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Reply to Comment on "Monitoring Network and Interfacial Healing Processes by Broadband Dielectric Spectroscopy: A Case Study on Natural Rubber"

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Abstract: Das *et al.* comment our publication on the use of broadband dielectric spectroscopy as a potential tool for monitoring healing processes in natural rubber. They argue that our interpretation of self-healing processes should be handled with care and that critical issues like rubber tackiness and sample fabrication for dielectric experiments were not properly addressed. We agree that tackiness in partially cured rubber does exist and that interpretation of dielectric experiments requires detailed insight into both the processes and the method, but we will try and re-argue below the correctness of our approach as reported in our publication.

Keywords: self-healing, natural rubber, polymer network, tackiness, dielectric properties

Das *et al.*¹ indicate that the "tackiness" behavior of long chain polymers might not be fused with the "self-healing" term. We fully agree that tackiness and self-healing should not be regarded as the same phenomenon. Yet, in intrinsic healing polymers the first is a must for full macroscopic healing to occur, as also stated by other scientists not involved in the present discussion.²⁻³ It is generally accepted that the overall macroscopic healing process in intrinsic healing polymers consists of three main stages:⁴⁻⁵ (i) 2D interface (self-adhesion); (ii) 3D interphase (long range diffusion processes at relatively short times); and (iii) randomization (homogenization at long time scales). At this point it should be noted that the complete randomization is only demonstrated if fracture does not re-occur at the prior damage site. The process of an interface/interphase formation involves short range physical and/or chemical interactions and molecule/chain inter-diffusion. Such processes are possible in both crosslinked and non-crosslinked polymers and lead to the macroscopic mechanical phenomenon recognized as (self-)adhesion reflected in a low or high bonding energy depending on the level of interaction/diffusion achieved. The term "tackiness" coincides with such processes and definition, although it is traditionally applied to the elastomers field alone. Thus, in our opinion polymers showing partial healing having reached the interphase formation (tackiness) can therefore use the term "healing" provided it is clearly stated that only partial healing is obtained, as we reported in our manuscript.⁶

In the specific case of elastomers, we, Das and many other authors agree that "tackiness" is present in all non-cured NR, and has been recognized as the first step for achieving self-healing. Interestingly this term has also been applied in the case of lightly crosslinked NR and ENR containing different reversible moieties and reactive points for irreversible crosslinking.^{3, 7-8} In line with this discussion, Das *et al.* state that their peroxide (DCP) cured NR compound recovers its mechanical strength at low strains. Notwithstanding the potential issues related to the remaining activity of the DCP, they consider that this recovery is nothing but the reflection

of the tackiness of the rubber. Indeed, we fully agree with this. From a healing terminology, and following our exposition above, the DCP-NR has partially healed (interface/interphase formation). The question remaining is related to the type of underlying processes that took place in the cases of discussion: short range interactions vs. some sort of polymer chain diffusion. To elucidate this point detailed spectroscopic and mechanical testing would be required, yet, some indications can be given based on previous works.⁹⁻¹⁰ With very low recovery of the strength and strain before mechanical failure it can be stated that the healing process does not go beyond the stage of interface formation related to short range interactions. Nevertheless, the samples presented in our work and that of Das *et al.* show some recovery of the mechanical properties beyond relatively low strains (at the measured crosshead speeds). This indicates there is a significant load transfer from the damaged/repaired zone to the bulk thereby leading to higher deformation (higher strains) before failure. This allows debating if the second stage of healing (interphase formation) has been reached, allowing claiming partial healing. Based on the fracture results we showed in our first manuscript⁶ one cannot conclude that only the first healing stage was reached (self-adhesion). At this point it should be noted that the results we report in the commented manuscript⁶ were obtained by locally analyzing the healed region by means of a fracture mode test, rather than the more commonly used stress-strain tensile testing. In fracture mode, the loads are localized at the fractured and healed plane while in tensile mode the loads, and therefore deformation, are distributed along the sample until final failure. This is a critical difference as it allows evaluating self-healing polymers more accurately as well as defining the transition between stages more easily. It should be noted that we also demonstrated in previous works that fracture and rheology, when properly combined, can be extremely powerful tools to even separate the contribution to macroscopic healing of different phenomena such as interfacial hydrogen bonding (short range interaction/adhesion) and molecular diffusion responsible for the different healing degrees as function of healing time.¹¹ This was also demonstrated for a disulfide crosslinked poly(urea-urethane) elastomer which is of different nature to the NR studied in^{6, 12} but containing similar type of reversible bonds.^{11, 13} Finally, we fully agree with Das *et al.* that not all systems showing tackiness can actually reach high healing degrees, but this was not our point and has not been suggested in any of our papers.

