Influence of the epoxy/amine stoichiometry on the thermomechanical properties of nanocomposites based on high T_g epoxy and organophilic clays

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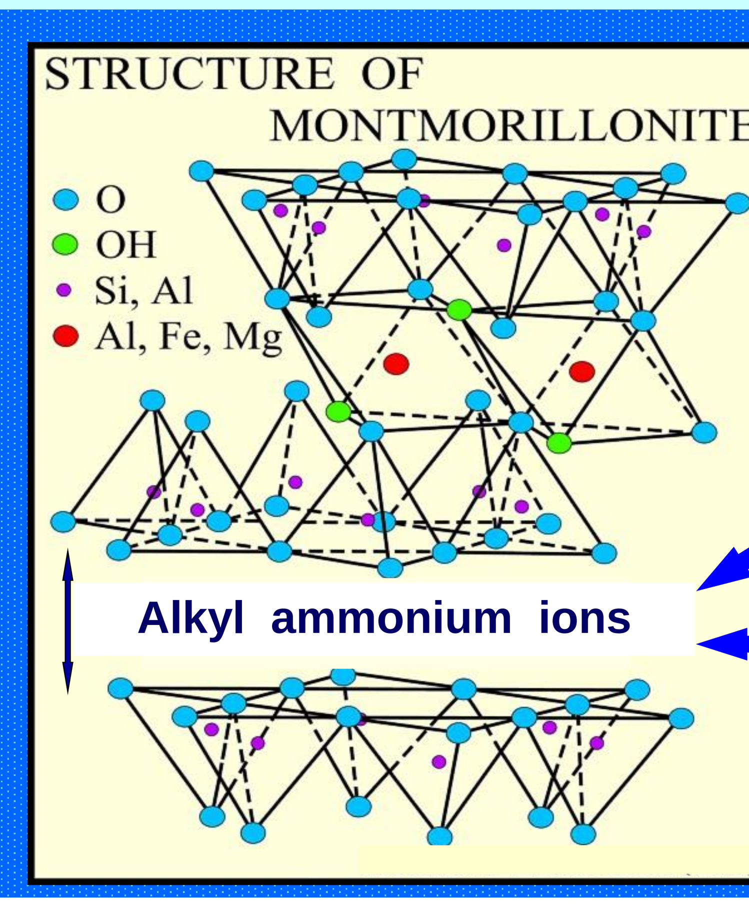
INTRODUCTION

In layered silicate-epoxy nanocomposites organic modification of the silicates makes them compatible with the epoxy which intercalates into the clay galleries. The effect of clay dispersion on epoxies of high T_g is not clear. Decreases of the epoxy T_g have been frequently reported. The presence of clay may cause stoichiometry imbalances that conduces to the formation of imperfect networks.

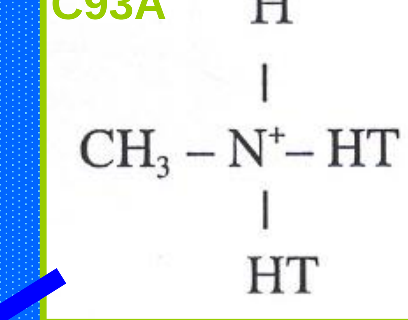
OBJECTIVE

To study off-stoichiometry effects in clay-epoxy nanocomposites by analyzing: its influence on curing, glass transition temperature, thermomechanical and mechanical properties of the nanocomposites.

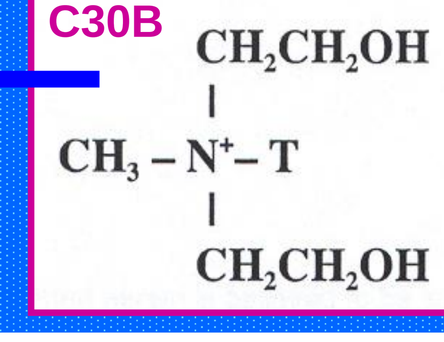


CLOISITES

C93A



C30B



T≡ tallow, HT≡ hydrogenated tallow: 65% C18, 30%C16, 5%C14

EXPERIMENTAL

Dispersion: Clay was dispersed in DGEBA at 120ºC Vacuum 80ºC. Adition of DDM 2min. Sonication.

