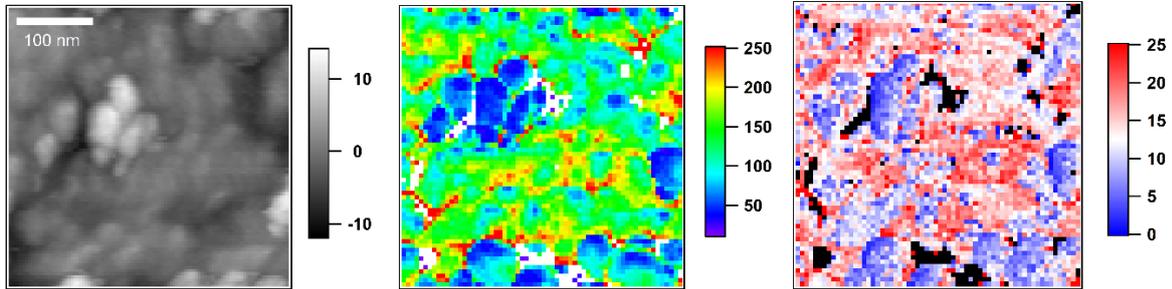
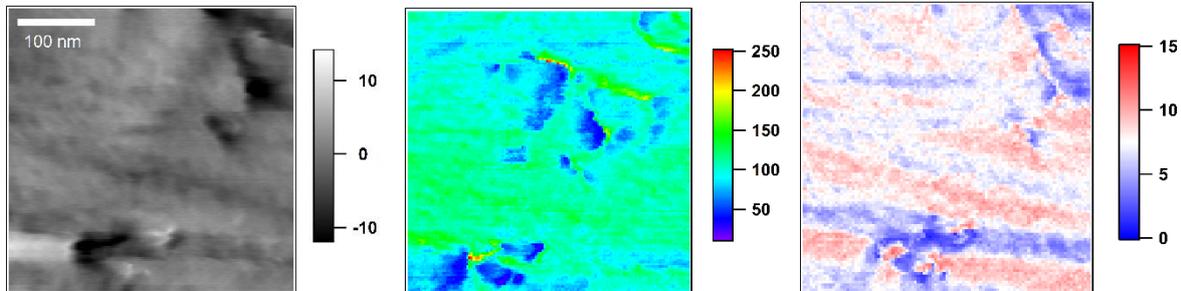


Supporting material

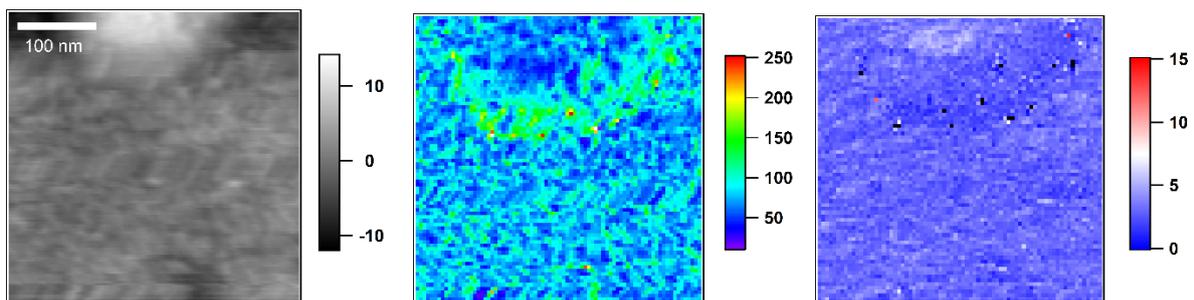
SM1:



SM1.1 Tapping mode topography (left) and ImAFM work of attractive forces W_{attr} (middle) and stiffness map of EP/BNP15. White pixels on the on W_{attr} map and black pixels on stiffness map indicates error. The color scale units of topography, W_{attr} and stiffness map are nm,nJ and arbitrary unit, respectively.



SM1.2 Tapping mode topography (left) and ImAFM work of attractive forces W_{attr} (middle) and stiffness map of EP/BNP2.5. The color scale units of topography, W_{attr} and stiffness map are nm,nJ and arbitrary unit, respectively.

