Polymer-based nanocomposites with nanoclay

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Abstract. In the last few years a huge number of papers were published in the topic of
nanocomposites. Mixing some kind of nanoscale additive into a polymer matrix provides an
extra advantage to create polymer-based nanocomposites with better properties. The clay
particles, like montmorillonite, can improve thermal, mechanical, rheological and barrier
properties and conductivity, although the structure of the platelets greatly influence their
behaviour. Moreover, nucleating and synergetic effect can occur, which also accomplish the
properties. This review discusses the properties changes of the polymer nanocomposites
reinforced with montmorillonite (MMT).

1. Introduction

Polymer nanocomposites can be widely used in many applications in the vehicle industry. The
nanoadditive have at least one dimension smaller than 100 nm. The nanoscale dimensions make the
macroscopic properties dimension-depending ones. The properties can be changed easily with only few
percent of nanoparticles [1-3]. Some parts of the mechanism of the nanomaterial effect have been
revealed, but not at all.

The influential factors come from both the matrix and additive properties, their proportion in the
mixture, the processing technology and parameters, e.g. processing temperature, applied pressure [4-7].
The cohesion between the matrix and the additive materials is essential. For this reason surface treatment
is required of the nanoadditives [8-10]. Carbon nanotube, graphene and several sort of clay particles
(ceramics) are used as nanoscale additives. Montmorillonite is mostly used and also kaolinite, bentonite,
hectorite, sepiolite, laponite etc. are used as nanoclay [11-12].

This work also summarises the main property changes in the nanocomposites and marks out a new
way for our research.

2. Structure of MMT

MMT is a very soft, fine-grained phyllosilicate, member of the smectite group. It has sandwich shape
from silica and alumina sheets. In Figure 1. its structure is shown in scanning and transmission electron
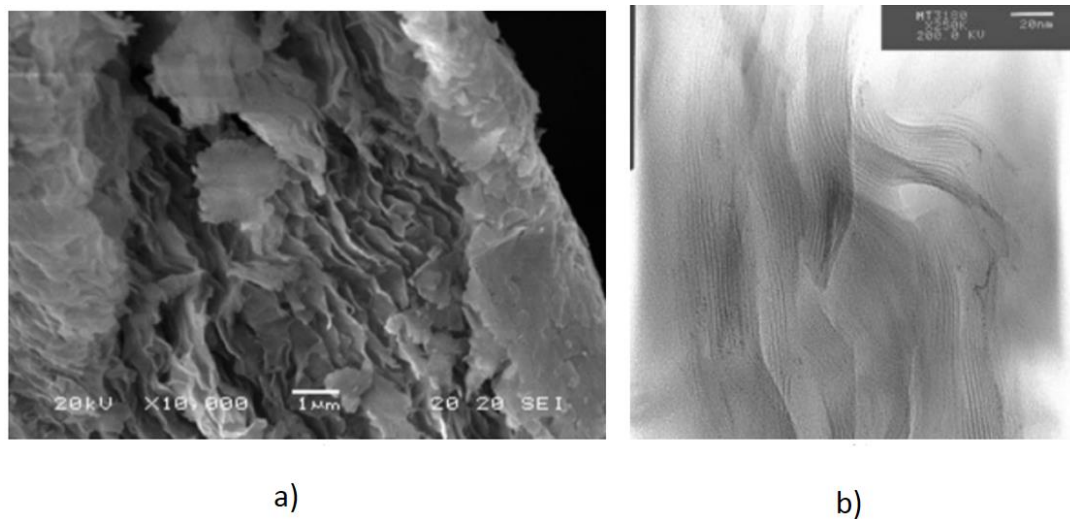microscopic (SEM, TEM) pictures.

Figure 1. Pictures of MMT: a) SEM, b) TEM [13-14]

It can form by precipitation from water solution as microscopic crystals. Chemically, it is hydrated sodium calcium aluminium magnesium silicate hydroxide $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$. It can contain other cations, like potassium or iron [15].

