Major Properties & Characteristics of Shape Memory Natural Rubber - A Critical Review

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***Abstract*- This paper aims at giving a detailed and critical overview on the major properties and characteristics of shape memory natural rubbers. The critical review enhances our knowledge over the storage strain, shape memory parameters, energy storage capacity, cold storage capacity, tunability, solvent sensibility, solvent aided programming and blended capacity of shape memory natural polymers. this detailed report over the major characteristics and properties of shape memory polymers shall surely help the scholars who are working in this field.**

***Index terms*- Shape memory, Mechanical Properties, Natural rubber**

I.INTRODUCTION

Natural rubber (NR) is a renewable raw material which is drawn from rubber trees in amounts of 10 million tons per year. Charles Goodyear developed a cross-linking process, referred to as vulcanisation, which transfers this sticky substance to an elastomeric material. Since the properties of cross-linked NR are broadly variable depending on the degree of cross-linking, NR is applied in many products; mostly tires. Despite great efforts, replacement of NR by synthetic industrial products is not possible up to now. This is due to the fact that no other elastomer is capable to support large stress up to 30MPa at strains of many 100%.

NR is amorphous at room temperature and forms crystals only upon strain, causing the observed self-reinforcement effect[1]. When releasing the stretching force the crystals vanish and the rubber restores its original shape. Over the last 80 years, nucleation and growth of the strain-induced crystals was explored in countless theoretical as well as experimental works using transmission electron microscopy (TEM), small- and wide-angle X-ray scattering (SAXS/ WAXS) while being stretched[2]. All the more surprising is that such a long known and extensively studied material is able to fascinate nowadays with completely new and unexpected properties.

In searching for innovative materials with new property characteristics, we follow the concept of cross-linking high polymers at the critical degree of cross-linking. This allows the polymer material to retain its properties in the molten state, but also offers the possibility to keep the macromolecules in a constrained, stretched state for unlimited time. [3]Due to the prevention of flow the stretched macromolecules cannot relax as they do in a typical polymer melt. This is important because self-organization of elongated polymer chains is often slower than relaxation processes. This way, we expect to imprint new properties into materials that are based on self - organization of stretched polymer chains with- out time constraint due to plastic deformation.

To this end, high polymers with interesting properties are chosen and chemically cross-linked with varying cross- linking densities. The resulting material is then investigated with dynamic mechanical analysis for determining the Young’s modulus in dependence on temperature. Figure 1 depicts an idealized graph, showing that the material with the critical cross-linking density acts like the melt but does not yield.

This experiment was applied to NR. The resulting lightly cross-linked material is surprisingly not a classical rubber but a material that is capable to respond and adapt to its environment in many ways. It is called shape memory natural rubber (SMNR) and its amazing properties are reviewed in this article.

II. PROPERTIES

2.1 Shape Memory of Lightly Cross-Linked NR

A shape memory polymer (SMP) is typically programmed by heating it above a certain temperature, called the trigger temperature Ttrig, brought into a new shape, and subsequently cooled below Ttrig to fix this new shape. This requires that the respective polymer has a glass transition temperature above ambient temperature or is partially crystalline at ambient temperature. NR lacks both prerequisites and should not be a SMP at all.

However, if lightly cross-linked NR is quickly stretched and kept in this state for several seconds it does not fully recover its original state. The material retains parts of its strain,[4] so it looks like the material is worn out. However, when applying just body heat to the stretched material by taking it into a fist, it fully recovers its original state. Thus, lightly cross- linked NR—referred to as SMNR—is indeed a SMP that can be programmed below its trigger temperature without plastic flow.In contrast simple stretching of a semi- crystalline polymer below its melting point results in only partially recoverable, mostly plastic deformation. This makes SMNR the first SMP that can be cold-programmed by simple stretching without any heat treatment.

This is possible, because NR is amorphous at room temperature in a relaxed state and can crystallise only upon strain (SIC). Typically, strain-induced crystals that are formed in such rubbers are unstable at room temperature and vanish when the stretching force is released. Only the cross-linking of NR right at the borderline between thermoplastics and elastomers allows formation of crystals upon strain that are sufficiently stable at room temperature to fix the network in a state of high elongation.

Commonly used NRs are for mechanical reasons higher cross-linked (degree of cross-linking X>1%). This might be the reason why the shape memory effect of this natural material was undiscovered for such a long time. Systematic studies showed that the trigger temperature of SMNR increases above room temperature whenever NR is cross- linked below a critical degree of cross-linking of Xc < 0.4%.

