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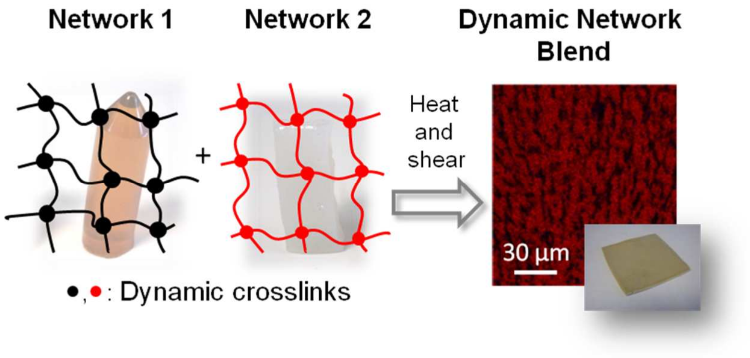

Is it possible to blend two immiscible polymer networks starting from their cured state? Here we present a simple thermomechanical approach that allows the blending of two dynamically crosslinked polymer networks. The blend presents superior mechanical properties than the starting materials, as shown by hardness, tensile tests and rheological measurements.

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**ARTICLE TYPE**

# Mixing the Immiscible: Blends of Dynamic Polymer Networks

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**A simple thermomechanical approach is used for the preparation of elastomeric blends starting from two dynamically crosslinked polymer networks, which are forced to mix and form a dynamic network blend (DNB). The new material presents superior mechanical properties than the starting materials, as shown by hardness, tensile tests and rheological measurements.**

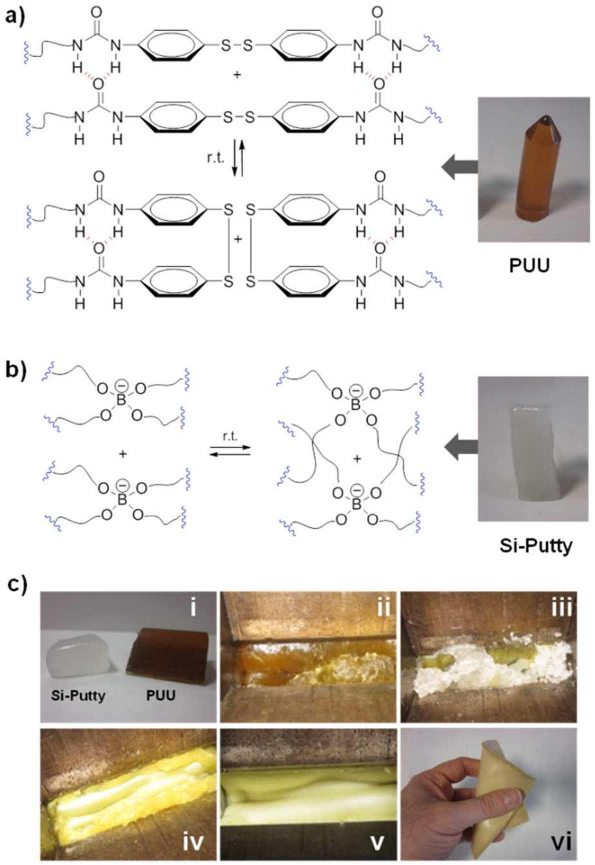
The very exigent demands of the industry of the 21st century are forcing scientists to continuously improve the existing materials. This is probably more noticeable in polymer chemistry, where new functionalities and enhanced properties are constantly required by the market. In this sense, one of the most economic and practical approaches towards the creation of polymeric materials with improved properties, would come from blending of different polymers. However, this is still an unresolved issue, due to the intrinsic immiscibility of polymers of different nature.[1] Several approaches have been recently proposed to overcome this problem, such as the development of block-copolymers and grafted polymers as compatibilizing agents,[2,3] reaction-induced blending[4] and the introduction of hydrogen bonding[5,6] or host-guest[7,8] functional groups in the side chains of the polymers. All these approaches have one thing in common: they try to make the polymers more compatible. However, the design of a blending strategy that does not involve compatibilisation of the different polymers would be highly desirable. Moreover, polymer blends are commonly referred to non-crosslinked systems like thermoplastic polymers, or systems including rubber/plastic blends and the so called thermoplastic vulcanizates (TPV) where only one component of the blend is fully crosslinked. The possibility of blending two polymer networks starting from their crosslinked state has never been carried out, to the best of our knowledge. In this communication we describe a very simple and convenient method for blending two polymer networks which are, in principle, “immiscible”, to obtain a blended network with enhanced mechanical properties.