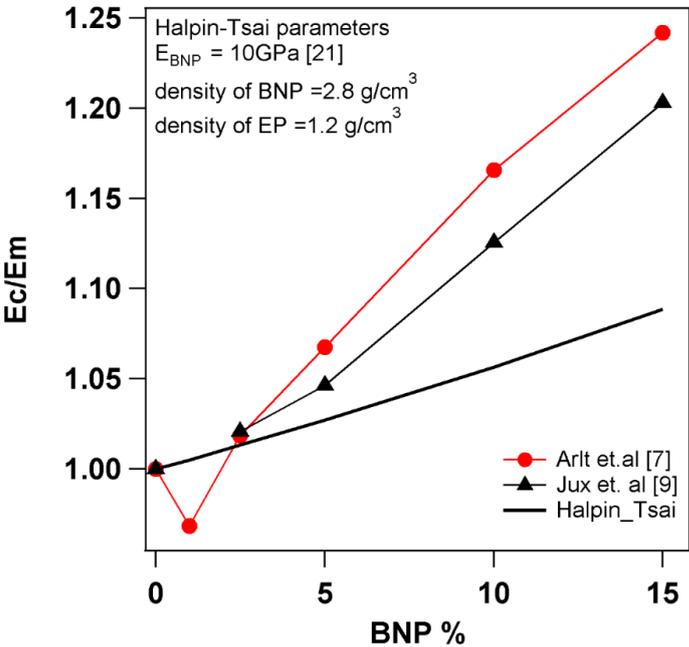


SM1.3 Tapping mode topography (left) and ImAFM work of attractive forces W_{attr} (middle) and stiffness map of neat epoxy EP. The color scale units of topography, W_{attr} and stiffness map are nm,nJ and arbitrary unit, respectively.

SM2: Comparison of experimental data with Halpin-Tsai model

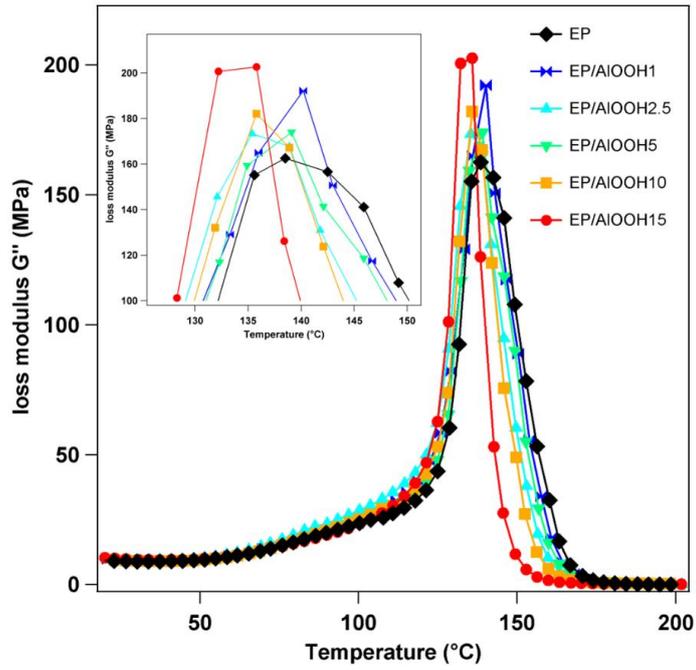
It was assumed that the drastic increase of elastic modulus of composite E_c with BNP is due to contribution of elastic modulus of BNPs which is in the range of 10 GPa. Halpin-Tsai and experimental

moduli are in the good agreement for only low particle concentrations (less than 5wt%). This shows that for low particle concentrations E_{BNP} is the main reason for increased modulus of the composites. However, from 5wt% Halpin-Tsai cannot follow the drastic increase of modulus. The disagreement between theoretical models and experimental mechanical behavior has been already observed in studies on several nanocomposite systems as it was usually attributed to the interphase modulus and also percolation of interphase. However, we believe that alteration of the modulus of matrix E_m as observed in our study is the reason for the disagreement with the theoretical model. Treating E_m as a variable parameter has never been taken into account in any theoretical modifications of Halpin-Tsai and hence it is noteworthy to be considered when such a behavior is observed.

