



SELF-HEALING POLYMER MATERIALS

Aim of this review is to make known some of the efforts and the results obtained by a few research groups in the world, striving to find and optimize self-repairing processes of polymer materials (passive vs. active protection). The mechanism of active protection is reviewed and compared with protection systems of living body, providing useful information on the development of advanced materials.

In recent years, the ever increasing growth of polymer-based composites as structural materials has been the source of new problems that are beyond the chemistry of the synthetic process itself. Namely, many applications not only require specific mechanical properties, but also demand a suitable resistance to potential damages during their use (repeated mechanical stresses, attack by chemical or physical external agents, etc.). Usually, the damages are made evident by the appearance of microfractures (cracks) that occur in the matrix and follow chain degradation. An immediate consequence of the degradation process is the decreasing of molecular mass as well as the variation of chemical composition of parts of the polymer chain.

So far, the exact localization of the events causing the start of degradation is almost always rather difficult and a repairing service practically impossible. Above all, most microfractures are produced inside the polymeric material and become visible only when

the mechanical resistance is irreversibly jeopardized.

Aim of the present review is to make well known some of the efforts and the results obtained by a few research groups in the world, striving to find and optimize self-repairing pathways of polymer materials, when these latter can face structural damages during their service. However, it is necessary to point out not only that, at present, the chemistry of the repairing process is not always fully developed, but also that the transfer of research results to potential applications still requires relevant additional time to be accounted for.

The interest for possible *in situ* self-healing approaches to apply to microfractures, wherever localized, is widely growing in the last few years and is centered on the development of self-repairing mechanisms activated by the damage itself (namely, by the start of microfracture formation) as a key point common to most researches. At present, the suggested protection mechanisms can be clas-

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sified into two different categories [1]:

- i) an *active protection* that promotes self-healing by “metabolic” reactions able to “internally” repair injuries caused by many kinds of external deterioration factors;
- ii) a *passive protection* when materials are protected by simple chemicals (e.g. light absorbers).

Metabolic or active protection

For this category, a very promising approach has been initially proposed by the researchers of University of the Illinois at Urbana-Champaign (USA), followed by other research groups: the repair process is based on the dispersion, within the polymer matrix, of microcapsules [2-4] or hollow glass fibres [5-8] filled with a healing monomer, whose initiator/catalyst of polymerization is dispersed in the matrix polymer. The occurrence of a microfracture colliding with a capsule or a fiber causes the break of their walls; monomer diffusion in the matrix to encounter the initiator/catalyst molecules determines its *in situ* polymerization and the microfracture filling. A subsequent heat treatment may be useful to complete the repairing process [9], although the recovery of the initial mechanical properties is hardly achieved. Apart from the choice of the optimum amount of capsule or fiber to be added to the polymer matrix (such content would influence mechanical properties of the composite), one of the most complex problems to handle is the choice of both the sphere or fiber diameter and wall thickness, and the physical characteristics of these latter. Indeed, it is required that they only break when the microfracture is formed and encounters the monomer “reservoir”, allowing its diffusion in the polymer matrix, not earlier and/or for different reasons. The numerous sys-



tems described in the literature and based on the above approach not only refer to polymer matrices, but also to applications for ceramic concrete, aerospace and electronic materials, etc. More specifically, the studies on polymer systems are aimed to their use in the aeronautical and transport field, in the road flooring, etc. However it is useful to remember here that, as mentioned above, the transfer of research results to the applied fields for various kinds of materials has not been yet completely achieved or at least made fully known in the open literature. Nevertheless, on the basis of the present knowledge, it is possible to assert that the protocol of a self-healing material synthesis consists of the following steps:

- a) Polymer choice as the matrix material on the basis of foreseen applications. In case of an epoxy resin (one of the most used structural polymers), it is necessary to prepare a suitable mixture of reactants adding to them, before full reaction, the polymerization initiator/catalyst of the monomer that will form the healing polymer.
- b) Insertion of the above monomer in capsules or hollow fibers, able to be easily broken when reached by the propagating microfracture.
- c) Mixing of the reacting mixture with the microcapsules or the hollow fiber network, followed by its hardening.
- d) Characterization of the obtained composite material.
- e) Evaluation of the mechanical properties during the working period in relation to the adopted recipe.