The structure and dispersion of the clay will affect the properties of the nanocomposite. According to the state of dispersion, the clay can be in immiscible, intercalated or exfoliated form (Figure 2.) [16].
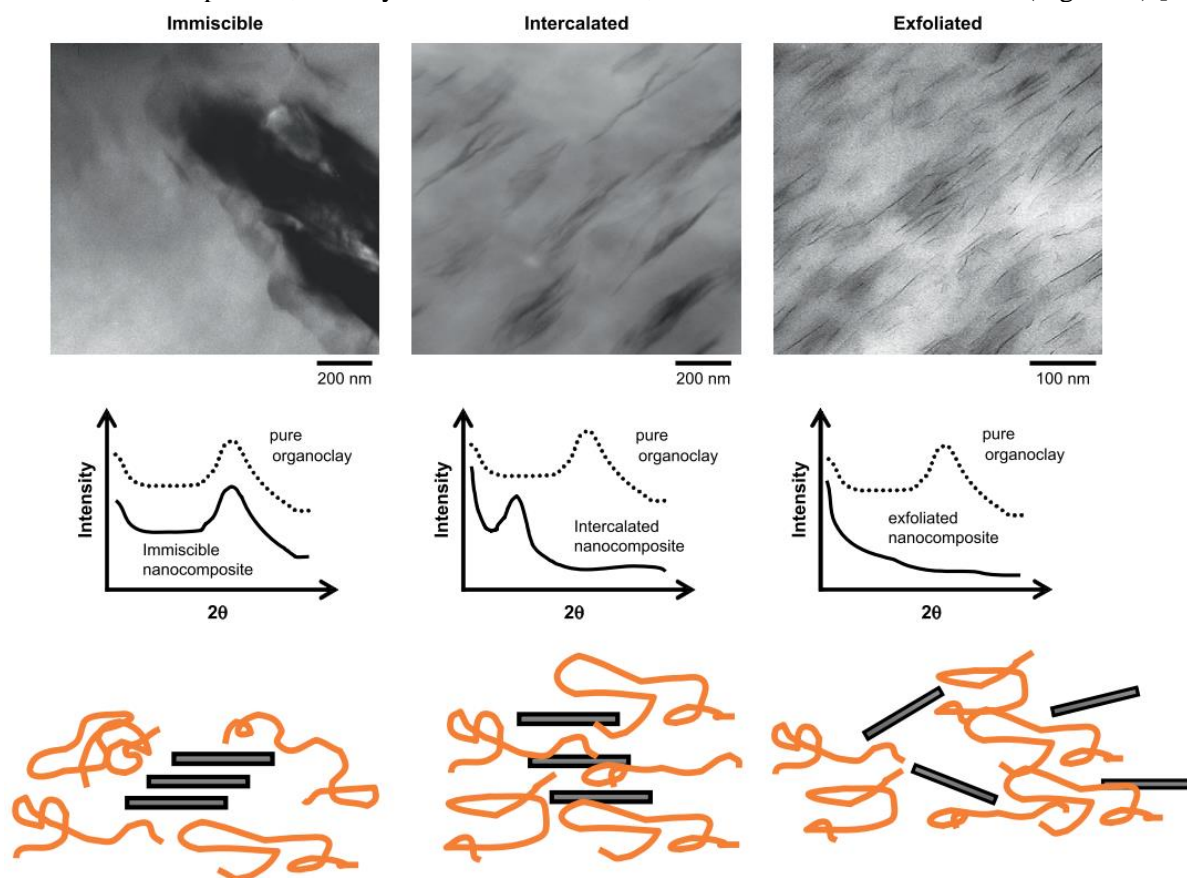

Figure 2. The structure and dispersion of the clay in polymers [16]

The immiscible particles have the worst properties, because the matrix material cannot get into the clay platelets. Intercalated form means a well-ordered structure with interaction between the layers and

the matrix material. Exfoliated montmorillonite has delaminated form, the additive can disperse in the matrix well. The state of the clay can be organophilized or as it is (native). The clay is mined, and it can be modified by organic substances in order to achieve better interaction between the materials [3, 6].

3. Matrix polymers

Matrix material can be thermoset (epoxy or polyester resin) or thermoplastic [17-18]. In the field of thermoplastics, the most used polymers are polystyrene (PS), poly(lactic acid) (PLA), polyethylene terephthalate (PET), polypropylene (PP), polyamide (PA), polymethyl methacrylate (PMMA), poly e-caprolactone (PCL), polyvinylidene fluoride (PVDF), polyethylenglykol (PEG), polyethylene (PE), acrylonitrile butadiene styrene (ABS), polyvinyl acetate (PVA), polyethylene oxide (PEO), polyimide (PI), etc. [19-24]. Matrix polymers influence the processing technology and determine the application field (e.g. the operating temperature).