The introduction of covalent reversible chemistry[9-13] in polymer systems has recently boosted a series of breakthroughs in materials science. Thus, the concept of polymeric entities that could reversibly change their constitution, so-called *dynamers*, was first introduced by Skene and Lehn.[14] Later, dynamic bonds were introduced into cured polymers, and amazing concepts such as Bowman’s *covalent adaptable networks* (CANs)[15,16] or Leibler’s *vitrimers*,[17] among others,[18,19] emerged as a new generation of dynamic materials. Recently, our group published a poly(urea-urethane) (**PUU**) which showed quantitative healing efficiency at room-temperature, without the need of any external stimulus or catalyst. This material was crosslinked by specific chemical moieties containing hydrogen bonds and aromatic disulfide bridges, which are in constant exchange at room-temperature (Scheme 1a). On top of the self-healing properties, this material could be reprocessed under heat and pressure, due to the reversible nature of the crosslinks.[20,21] However, this material presents limited mechanical properties (0.8 MPa tensile stress at break), and therefore needs to be improved in order to permit its use in the widest range of industrial applications.

In an effort to improve its mechanical properties, we came out with the idea of synthesizing an interpenetrated double network (DN), inspired by the work of Gong and co-workers,[22,23] who demonstrated that some specific hydrogel DNs present superior mechanical properties compared to each of the single networks. Thus, the idea was to use a simple and fast method for the preparation of bulk elastomeric DNs, starting from two different polymers, both crosslinked *via* dynamic chemical bonds. The aim was to study if two chemically crosslinked networks could be thermomechanically forced to interpenetrate and form a double network, by means of a process that could remind very much of a popular magic illusion known as “Chinese rings”. This could be understood as a new approach for blending polymers, without the need of making them more compatible.

Thus, the second network chosen for making the blends in combination with **PUU** was a silicone putty.[24] This material is composed of a hydroxyl-terminated poly(dimethylsiloxane) (PDMS) crosslinked with boric acid, where the resulting borate ester bonds are also in constant exchange (**Si-Putty**, Scheme 1b). This silicone network possesses intriguing rheological properties, which gave rise to the creation of a popular toy known as “Silly Putty” back in the 1950’s. It is worth noticing that PDMS, for its mainly inorganic nature, is completely immiscible with the vast majority of organic polymers. Thus, the objective of this work was two-fold: Firstly, to explore the possibility of blending two completely immiscible polymer networks starting from their cured state; and secondly, to demonstrate the synergistic effect of the process, by improving the mechanical properties of the elastomeric **PUU** by blending it with a silicone network which was softer.

The blending process was carried out starting from cured **PUU** and **Si-Putty** (Scheme 1c-i), using a very simple thermomechanical method. First, a piece of **PUU** was added to an internal batch mixer without heating (Scheme 1c-ii). Such equipment, typically used for mixing or compounding rubber and plastics, consists of two rotating blades encased in segments of cylindrical housings, and causes very high shear levels. Then, the second polymer was added, **Si-Putty**, while continuous mixing. At this stage the two polymers remained immiscible, even after prolonged mixing times (Scheme 1c-iii). Then temperature was raised to 150 ºC and the polymer networks started to blend (Scheme 1c-iv). After 1 hour mixing at 150 ºC, the blend was obtained as a homogeneous elastomeric material (Scheme 1c-v). It was found that both heat and shear were necessary for the correct formation of a homogeneous blend. As both the aromatic disulfide metathesis and the borate ester exchange occur at room-temperature, this could only be explained by the presence of the strong hydrogen-bonds between the urea protons and adjacent carbonyls (Scheme 1a). FTIR experiments performed in our previous work showed that such H-bonds in **PUU** are disrupted at temperatures above 110 ºC.[21] Thus, the blending of the two networks needs to be carried out above such temperature.