Another point of concern by Das *et al.* relates to our interpretation on the underlying mechanism responsible for the ‘healing’ behaviour observed. In their comment Das *et al.* state that till date there is no firm evidence to establish reversible disulfidic mechanisms as responsible for the self-healing nature of rubber matrices (uncrosslinked or lightly crosslinked). Their statement is in disagreement with many publications by us and others on this topic.^{7, 13-16} In the companion paper to the paper being discussed,¹² Electron Spin Resonance (ESR) was used to prove the temperature-driven formation of sulfur radicals with the healing temperature and its disappearance when cooling (reforming the disulfide bridges). The breakage of the disulfide bridges during the healing process allows for a substantially higher mobility than in a partially crosslinked polymer with irreversible crosslinks. Similar results demonstrating a temperature-driven sulfur radical reactions ($S-S \rightleftharpoons S^{\bullet} + S^{\bullet}$) were also obtained for other disulfide based healing systems.¹⁷⁻¹⁸ Despite the clear indications pointing at the radical formation followed by radical re-association controlling the healing process we agree that more dedicated research would be beneficial.

Das *et al.* also express their doubts about the clarity of our dielectric measurement protocol and sample fabrication to quantify macroscopic healing. In our measurements, the upper electrode acts on the whole flat surface and not only on the damaged area. The damage area is perpendicular to the contact disks. The collected dielectric spectrum represents the average of all chain motions in the sample being highly susceptible to heterogeneities, which is what

damages and healed zones are. In fact, in the case of macroscopic damages such as cuts, the presence of contact discontinuity (air gaps between the two cut faces or even after the so-called adhesive/tack taking place) inhibits the completion of the dielectric measurement as we stated in our manuscript.⁶ To further support the measurements and interpretations in the same manuscript we reported similar dielectric behaviour regardless the type of damage, *i.e.* macroscopic cuts and network damage by straining cycles, as well as repeated the measurements at least two times. BDS is therefore a technique to evaluate if some sort of interphase restoration has taken place (requiring some chain interdiffusion). At this point we can indeed discuss if the technique is suitable for quantifying healing degrees (*i.e.* percentage of healing) or if it must be considered an on-off test. We agree that for this to be answered more dedicated studies are necessary.

In terms of interpretation, Das *et al.* suggest that the different results between the pristine and healed samples could be an effect of the microstructure of the rubber chains due to unavoidable crosslinking, aging and/or degradation of non-rubber components or proteins of the natural rubber. Interestingly, we did address this point in our manuscript.⁶ We indicated that such differences could be due to the formation of an heterogeneous network structure at the healed interface (with respect to the bulk) in the case of the macroscopic cut, or due to a change in the bulk architecture of the strained and healed sample, or/and due to further crosslinking of the bulk polymer. Of these options, two relate to healing processes and one relates to unwanted crosslinking. To discard the effect of the last one governing the healing process we reported the results and analysis of pristine (non-damaged) samples subjected to the same healing thermal treatment. The results suggest that no detectable further cross-linking took place under the selected thermal healing conditions.⁶ We do not deny that the “unavoidable crosslinking process” Das *et al.* comment will indeed take place, as we also reported in our follow up manuscript¹² in relation to the loss of healing efficiency in NR by disulfide exchange. Yet, these processes cannot be considered as the origin for the different dielectric results between pristine and healed samples which are more due to the formation of a healed region architecturally different to the bulk material (an heterogeneity). Unfortunately, Das *et al.* missed our second publication when submitting their ‘comment’.

Das *et al.* consider that the dielectric analysis we presented is an over-interpretation of the dielectric behavior of self-healing rubber compounds. They tried to illustrate this with an example stating that the dielectric behavior of sulfur cured nitrile rubber (NBR) changes when cured at different times. Indeed, the dielectric behavior changes with curing, as we also showed in our studies. We give strong evidences on how dielectric parameters such as dielectric loss, dielectric strength, shape parameters and relaxation times change with curing degree. Unfortunately, the example shown by Das *et al.* obviates several aspects due to its analysis simplicity. The interpretation of the results of the dielectric behavior of the pristine, damaged and healed NR compounds presented in our research is more systematic than the not fully appropriate case presented by Das *et al.* Nevertheless, we agree that it is too early to make an undebatable statement about the use of BDS to evaluate the healing state or degree of polymers. In our original manuscript⁶ we already stated that more dedicated work is needed to demonstrate the potential of BDS to capture the degrees of healing but we are happy to repeat it here.

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