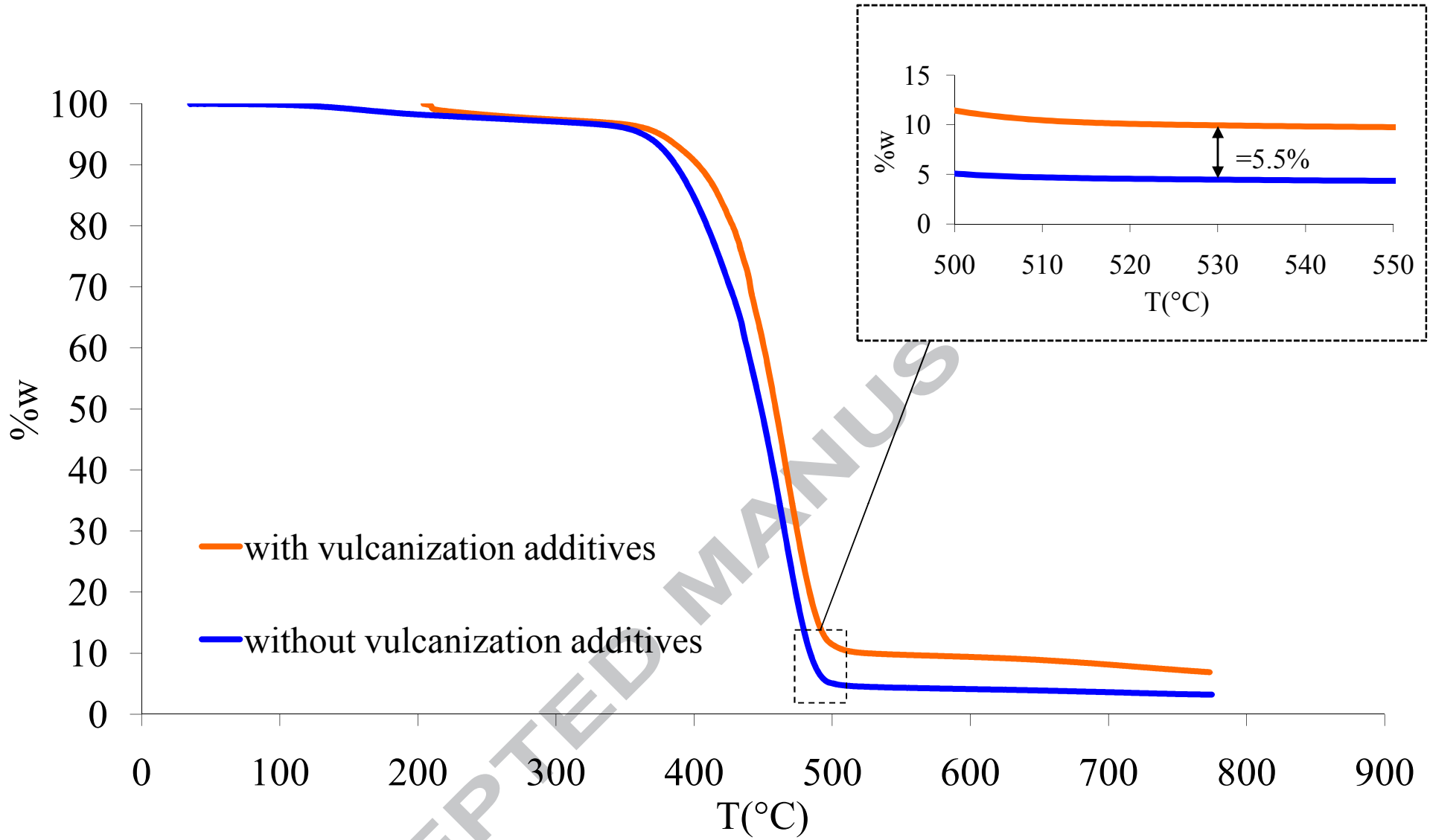

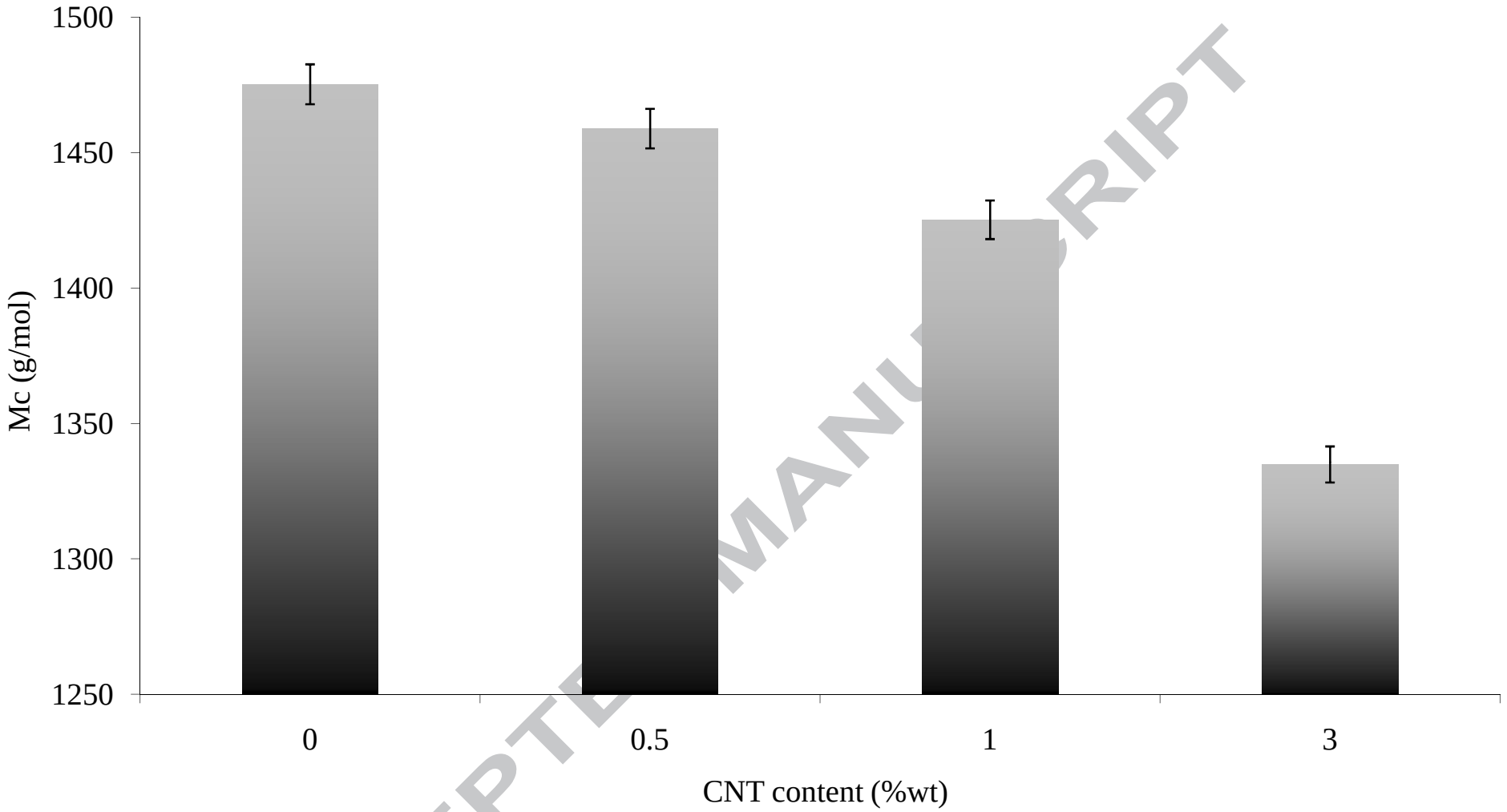