Preparing polymer-based nanocomposites can be in different methods. Precipitation means that a suspension or solution of modifier is added to the polymer solution. The solution should not dissolve the polymer. In sol-gel reaction, the nanocomposites are made by crosslinking from polymer/oligomer solution. With in-situ polymerisation, layered silicate nanocomposites can be prepared. In this reaction the monomers transform into polymer chains among the layers. Melt intercalation means that polymer powder or granulates and silicate are mixed together while the polymer is melting. An often-used method is also the exfoliation, in which nanoadditives are mixed to the polymer melt. The shear forces separate the silicate layers, so the cohesion between the matrix polymer and additive are assured [16].

4. Properties of the nanocomposites

Montmorillonite-based nanocomposites are relatively new materials, so the behavioural changes of the properties should be investigated.

4.1. Thermal properties

Generally, MMT increases the heat stability, while the incorporation of nanoclays reduces the mobility of the polymer chains [25]. Nanoclays also hinder the out-diffusion of the volatile substances [2]. As it is shown in Figure 3., the same percent of weight loss occurs at higher temperature adding MMT to polystyrene (PS). The number after PS means the MMT content, and FPS5 was made by another preparing method (dry mixing) with 5 wt% of MMT. The other three sample were prepared by solution blending method.
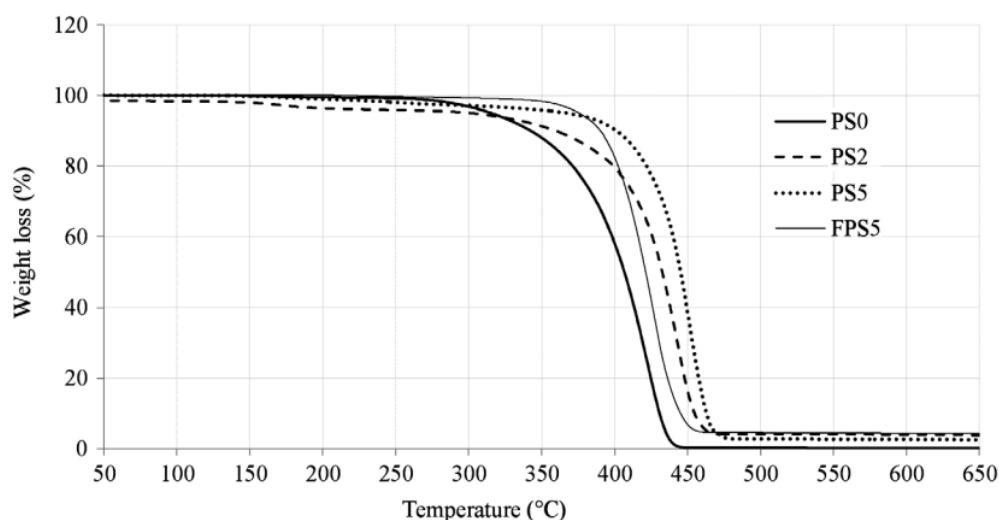

Figure 3. TGA curves of MMT filled PS [2]

In several cases intercalated MMT accelerates biodegradation of compostable materials (PLA), because the clay accumulates heat, so it functions as heat source [26]. The characteristic temperature