2.2 Storable Strain And Shape Memory Parameters

In general every polymeric material with Tg or Tm above room temperature is an SMP. Programming of non–cross- linked high molecular weight polymers is an application tool for disposables and results in partial recovery only. Full recovery is required for applications that depend on reversible and defined shape memory. This is only possible for cross-linked systems. Only a few SMPs are able to store fully recoverable strains significantly above 300%, being radiation cross-linked PE and a specific polyacrylate system.43 Due to its lightly cross-linking, SMNR is a candidate that might be capable to store extremely large strains. As expected, the effective amount of stored strain Ɛstored mainly depends on the degree of cross-linking of SMNR. The highest value was found to be Ɛstored = 990% for SMNR having a degree of cross-linking of 0.12%. SMNR with lower degrees of cross-linking plastically flows during programming and thus no full recovery of the original shape is achievable.

Figure 2 shows the development of stored strain over 10 shape memory cycles for differently cross-linked SMNRs programmed at a temperature of 20 8C as well as 80 8C.44 As seen, the programming temperature only slightly affects the maximally storable strain.

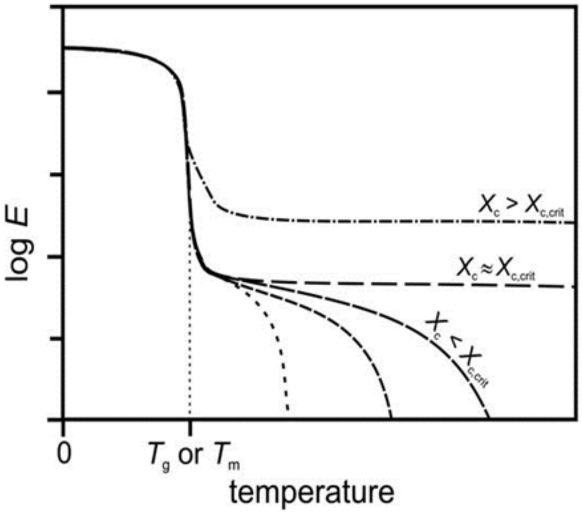

FIGURE 1 Cross-linking at the borderline between elastomer and thermoplastic material, illustrated with a classical log E versus T plot. [2]

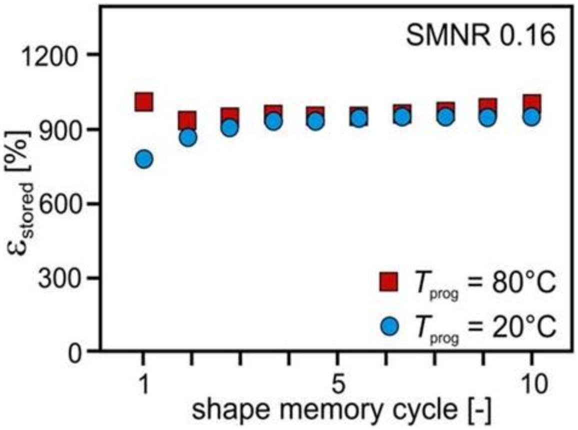

FIGURE 2 Stored strains Ɛstored for differently cross-linked SMNR programmed at temperatures of 20 8C and 80 8C [2]

Besides the maximally stored strain, also the fixity ratio Rf as well as recovery ratio Rr were determined over 10 shape memory cycles. Depending on the degree of cross-linking we found for all SMNRs fixity ratios between 90% and 95% that keep nearly constant over at least 10 shape memory cycles. The development of Rf and Rr of differently cross-linked SMNRs that were programmed at 20 8C and 80 8C, respectively, is shown in Figure 3.

The recovery values are marginally lower within the first two shape memory cycles than those determined at Tprog 5 20 8C, because of plastic deformation at the program- ming temperature Tprog 5 80 8C. Thus, SMNRs that were programmed at higher temperature have to be conditioned by applying 1–2 shape memory cycles to obtain full recovery.

So far only our recently reported lightly cross-linked polyethylene shows higher values of stored strain, indicating the superior properties of SMNR.

2.3 Energy Storage Capability of SMNR

SMPs not only store strain but also stores stress that corre- sponds to a certain amount of energy. Since most SMPs store fairly low strains, there has not been spent much effort in the determination of stored work in SMPs so far. Antha- matten and coworkers were the first who evaluated numerous SMPs concerning their principal energy storage capacity and estimated an upper bound for the achievable work energy density to be 30 J/g, assuming SMPs as neo-Hookean solids.