**Scheme 1** Dynamic crosslinking structures of the two polymer systems used in this work. a) **PUU** is crosslinked with H-bonds and aromatic disulfide bridges, which undergo reversible metathesis reactions at ambient conditions. b) **Si-Putty** is crosslinked with borate ester groups, also at constant exchange at ambient conditions. c) Photographs showing the preparation procedure of DNBs: i) **Si-Putty** and **PUU** were used as starting materials. ii) First, **PUU** was introduced in an internal mixer at ambient temperature. iii) Then, **Si-Putty** was added, but the two polymers remained unblended. iv) Temperature was raised to 150 ºC, and the two networks started blending. v) After 1 hour at 150 ºC a homogeneous material was obtained. vi) The hot mixture was removed and hot-pressed in a flat mould. After cooling, the DNB material was obtained in the form of a film.

In order to obtain the materials in the form of films (Scheme 1c-vi), the blend was then placed in a 2 mm thick square mould and pressed at 150 ºC for 10 minutes.[§]

Three different blends were made by varying the ratio of **PUU** and **Si-Putty**, as shown in Table 1. A homogeneous elastomeric material was obtained in all cases (see supplementary movie), which, due to the reversible nature of the crosslinks could be named as *dynamic network blend* (DNB).

**Table 1** Composition and mechanical properties of the different DNB samples prepared

| Sample name | PUU (%wt) | Si-Putty (%wt) | Hardness (Shore A) | Tensile strength (MPa) |
|---|---|---|---|---|
| **PUU** | 100 | 0 | 10 | 0.8 |
| **DNB$_{75}$** | 75 | 25 | 20 | 1.3 |
| **DNB$_{50}$** | 50 | 50 | 30 | 1.9 |
| **DNB$_{25}$** | 25 | 75 | 17 | 0.5 |
| **Si-Putty** | 0 | 100 | - | 0.1 |

The microstructure of the obtained blends was analysed by FE-SEM. If interpenetration occurred at molecular level like in DNs, microphase separation would not be expected to occur. Fig. 1 shows the electron micrographs obtained for each of the DNBs and their corresponding EDX mappings of silicon element. In the three DNBs prepared, a co-continuous microphase structure was observed, especially in **DNB$_{50}$,** indicating that the blending process was effective only at a microscopic level. Interestingly, co-continuous blends of non-crosslinked polymers are known for possessing better mechanical properties than their components.[25] This is because in co-continuous structures the mechanical properties reflect a greater contribution of both components, whereas in dispersed structures the properties of the blend are dominated by the matrix component. However, to the best of our knowledge, co-continuous blends of polymer networks have never been prepared so far.

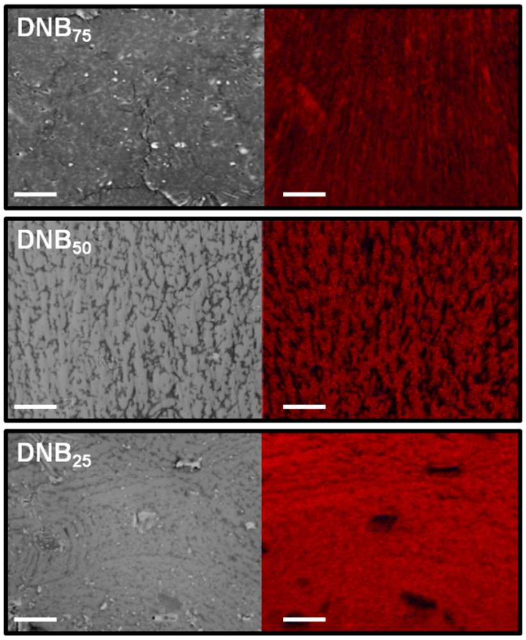


**Fig. 1** FE-SEM micrographs of different **DNBs** (left) and their corresponding elemental mapping of Si obtained by EDX (right). The red colour indicates presence of Si. Scale bar corresponds to 30 micron in all cases. Samples were prepared by cryo-fracturing in liquid nitrogen.

Differential scanning calorimetry (DSC) has been extensively used to detect the effective formation of miscible and immiscible polymer blends. In miscible systems, the glass transition temperature ($T_g$) of the blend is usually observed at an intermediate value between the $T_g$ values of the starting polymers. Unfortunately, characterization of the DNB materials by DSC did not give any information in our case, since a wide peak corresponding to the $T_m$ of the PDMS component masked the zone where the $T_g$ of the DNBs was expected to appear.