values can also change, e.g. glass transition temperature (Tg) or melting temperature (Tm). The segmental motion occurs only at higher temperatures at an increased Tg, so the matrix material will be stiffer in this region.
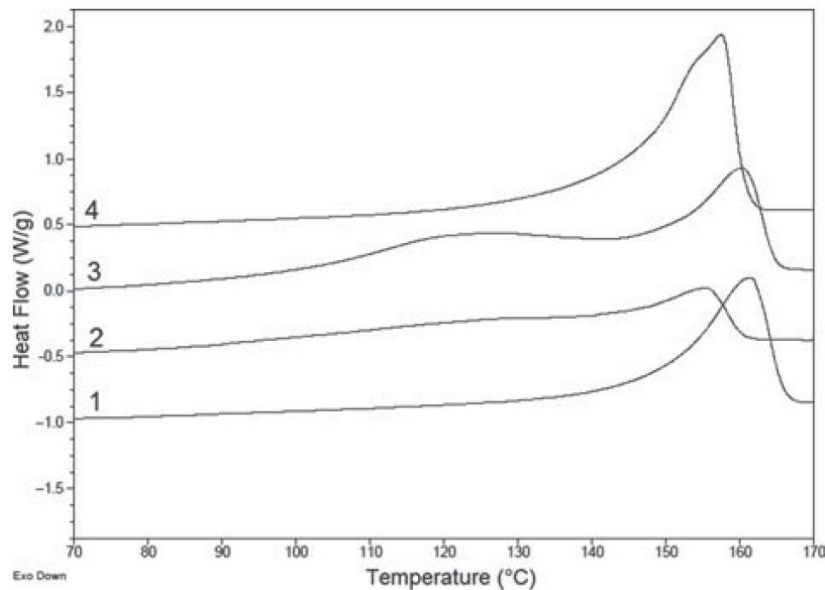

Figure 4. DSC curves of polypropylene (PP) with different clays [26]

In Figure 4. the melting ranges can be seen by Differential Scanning Calorimetry (DSC) method. **1** is for PP without clay, the other three curves for PP with clay: **2** for 16.9 wt% of Cloisite 30B, **3** for 1.1wt% of Cloisite 15A, **4** for 9.9 wt% of Claytone HY. Adding clay to the matrix polymer, the melting range is broadening and also the crystalline structure changes [26].

4.2. Barrier properties
The increased barrier property means reduction in gas (oxygen or carbon dioxide) or water vapor permeability [27]. The oxygen permeability plays an important role in oxidative degradation.
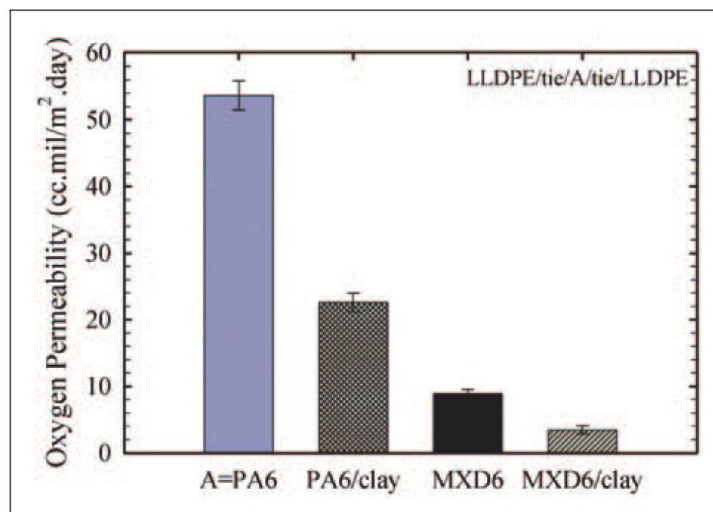

Figure 5. Oxygen permeability of PA/LLDPE blends with and without clay [28]

In Figure 5 and 6, it can be seen that with addition of clay, the oxygen permeation and the water vapor permeation of polyamide 6 (PA6)/linear low density polyethylene (LLDPE) and poly(m-xylene adipamide) (MXD6)/LLDPE blends reduces at least by 50% and by 27%, respectively [28].
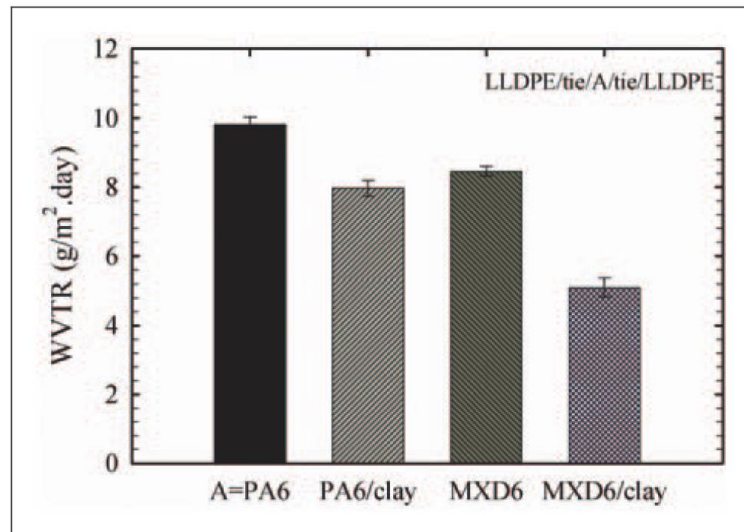
Figure 6. Water vapour transmission rate of PA/LLDPE blends with and without clay [28]

PVA membranes with chitosan and MMT content show improved methanol barrier properties [29]. Adding MMT is also an efficient method to prevent water uptake, which tenderize plastics [30]. Clay can block the flow of water the same way, as it does with heat.