SMNR can be strained to many 100% while supporting large tensile stress of up to 20–30 MPa. Therefore, it should be well suited to store significant amounts of mechanical energy. In order to explore this, the energy Wstretch, needed for programming SMNR, as well as the elastically stored energy Wstored, which is released upon triggering, were calculated from shape memory cycles by integrating force versus extension, as exemplarily shown in Figure 4.

It was found that SMNR is capable to store mechanical ener- gies (Wstored) in a range of 1.34–4.88 J/g with efficiencies (g5Wstored/Wstretch) between 26.22% and 48.32% depend- ing on its degree of cross-linking and programming strain.

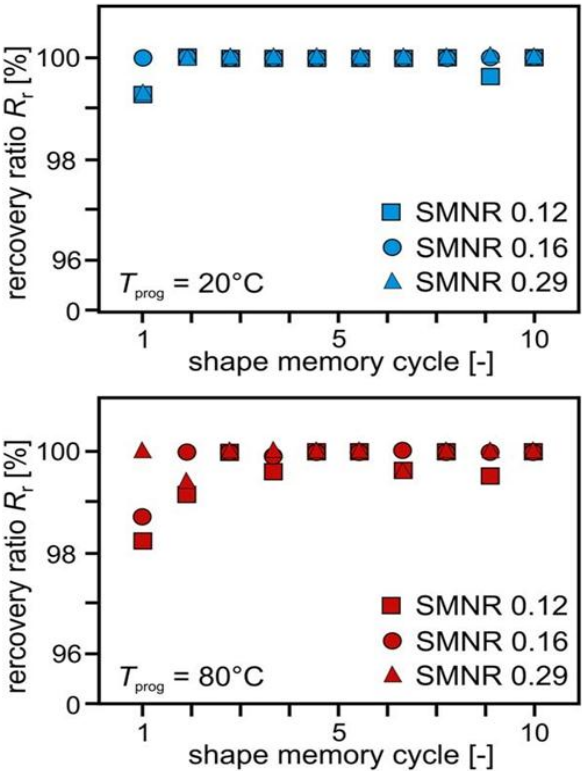

FIGURE 3 Recovery ratios Rr for differently cross-linked SMNRs programmed at temperatures Tprog of 20 8C and 80 8C [4]

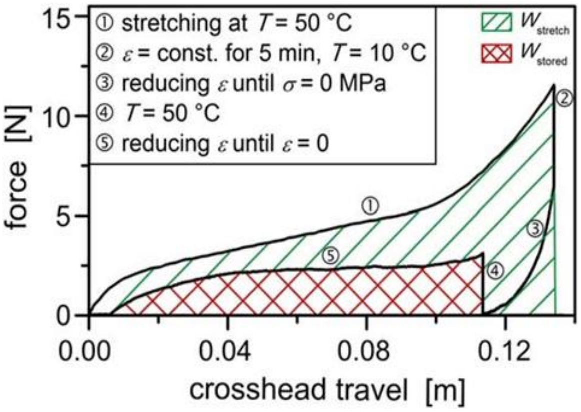

FIGURE 4 Force versus extension plot of a shape memory cycle for evaluation of stored energy Wstored and efficiency g of SMNR [5]

2.4 Cold Storage Capability of SMNR

An interesting way to cool a material is to release strain of an elastomer. Because the internal energy DU of a rubber remains nearly unchanged during deformation (DU 5 DQ – DW50), the performed work DW is directly released as heat DQ during the stretching process and vice versa taken up during its relaxation. This behaviour is well known for NR which shows a super-cooling of up to 10 K by releasing an elongation of k 5 5 (400% strain). In contrast [15] to common entropy-elastic materials NR forms crystals upon strain (SIC) which additionally contribute to the cooling of the rubber during relaxation, because the necessary heat of fusion Dhf is taken up from the surrounding. Altogether the stored cold corresponds to the sum of Dhf and DW. Due to the extremely large strain storage we found supercooling of SMNR of up to 20 K below ambient temperature upon shape recovery. Thus, SMNR does not only store large amounts of strain and mechanical energy, but can also be used for storage of “cold.