Curing protocols

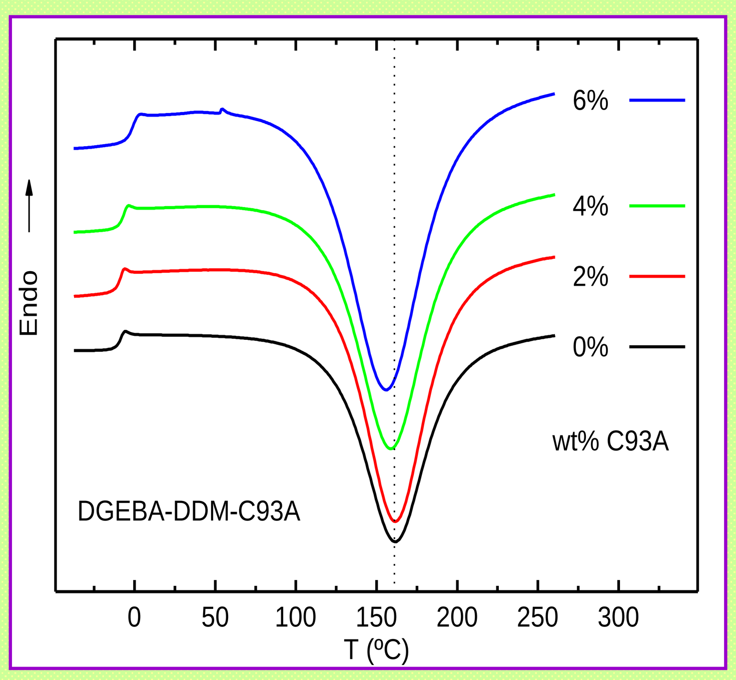
- **I** dynamic curing in the DSC at 10ºC/min
- **II** curing in oven: 2h-120ºC + 1h- 180ºC

Materials

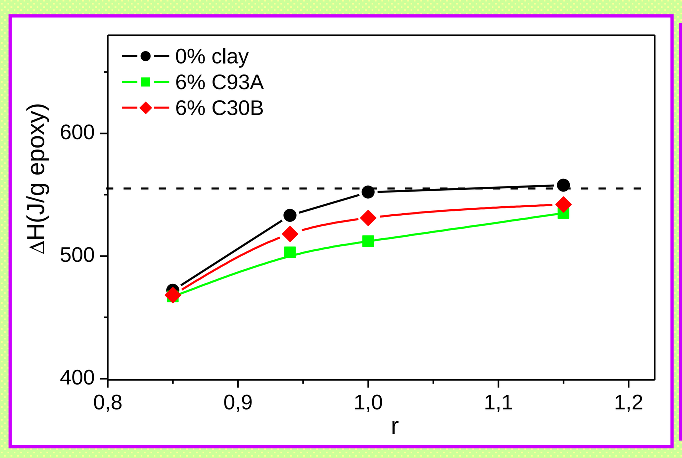
- **Cloisites:** C30B and C93A
- Diglycidyl ether of bisphenol A, **DGEBA**
- 4,4'-diaminodiphenylmethane, **DDM**
- **Stoichiometric ratio: r = HN/-O-** = 0.85 to 1.15