Relevant information was obtained from Fourier Transform Infrared (FTIR) analysis of the different DNB samples. The results revealed a shift of various peaks corresponding to PDMS chains of the **Si-Putty** network. Thus, Si-$CH_3$ rocking vibration and Si-bonded $CH_3$ symmetric bending peaks from the bare **Si-Putty**, underwent a progressive shift to higher frequencies while increasing the **PUU** content in the blend, from 786 and 1257 $cm^{-1}$ to 795 and 1259 $cm^{-1}$, respectively (Fig. 2). Such surprising behaviour could hardly be explained in a system where the two phases are separated in several micron-sized domains. These FTIR shifts could only be explained by the existence of an effective interpenetration at the molecular level. Thus, from these results we hypothesise that such molecular level interpenetration could actually exist to some extent at the edges of the microdomains.

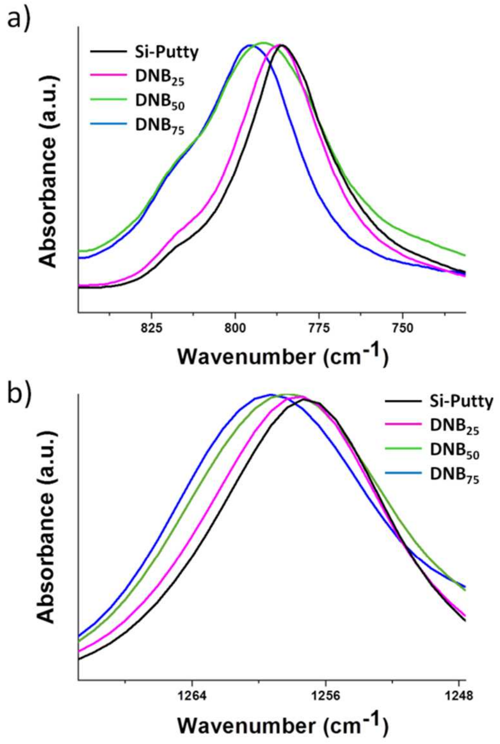


**Fig. 2** Fragments of FTIR spectra of bare **Si-Putty** and different DNBs, where shifts are observed in the Si-$CH_3$ rocking vibration band (a) and the Si-bonded $CH_3$ symmetric bending band (b).

To analyze the eventual effect of blending on the rheological properties, dynamic viscoelastic functions under linear conditions were measured. In the case of **Si-Putty** (see Figure S5), frequency scans at a temperature of 25 ºC revealed the constitution of an elastic gel, with a constant elastic modulus G' = Ge = $10^5$ Pa detected at high frequencies. Frequency scans at different temperatures allowed building a master curve (see Figure S6) from which a relaxation time τ = 1.4 s at 25 ºC could be obtained. This indicated that at times t < τ = 1.4 s or frequencies above 0.7 rad·$s^{-1}$ the borate ester bonds in **Si-Putty** (Scheme 1b) held on constituting a network, whereas at times t > τ = 1.4 s or frequencies below 0.7 rad·$s^{-1}$ the network did not stand, and G'' > G'.

However, for **PUU** (see Figure S7) the dependence of both G' and G'' on frequency indicated that under the experimental conditions used, the crosslinks which undergo reversible metathesis reactions were not able to maintain a stable network. This would correspond to a weak gel case, as considered by de Gennes,[26] in which the time span of bonding-nonbonding reactions is so short that very high frequencies would be necessary in order to observe a constant G' value or equilibrium elastic modulus.