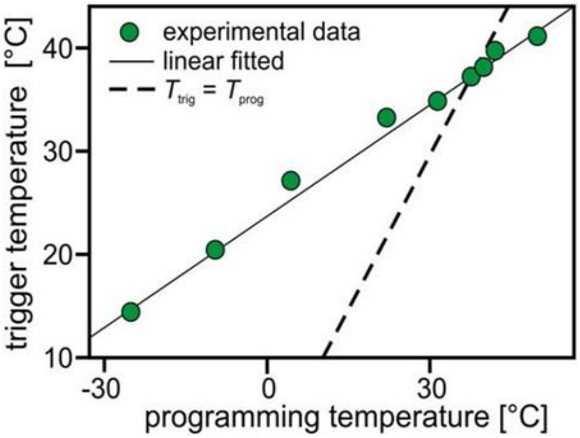

FIGURE 6 Plot of trigger temperature Ttrig against programming temperature exemplary for SMNR with a degree of cross- linking of 0.2% [6]

Tunability of Trigger Temperature

Compared with other SMPs the trigger temperature of SMNR is no material-dependent constant. Firstly, it depends on the network topology, especially on the degree of cross-linking and the distribution of cross-links. Ttrig decreases with increasing degree of cross-linking and undercuts room temperature when the degree of cross-linking increases above 0.4%. Secondly [14] and more interestingly, the trigger temperature of an SMNR sample with a certain degree of cross-linking can be altered in a broad range by varying strain-rate and temperature during programming. While the strain-rate has only a weak influence on Ttrig, the temperature during programming can be used efficiently to adjust trigger temperatures in the range of 225 8C to 45 8C (see Fig. 6). Thus, SMNR is one of a few SMPs with tunable trigger temperature.

Since polymer crystals are highly anisotropic it is obvious that they are more stable along the covalently bonded macromolecular backbone than perpendicular to this direction. Moreover, the strain-stabilizing polyisoprene crystals in programmed SMNR are highly oriented parallel to the direction of applied strain during programming. Thus mechanical stress can be applied selectively by applying external load parallel or respectively perpendicular to the programming direction of SMNR (see Fig. 7). Such a selective stressing of strain-stabilizing crystals in programmed SMNR should influence the stability of these crystals and thus its trigger temperature.

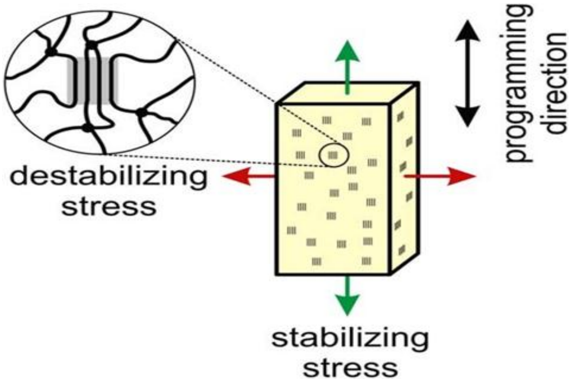

FIGURE 7 Influence of external mechanical stress on the stability of strain-stabilizing crystals in programmed SMNR. [7]

We actually found, that external mechanical stress has indeed an influence on the trigger temperature Ttrig of programmed SMNR. As shown in Figure 8, the trigger temperature of programmed SMNR can be effectively decreased in dependence on the amount of applied transverse mechanical stress and the initially programmed trigger temperature of SMNR. Higher initial trigger temperatures cause higher stress sensitivities[13] DTtrig/Drt. Since transverse stress can princi- pally be used to melt the strain-stabilizing crystals in SMNR and thus trigger the sample, this effect is referred to as stress-induced melting (SIM). Vice versa, the trigger temperature is increased linearly by applying stress parallel t0the elongation-stabilized direction, which is referred to as stress-induced stabilization (SIS).

2.5 Solvent-Sensing Via SMNR

Since all suited solvents cause complete recovery of a programmed SMNR, any qualitative and quantitative information on the trigger capability of these different solvent vapours is lost. In order to gain this lost information a rarely used technique was applied where the ends of the programmed SMNR [11] are fixed and the stress-answer is measured while the sample is triggered by exposing it to different kinds and concentrations of solvent vapours. It was found that SMNR under constrained condition responds with a tensile-stress when exposed to suited solvent gases. This stress-answer is composed of a reversible stress Drrev and an irreversible stress Drirr that remains after the solvent is removed (see Fig. 8).

The reversible stress-answer Drrev is highly sensitive to the applied vapour pressure pi and follows a parabolic-like progression for the solvents toluene, chloroform, n-heptane, cyclohexane, and tetrahydrofuran. Besides the reversible stress-answer Drrev of constrained SMNR, which allows in- situ solvent vapour pressure monitoring,69 also the irreversible stress-answer Drirr carries valuable information. It was found that Drirr depends linearly on the maximally applied solvent gas pressure pi,max to that the sample was exposed to in the past. Since this information can be erased by a heat treatment, constrained SMNR can also be applied as erasable non-volatile information storage device for applied solvent gas pressures in the sense of an "erasable programmable read-only memory" (EPROM).