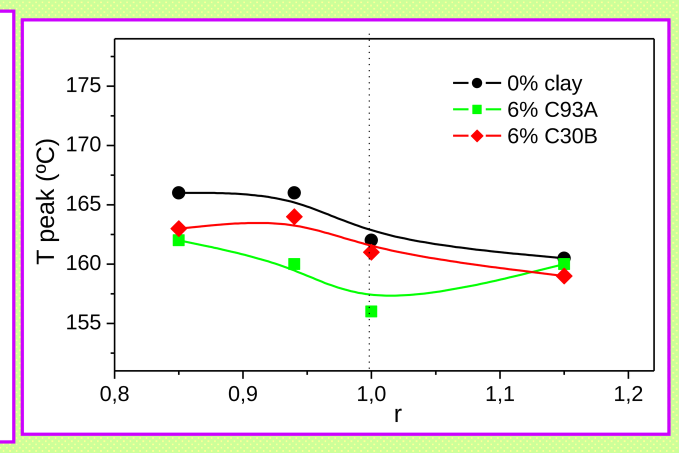
RESULTS AND DISCUSSION

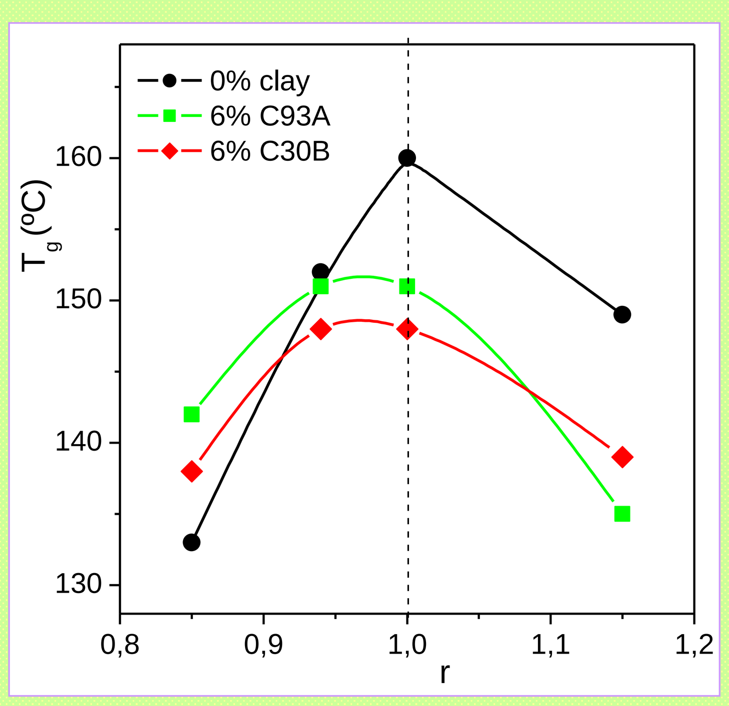
DSC: Dynamic curing of clay-epoxy dispersions



C93A-DGEBA-DDM and C30B-DGEBA-DDM the exothermal peak temperature shifts to lower values → the clays accelerate the curing reaction





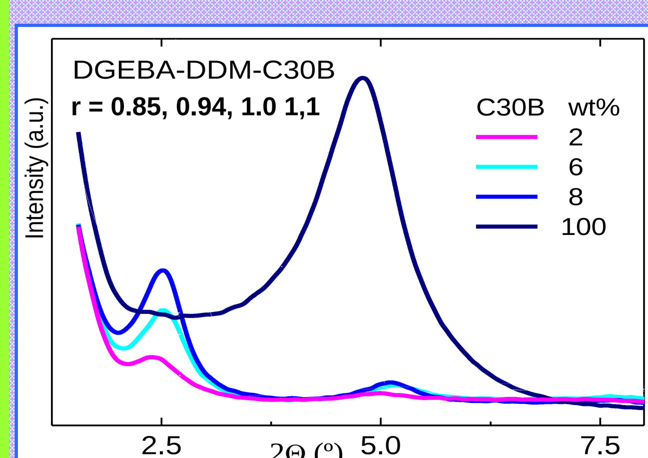


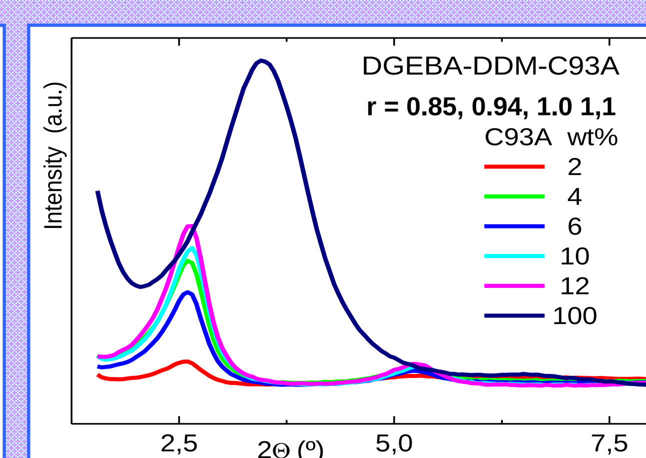
ΔH (J/g epoxy) is lower in nanocomposites than in neat epoxy for r >0,85. The lowest values of ΔH (J/g epoxy) were observed in C93A nanocomposites.