4.3. Nucleation effect

Montmorillonite can function as nucleation agent. In general, crystallinity in polymers will be more dispersed and occurs at higher temperature [26, 31, 32]. In some cases, crystallinity slightly increases [32-33]. It is revealed that nanofiller content decrease the characteristic time of crystallisation of the polyamide (PA11) matrix in isothermal conditions, and that the nucleation efficiency of organophilized montmorillonite (OMMT) is higher than of sepiolite (Figure 7.) [34].
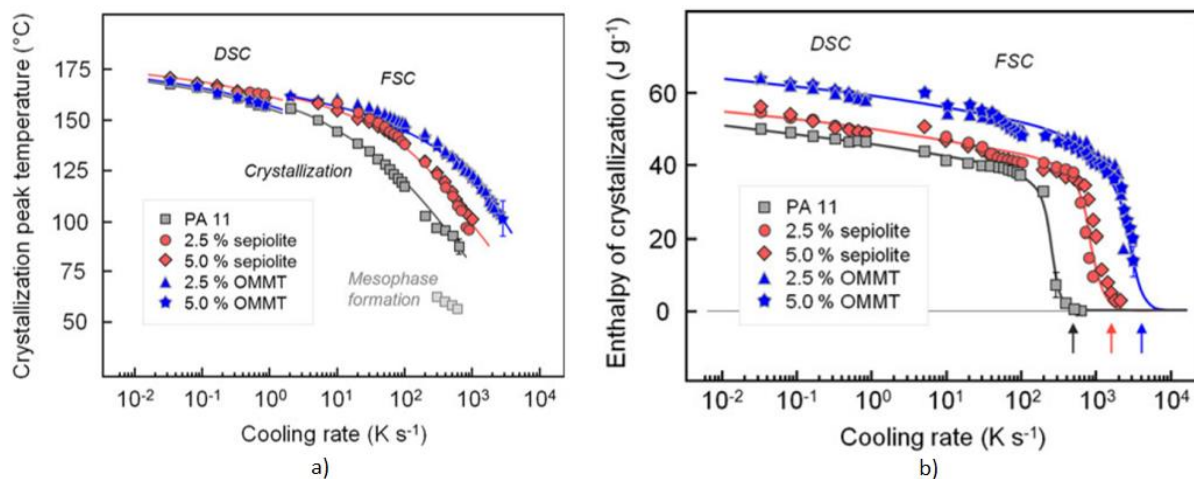

Figure 7. Peak temperature (a) and enthalpy of crystallisation (b) of PA11/clay nanocomposites [34]

During non-isothermal measurements, nanoclays are also effective nucleating agents, so their presence reduces the degree of super cooling required for crystallisation [35].

4.4. Mechanical properties

Mechanical properties of polymer/MMT nanocomposites are the most investigated ones. Tensile properties significantly depend on the dispersion characteristics of montmorillonite particles in polymer