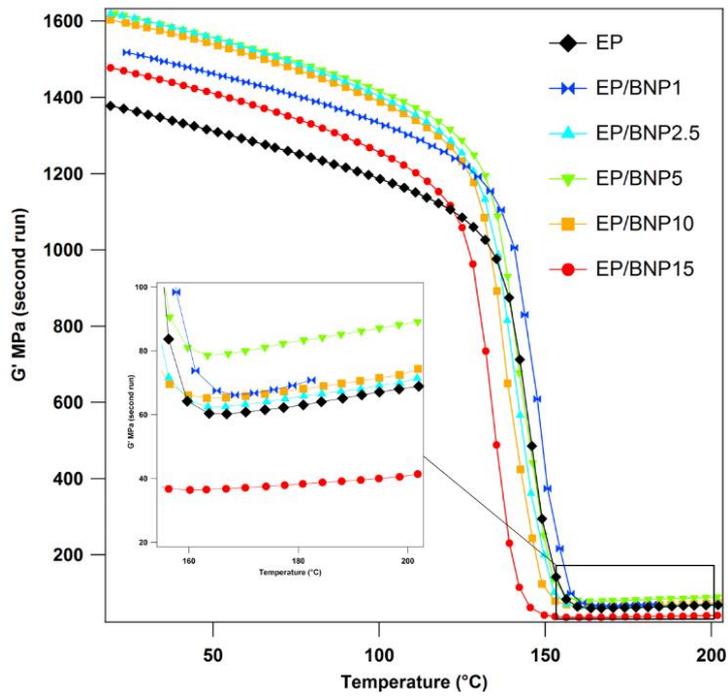


SM2. comparison of experimental elastic modulus of the EP/BNP nanocomposites from previous studies with the theoretical model Halpin-Tsai

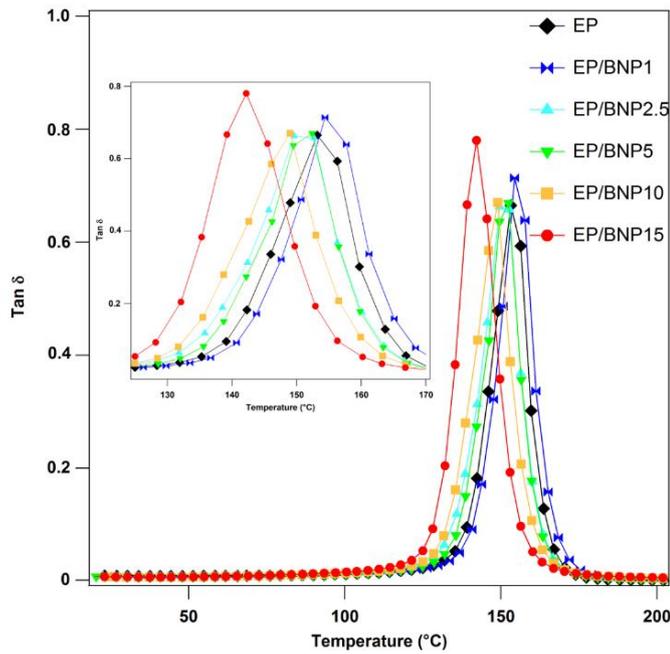
SM3: Supplementary DMTA results



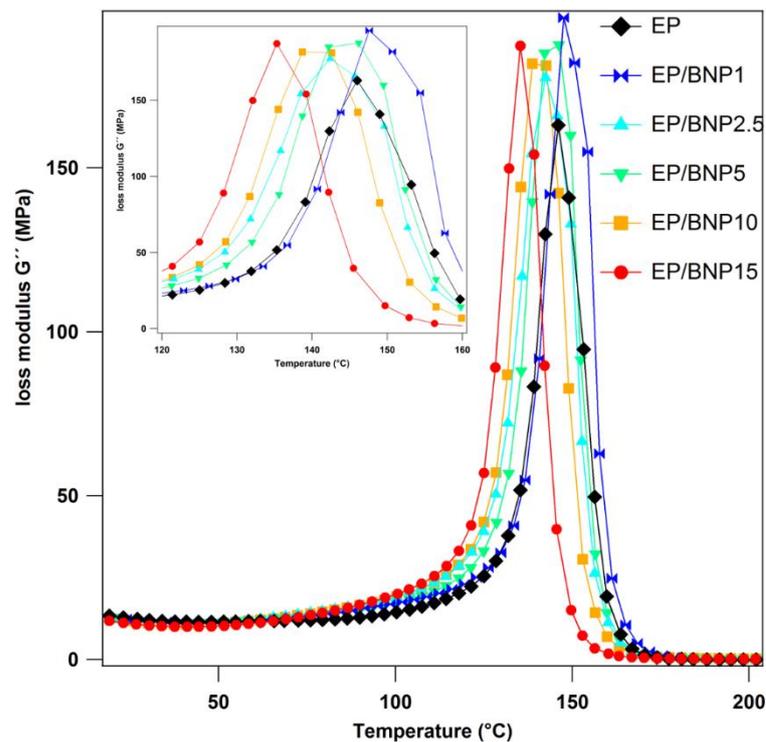
SM3.1 Loss modulus spectra of anhydride-cured epoxy with different BNP mass fraction (first run)