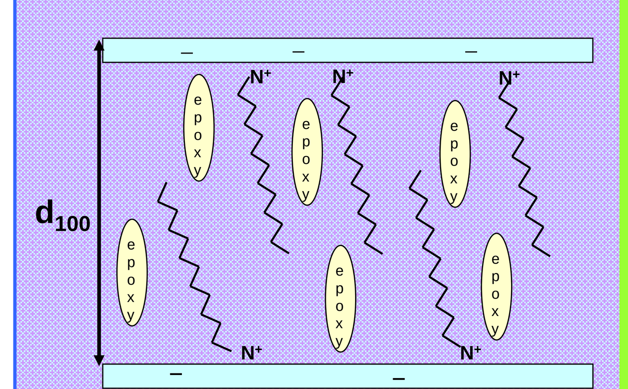
The curing reaction slows when r increases

- Neat epoxy thermosets: T_g maximun appears at r = 1
- Nanocomposites: the maximum of T_g occurs at r < 1
- For r > 0,94 the presence of clays lowers T_g
- For r ≈ 0,85 the presence of clays raises T_g

WAX-ray Diffraction of nanocomposites





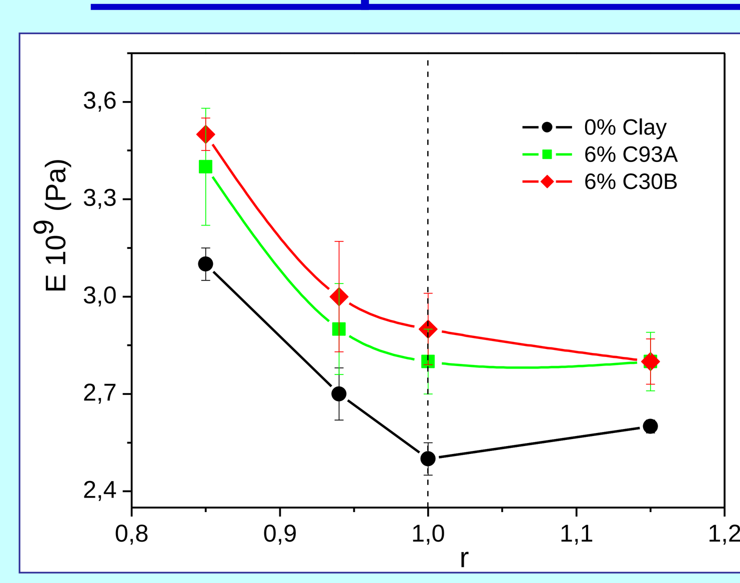


Basal distance d_{001} (nm)

Clay	neat clay	clay-epoxy nanocomposite
C30B	1.82	3.4
C93A	2.56	3.3

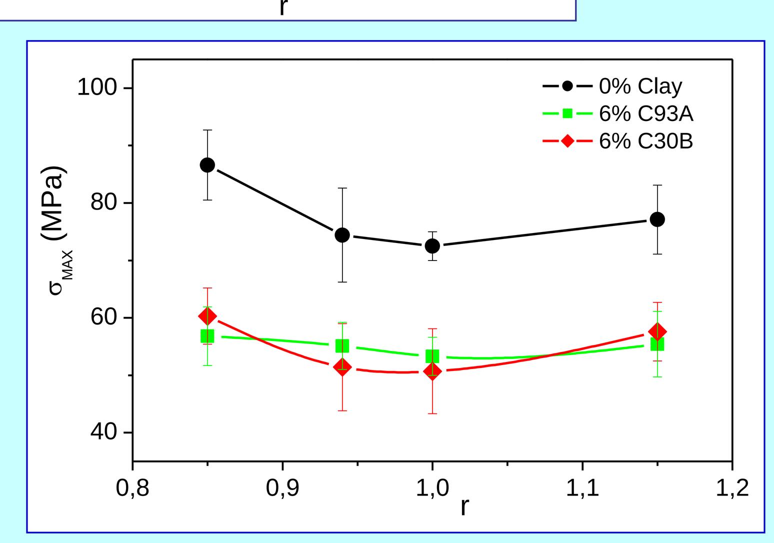
Nanocomposites show intercalated structures Δd_{001} C30B > Δd_{001} C93A