Obviously, every point of the above list requires a wide knowledge of all variables affecting the final result: for instance, at point c), in the case of monomer-filled hollow fibers, it is relevant to consider, as previously mentioned, the diameter of the fiber referred to the wall thickness, the fiber/resin volume ratio and so on. Hucker *et al.* describe in detail the above aspects in [8], where it is also pointed out that the obtained results are not fully interpreted so far.

In order to optimize the self-repairing process, it would also be useful to consider other two aspects in addition to the aforementioned steps:

- evaluation of the adhesion between matrix and microcapsule/hollow fiber walls;
- detection of microfractures under repair.

Non-metabolic or passive protection

The self-healing methods of the second type are mainly based on the evaluation of polymer molecular/structural changes during the deterioration step, with specific attention to the relevant decrease of molecular mass that always cause a worsening of mechanical properties. At the beginning of year 2000, some UCLA researchers

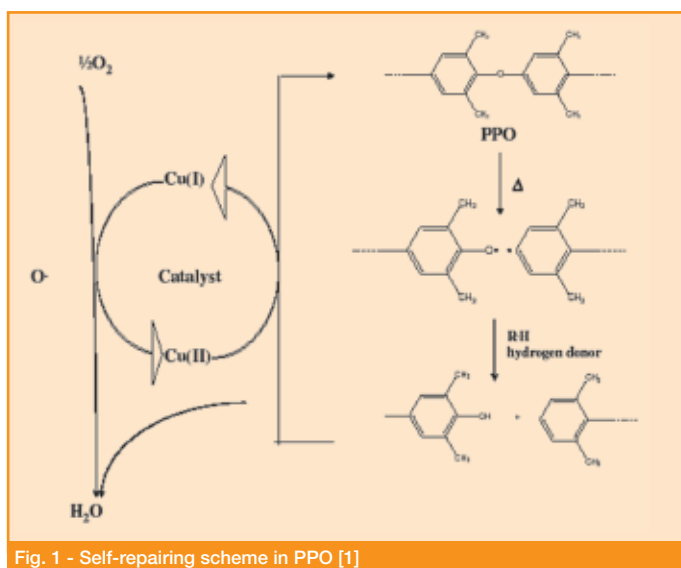


Fig. 1 - Self-repairing scheme in PPO [1]

have developed the synthesis of a transparent plastic material, called Automend®, that (without any chemical substance added) is able to repair microfractures by simple heating at ca. 120 °C [10]. At this temperature, a fraction of the inter-molecular bonds is broken and the polymer chains acquire mobility and fill the microcracks possibly formed. The polymer crosslinks are restored by simple cooling. Obviously, the above process is quite different from the previous one, which is based on a kind of adhesive that seals two or more pieces together after the fracture. While the “scaling” is able to recover only ca. 40% of the pristine mechanical properties. Automend can be repeated several times and gives a claimed recovery of ca. 60% of the pristine properties; moreover, after the repairing treatment, the fracture becomes fully imperceptible. By this approach, applications in optical field can be envisaged, and not only them: since microwaves can be transmitted from the polymer material, it is possible to use this latter for electronic applications, as radars or communication devices. Indeed, it is a remarkable property of Automend that, if an electronic system can be heated and cooled at specific frequencies, it will strive to self-repair during the heating step, automatically eliminating the damages possibly produced during the cooling step.

Recently, a new interesting method has been developed by Takeda *et al.* [1]. Their approach is based on the use of “inverse reactions”, as referred to those causing the damage: these “inverse reactions” induce chain recombination and recovery of the pristine properties. The following examples, applicable to thermoplastic polymers, will show that these methods do not require complex experimental protocols, but a deep knowledge of the degradation chemistry of the specific polymer under study is needed, *i.e.* modes of chain breaking, identification of newly formed groups together with possible reactions able to restore the chain length, potential repairing agent able to help the restoration process. An example, widely quoted, is that of poly(phenylene oxide) (PPO) [1]. This high performance polymer, characterized by a very high stiffness, is damaged by heat, light, mechanical stress. The polymer chain is broken with an initial formation of radicals, able subsequently to capture hydrogen from a hydrogen donor. The repairing scheme is shown in Fig. 1.