SM3.2 Shear storage modulus of anhydride-cured epoxy with different BNP concentrations (second run)



SM3.3 loss tangent of anhydride-cured epoxy with different BNP concentrations (second run)



SM3.4 loss modulus spectra of anhydride-cured epoxy with different BNP mass fractions (second run)

the quantitative analysis of the $\tan \delta$ and storage modulus of the second run for all compositions are evaluated from second run spectra (SM4,5 and 6) and listed in Table 2. For all compositions, T_g did not show any significant change from first to second run. However, the width of $\tan \delta$ peak drops for all samples to a minimum value of 14 K. This is the width which the EP/BNP15 nanocomposite has already reached during the first run and seems to be the minimum value that can be reached.

Table 2. Analysis of storage shear modulus and $\tan \delta$ curves of the dynamic mechanic spectra for each composition (second run)

composition	Storage modulus G' at room temperature (MPa)	Absolute value of Energetic elasticity G_e (MPa)	Crosslinking density ν (mol m^{-3}) * 10^6	Glass transition temperature T_g ($^{\circ}\text{C}$)	Width of half-height (K)	Peak Height (a.u.)
EP	1378	52	8.3	153	14	0.66
EP/BNP1	1518	80	9.17	154	14	0.71
EP/BNP2.5	1619	40	8.45	150	15	0.66
EP/BNP5	1620	45	10.64	152	14	0.66
EP/BNP10	1603	29	8.7	149	14	0.67
EP/BNP15	1478	17	4.9	142	14	0.78

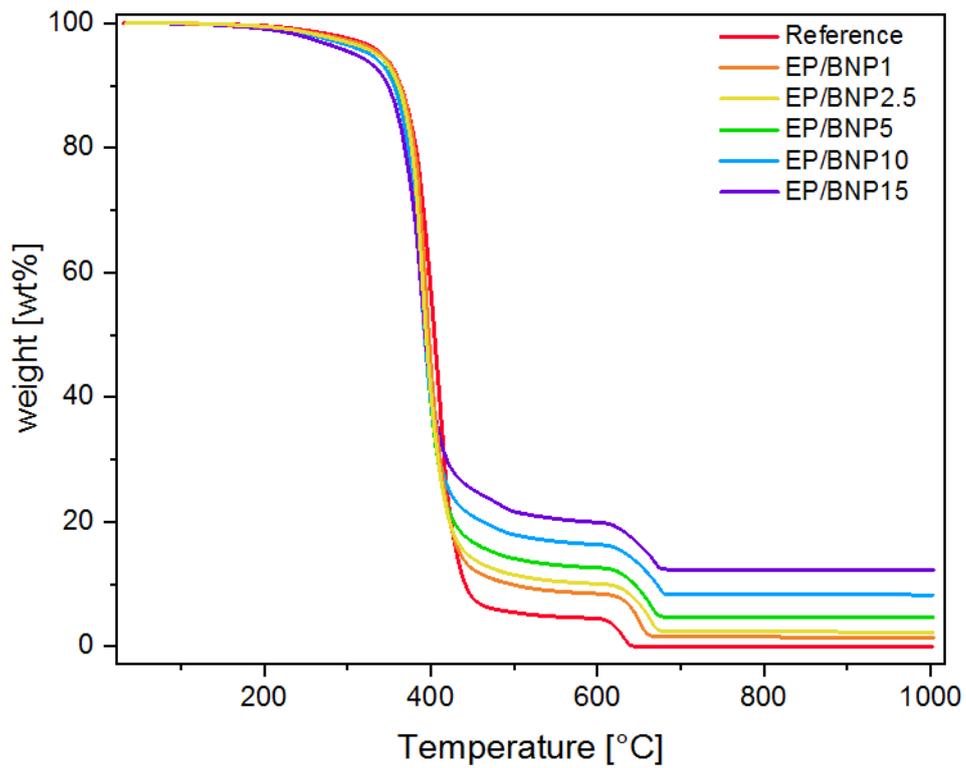
Comparison of the crosslinking density values of first run with second run in Table 1 and Table 2 shows that for all compositions, the crosslinking densities are shifted to higher values while G_e shows a considerable decrease. Following the argumentation of Pohl et al. [1], a decrease in G_e values implies that the response of the network is more entropic. High values of G_e during the first measurement implies that the elastic response of samples at rubbery state was govern more energetically. According to Pohl et al., energy contribution G_e can be originated from physical entanglements and intermolecular forces. Thus, a decrease of G_e values in the second run implies that by exposure to high temperature, chemical crosslinks replace the physical interactions.