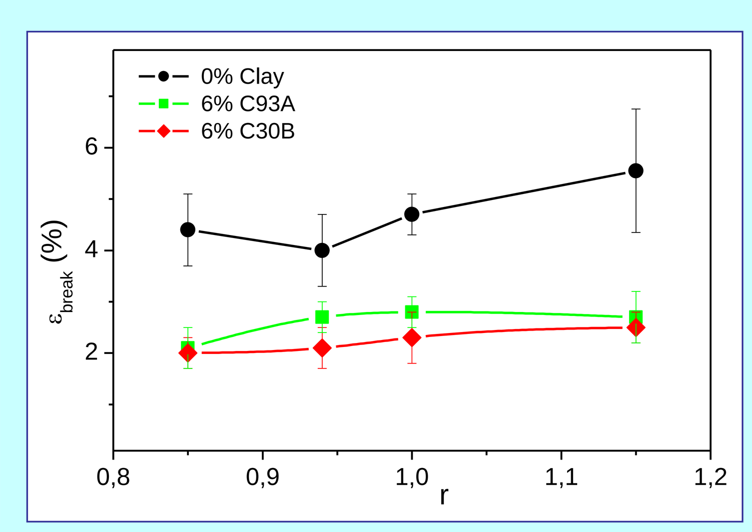
Nanocomposites cured under protocol II: Tensile tests at 25ºC



Glassy state: the highest modulus is observed in epoxy-rich compositions (r < 1).

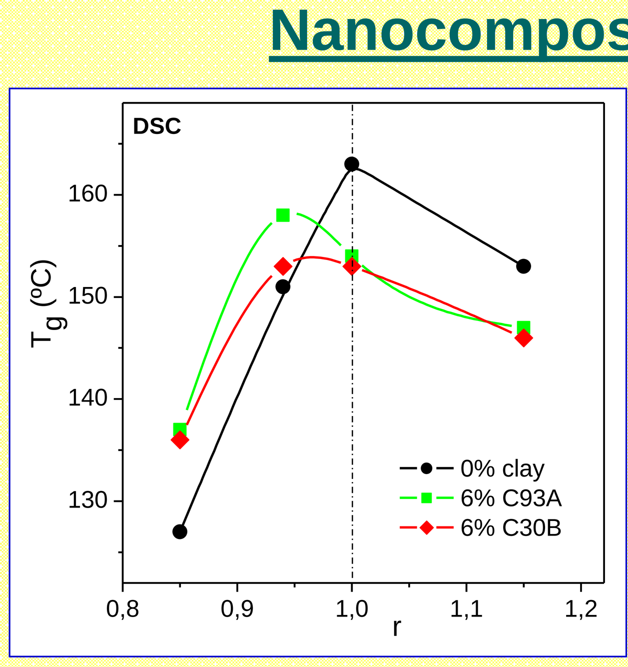
A minimum in the modulus appears at r =1 for neat epoxy thermoset, this behaviour has been explained in base of network topology and packing density.