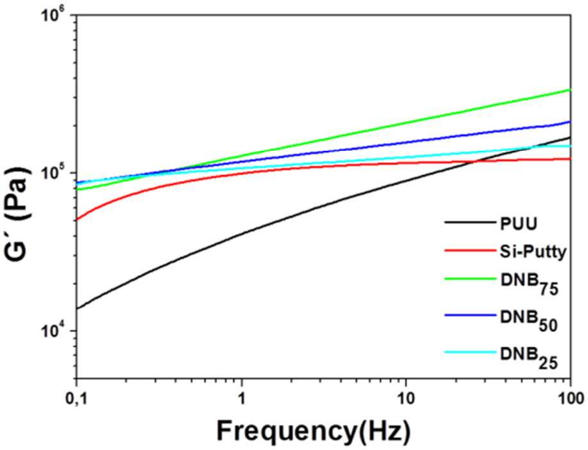


**Fig. 3** Elastic modulus for the starting polymer networks and their blends registered at T = 25 ºC.

Dynamic viscoelastic results of the different DNB samples (Fig. 3), indicated that these blends were not able to constitute stable, frequency/time independent networks, under the experimental conditions of our work. Interestingly enough, the instability of the network, reflected by the slope of G', increased gradually with the content of **PUU**. Most significantly, a synergistic effect due to the creation of the DNB was clearly observed, since G' values of the blends were higher than those of the individual components. This constitutes a rheological evidence of the effective blending of the two polymer networks,[27] and is in good agreement with the enhancement of the mechanical properties observed for co-continuous blends.[25]

In view of the promising results disclosed in the basic characterization of the blends, their end-use properties were also investigated. As shown in Table 1, the Shore A hardness of the different DNBs varied from 17 to 30, whereas the original **PUU** showed a value of 10. The maximum value, 30, corresponded to **DNB$_{50}$**. Interestingly, all DNBs presented a superior hardness than the starting **PUU**, although this was blended with a much softer **Si-Putty** material. This suggested again that the blending process has a synergistic effect on the mechanical properties of the material, in agreement with the co-continuous blends of non-crosslinked polymers reported in the literature.[25]

The mechanical properties of DNBs were further analyzed by performing tensile strength measurements, using dumbbell-shaped specimens. Fig. 4 shows stress *vs*. strain curves obtained for the starting materials and the different DNBs. Bare **PUU** showed a tensile stress of 0.8 MPa and a strain of 2300% at break, as reported previously.[20] **Si-Putty** was a non-elastic material, having very poor stress resistance. Interestingly, **DNB$_{50}$** gave the maximum performance in terms of stress resistance (1.9 MPa). In this case, the elongation at break was 1600%, significantly lower than the one obtained for bare **PUU**. **DNB$_{25}$** gave poorer mechanical properties (0.54 MPa stress and 976% elongation at break), whereas **DNB$_{75}$** presented superior mechanical resistance compared to bare **PUU** (0.88 MPa stress and 2307% elongation at break). It is worth noticing here the fact that blending **PUU** with a soft material such as **Si-Putty** in a 50:50 ratio resulted in a new material with a 2.3-fold higher stress resistance. This demonstrates that the strategy of creating dynamic network blends can also be used for the obtaining of elastomers with enhanced stress resistance.

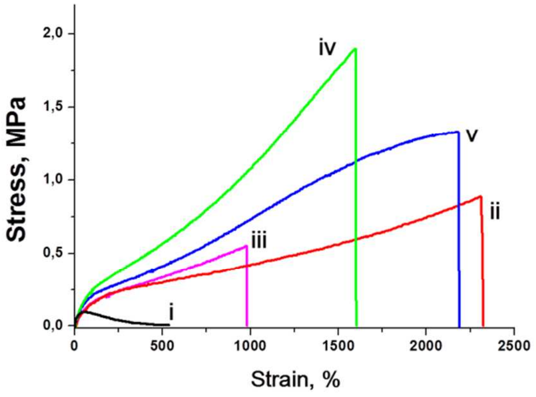


**Fig. 4** Stress *vs*. strain curves until rupture of **Si-Putty** (i), **PUU** (ii) **DNB$_{25}$** (iii) **DNB$_{50}$** (iv) and **DNB$_{75}$** (v).

## Conclusions

In summary, two dynamic polymer networks have been blended by a very simple thermomechanical method. This has resulted in the formation of elastomeric DNBs which present a co-continuous microstructure. Interestingly, such DNBs present better mechanical properties than both of their precursors, being the 50:50 blend the best performing material according to tensile strength measurements. This constitutes a novel approach for blending polymer networks in a synergistic manner, and opens the way towards the facile design of new polymeric materials with superior mechanical properties. The simplicity of the process, as well as the wide variety of dynamic chemistries available, makes the method useful for the development of advanced polymeric materials for the exigent industrial needs of the 21st century.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: Synthetic procedures, FTIR and rheological data and a short movie showing the preparation of the DNB. See DOI: 10.1039/b000000x/

§ When heated over extended periods of time over 150 ºC, a visual change in the appearance of the samples was observed, due to an extensive phase separation.

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