unfilled epoxy in the second run shows 10% increase in glassy state storage modulus compared to the first run. Nevertheless, for EP/BNP15, the difference between glassy state modulus in first and second run is only around 2%. Also, the increase of crosslinking density in second measurement for EP/BNP15 is small compared to unfilled epoxy and other compositions. It is noteworthy that 5wt% nanocomposite(EP/BNP5) has a distinctive behavior as exposure to high temperatures affects the mechanical properties of this composition more than others: The measurements in second run show that both crosslinking density and glassy-state modulus reaches the maximum value among all other compositions. In composites less than 5wt% (EP/BNP1 and EP/BNP2.5), the changes in crosslinking density is not considerably large. Thus, somewhere between 5wt% and 10wt%, the crosslinking density starts to decrease and reaches its minimum value at 15wt% particle concentration. Therefore, a particle concentration between 5% to 10% appears to be a critical composition. The same tendency is

observed in glassy state modulus from the second run. At low concentrations, the glassy state modulus increases and reaches a maximum value for EP/BNP5 then shows a slight trend of decrease for higher concentrations. The reason behind the behavior is not yet understood. However, a concentration threshold makes it reasonable to assume two competing effects of network formation, resulting a higher crosslinking at a BNP content between 5% and 10%.

SM4. Thermogravimetric analysis

To characterize the pyrolysis behavior (thermal decomposition) of the materials thermogravimetric analysis (TGA) was employed. Figure X shows the mass loss rate curves of a pure epoxy and nanocomposites with various BNPs content. A minor decomposition process of approximately 0.2 wt% for the unfilled epoxy to 0.7 wt% for the nanocomposite with the highest BNPs content at ca. 150 °C corresponds to the pyrolysis or desorption of the anhydride, which did not take part in the cross-linking reaction. Furthermore, at ca. 250 °C another decomposition reaction is observed as a change in the mass loss curve of about 2.5 to 4 wt% for the pure EP to the EP/BNP15, respectively. This results from the thermal degradation of the un-reacted DGEBA monomer. The decomposition products at 150 and 250 °C were investigated with a Mass Spectrometer (MS). At the lower temperature the gas contained CO₂, which is a typical decomposition product of an un-reacted anhydride bonds, whereas at the higher temperature phenyl group was detected, resulting from a decomposition of the un-crosslinked DGEBA monomer. A more detailed discussion about the TGA-MS results will be published elsewhere. The main step of approximately 90 wt% for EP, decreasing with increasing BNPs content to 70 wt% for EP/BNP15, corresponds to the degradation temperature (T_{deg}) of the samples. A shift of the T_{deg} from approximately 408 °C for EP to 388 °C for EP/BNP15 indicates that the introduction of BNPs causes an earlier decomposition of the composites, which might result from a change in the network structure, as the nanofiller is added to the matrix. The last step in the mass loss curve for all the samples corresponds to the oxidation of the material. Lastly, the incorporation of the BNPs leads to an increase in the char yield as expected than the inorganic BNP do not decompose completely. This clearly proves that all experiments with temperatures up to 200°C are not superimposed by problems of the thermal degradation of the different networks.



1. Pohl, G., H. Goering, and D. Joel, *ON THE DETERMINATION OF NETWORK DENSITY IN POLYURETHANES*. *Plaste und Kautschuk*, 1983. **30**(4): p. 196-200.