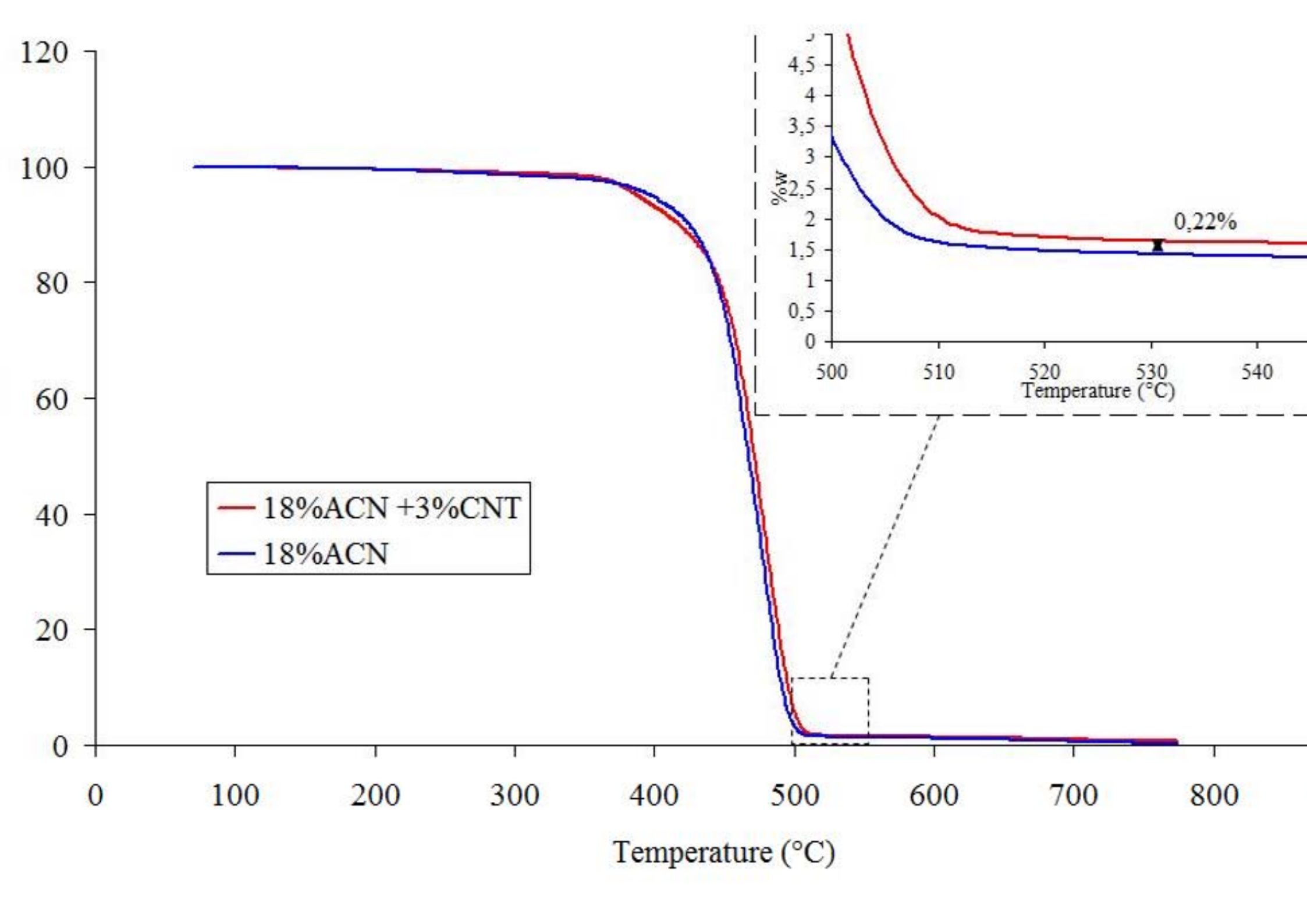
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