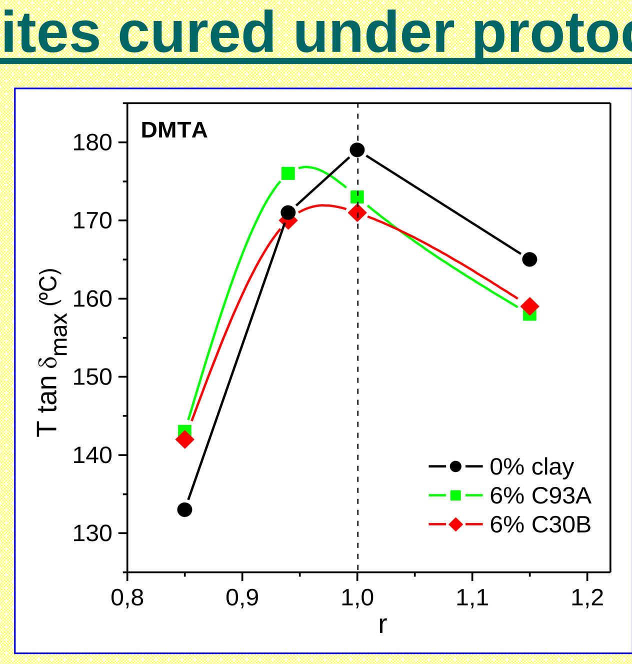


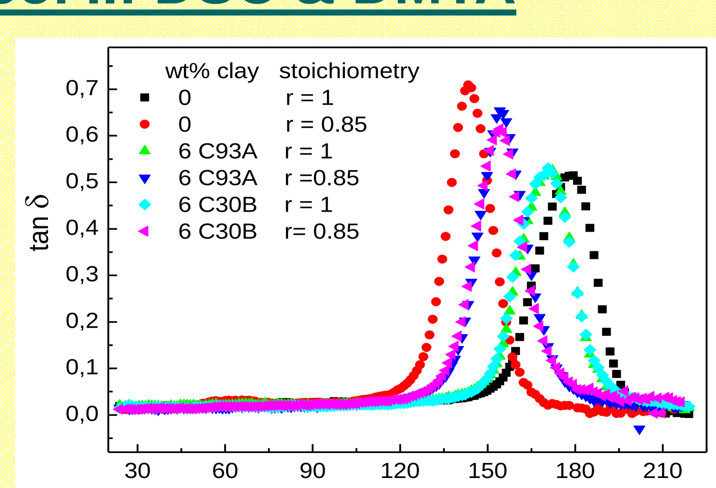


Glassy state: clay-epoxy nanocomposites show higher modulus, lower strenght and lower elongation to break than neat epoxy thermosets

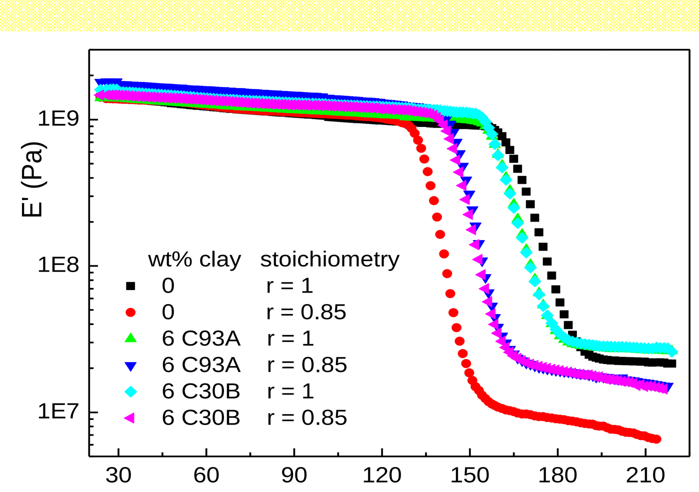
Nanocomposites cured under protocol II: DSC & DMTA

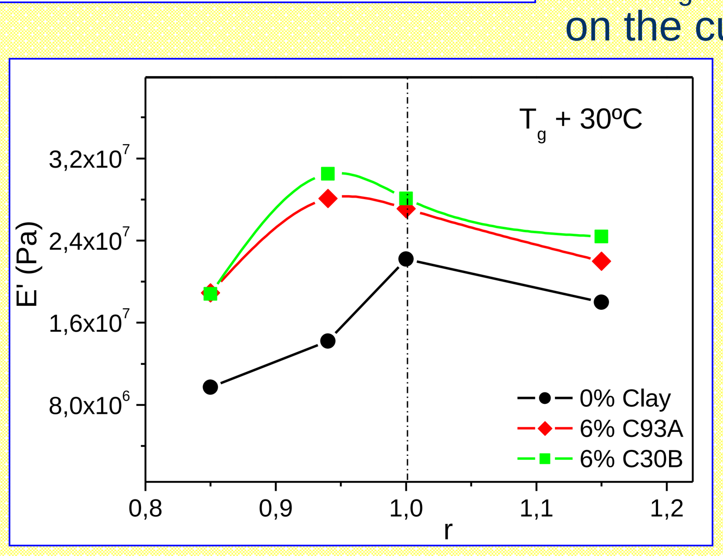






The T_g-r trend is almost independent on the curing protocol





E'_{rubber} and T_g show similar behaviour: maximun values in T_g and in E'_{rubber} are coincident → highest crosslinking density

Rubber state: clay–epoxy nanocomposites have higher E'_{rubber} than neat epoxy thermosets for r ≤ 0.94, but lower for r > 1.

CONCLUSIONS

- **Stoichiometry is an important factor determining epoxy thermoset properties, both in epoxy neat thermosets and clay-epoxy nanocomposites.**
- **Similar property-stoichiometry trends are observed in epoxy neat thermosets and clay-epoxy nanocomposites, but the behaviour of nanocomposites is shifted toward lower stoichiometric ratios.**
- **The presence of clays modify the stoichiometry, curing and properties.**