If Cu(II) has been previously added to PPO, it forms a complex with each end of two different chains, withdrawing two electrons from them, thus reducing to Cu(I). The polymer chains combine, eliminating two protons from their ends. The deactivated Cu(I)-containing molecules migrate inside the polymer until two of them meet and react with an oxygen molecule oxidizing and leading to corresponding Cu(II) species. The oxygen anion reacts with two protons to form a water molecule that can migrate out of the polymer. Several experiments have been carried out to check the above mechanism. The mobility of the chains was supposed to be one of the key factors in accelerating the self-repairing reaction, because the two ends of PPO chain, which is one of the most rigid plastics, and the copper ion must meet each other at the same time. The experimental results show that the rate of recovery increases with decreasing initial molecular mass, thus supporting the assumption that the self-repairing reaction depends on the chain end concentration and mobility. The rate of recovery was also expected to be dependent on oxygen partial pressure in the surroundings.

Another example of self-repairing system is that of one of the most useful engineering plastics: polycarbonate (PC), prepared from bisphenol-A and phosgene [11]. The decrease of PC molecular mass [12-17] is caused either by heat or by acid hydrolysis. The above

Materiali polimerici autoriparanti

Obiettivo del presente articolo è quello di illustrare in maniera concisa i risultati ottenuti da alcuni gruppi di ricerca statunitensi, giapponesi ed europei nella realizzazione e ottimizzazione di nuovi processi di autoriparazione in materiali polimerici ad alte prestazioni.

RIASSUNTO 

decrease causes severe worsening of the mechanical strength. The easy recombination of the two parts of the chain occurs if sodium carbonate is present within the polymer matrix. This chemical makes the medium weakly alkaline, thus favoring the inverse reaction. The detailed scheme of the repairing action is given in [1].

The application of the above repairing method is simple in essence, but requires, as already underlined, an accurate study of the chemical processes and pathways occurring in chain breaking and chain repairing steps.

Another typical biomimetic process is that foreseen for hollow glass fibers in aerospace applications. The above fibers, filled with an uncrosslinked polymer, behave like the human skin, leaving the polymer to flow from the actual points of cut (similarly to blood from the wound) to the damaged area to repair. Obviously, in the case of glass-reinforced polymer composites, the breaking of the glass fiber cannot be eliminated, but the repaired matrix (e.g. epoxy) gives back ca. 90% of the pristine mechanical strength and can be, although temporarily [18, 19], a remedy to the damage. The experiments made at the University of Bristol, UK, are encouraging for future applications.

Finally, we want to recall here that at the end of the past century, some researches have been carried out on new polymers, characterized by repetition units linked together by reversible bonds or interactions, weaker than covalent bonds, such as hydrogen bonds, π - π and hydrophobic interactions, and coordination bonds. The main characteristics of their synthesis is based on the relevant aspect that the chain must grow up to critical dimension/size before further monomer addition becomes favorable according to the



nucleation-lengthening model. In this way, macromolecules with a tertiary structure are spontaneously obtained. It is possible to envisage applications of the above polymers in the fields of catalysis, non linear optics, magnetic and electrical molecular materials, and for drug release devices. Moreover, the polymers so obtained are sensitive to external stimuli such as temperature, so that bonds can be broken and formed again, thus allowing the reassembling of the polymer structure. It is evident that the latter property is very useful, as it paves the way to new self-repairing materials.

Within Consortium INSTM a group of researchers, devoted to study alternative approaches on self-healing processes, has been recently established. Researchers of the NIPLAB Centre, added with research units from University of Sassari, Milan and Parma (about 20 persons in total) are actively working on this theme in the perspective to involve researchers of other European Countries in a future joint project.

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