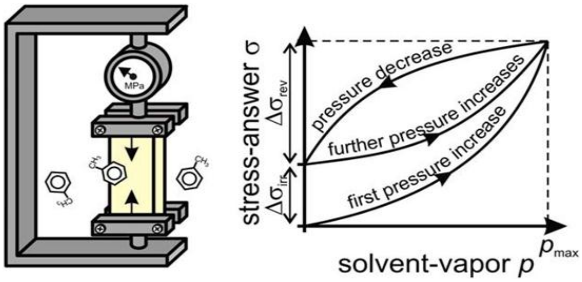

FIGURE 8 Solvent-induced stress-answer of SMNR [7]

Unexpectedly, it was found that a solvent-treated programmed SMNR is not triggered completely after unclamping but still fixes a large elongation. Even the trigger temperature was significantly higher than that of the originally programmed SMNR.

2.6 Solvent-Aided Programming of SMNR

Detailed studies revealed that solvent vapors can be effi- ciently applied not only for increasing the trigger tempera- ture of SMNR after programming but also for discretizing its trigger process. To this end, SMNR is firstly cold- programmed, which results in a relative low trigger tempera- ture but extremely narrow trigger range beneath 1 K. Secondly, the strain of the programmed SMNR is kept constant while exposing the constraint SMNR to a suited solvent. This way, Ttrig can be increased by 10 K while maintaining a narrow trigger range of less than 1 K. Furthermore, such solvent treatment enables programming even of NR vulcanizates with degrees of cross-linking above 0.4% that cannot be pro- grammed conventionally to trigger temperatures above room temperature (see Fig. 9).

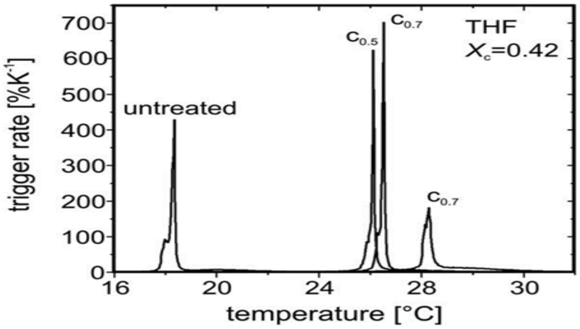

FIGURE 9 Trigger rate versus temperature plot of NR with a degree of cross-linking X of 0.42%, conventionally programmed at 20 8C and solvent-aided programmed using different concentrations of tetrahydrofuran vapor [8]

2.7 Shape Memory Blends With NR

Compared with the above described lightly cross-linking of NR there are further approaches reported in the literature to gain a shape memory effect on the base of NR. One possibility for fixing a temporary state is to increase the glass transition of the NR network above room temperature and use it as SMP directly. A suited chemical modification to this end is the epoxidation of NR and subsequent cross-linking by 3- amino-1,2,4-triazole or zinc acrylate using the oxa-Michael reaction. SMPs with varying Tg values (20 8C – 46 8C), stored uniaxial strains of about 60%, excellent shape fixities and shape recoveries were demonstrated.72–75 Other approaches are based on unmodified NR that is blended and cross-linked with high polymers like polylactide or poly(lactic acid).

Another more facile approach to gain a shape memory effect was followed by Cavicchi and Coworkers who blended generic sulfur cross-linked NR with oligomeric waxes (Fig. 10). The rubber bands were swollen in molten stearic acid at 75 8C resulting in a loading of 35 wt %. When cooled the crystallization of the stearic acid formed a percolated net- work of crystalline platelets. The microscopic crystals and the cross-linked rubber produce a temporary and a permanent network, respectively. These two networks allow thermal shape memory cycling with deformation and recovery above the melting temperature of stearic acid and fixation below that temperature. The shape memory rubber bands exhibited fixity and recovery ratios of up to 100%, and stored strain up to 70%.

III. CONCLUSIONS

Even if the phenomenon of the shape memory effect of NR is not understood yet in all details it is certain that all discovered effects are related to the lightly cross linking of SMNR at the borderline between thermoplastics and elastomers. Nevertheless we were able to use the experience made with the example of SMNR to significantly broaden the profile of properties of classic thermoplastics like polyolefins and polyvinylidenefluoride. The insights on lightly cross- linked NR, reported in this article, show that unimagined properties still slumber in long known classic materials that are assumed to be fully understood. Future work will focus on coupling shape-memory properties of highly stretchable polymers such as SMNR with switchable surface ripples, ultra hydrophobic surfaces, amphiphilic character, and optical properties.

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