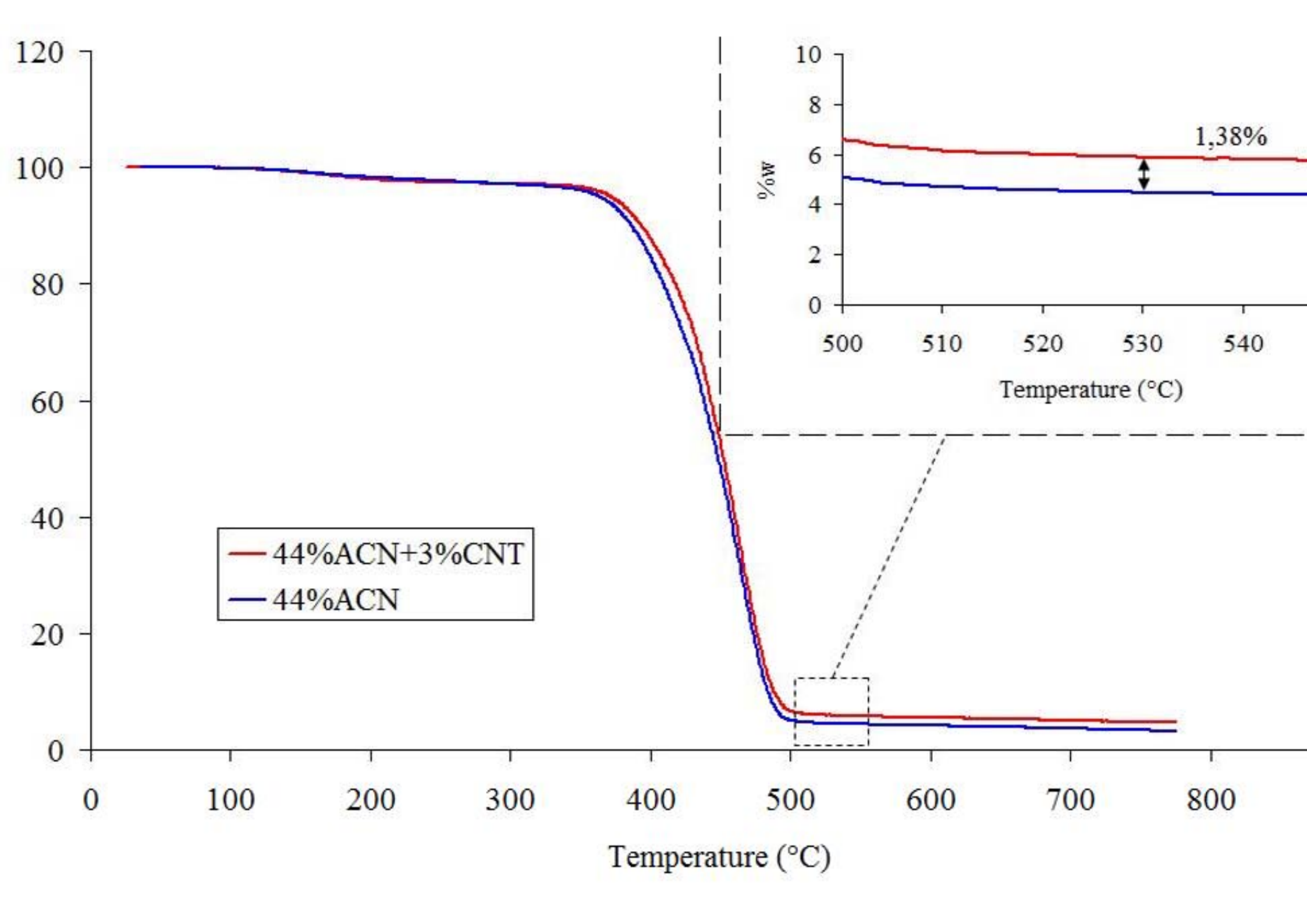
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8
6
4
2
0
%W
1,38%
500
510
520
530
540
Temperature (°C)