matrix [36]. The MMT improves the macro- and microstructure of the composite. The tensile properties will be better, both tensile strength and elongation at break increases (Figure 8.) [37].
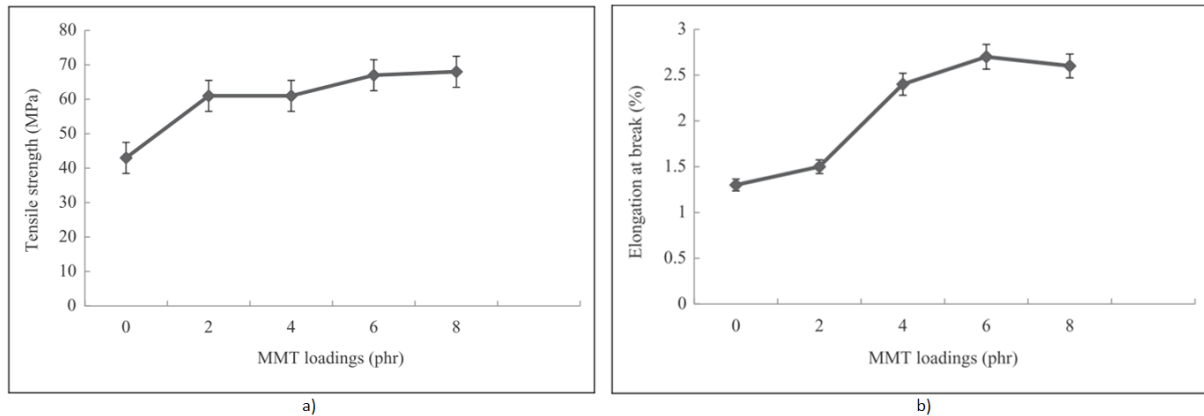

Figure 8. Tensile strength (a) and elongation at break (b) of MMT loaded PLA [37]

Adding MMT into PA6, the creep recovery, storage modulus and also loss factor decreases, explained by the reduced molecular motion [38]. Properties, like Young's modulus is seem to have a maximum value, which occurs at 3-5 wt% MMT content (Figure 9.) [37, 39].
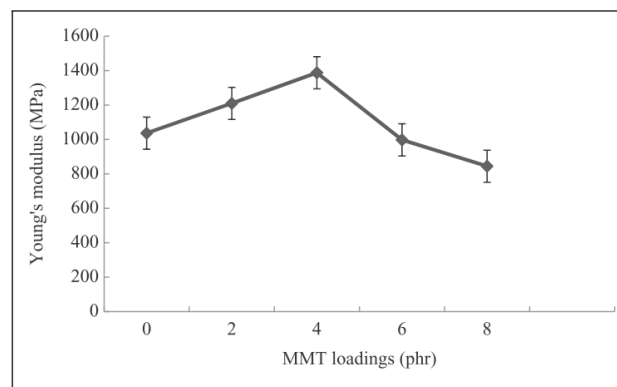

Figure 9. Young's modulus of MMT loaded PLA [37]

The structure is likely to transform above a certain percentage of clay, from intercalated or exfoliated into aggregated parts. However, MMT is a soft clay, the hardness and the fracture toughness of the composites changes [40-42].

4.5. Rheological properties
The melt flow index (MFI) decreases with the increased filler content (Figure 10.) [31]. The nanofillers were bentonite (Nanoclay 1) and montmorillonite (Nanoclay 2). It means that the viscosity increases in this region. In low frequency region, higher complex viscosity of the nanocomposites is observed compared to the neat polymer, while there is strong interaction between the matrix and the clay [21]. These interaction hinder the motion of polymer chains. The nanocomposites show dominant shear thinning behavior. Therefore at higher frequencies, the viscosity curve sharply decreases.
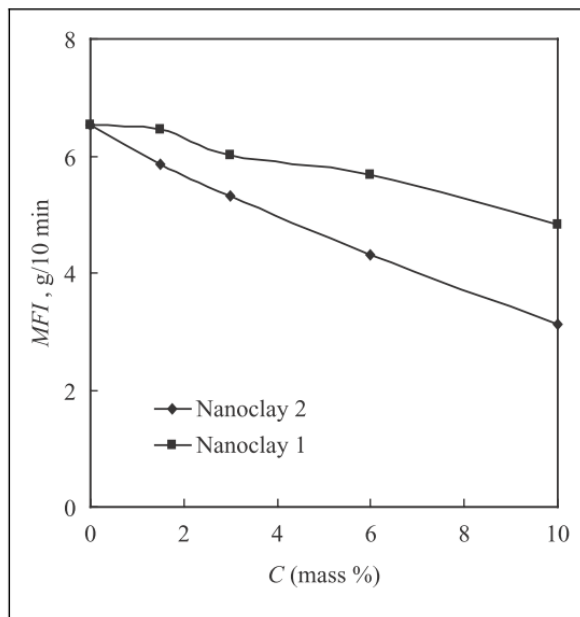
Figure 10. MFI values of poly(vinylidene fluoride-co-hexafluoropropylene with clay content [31]
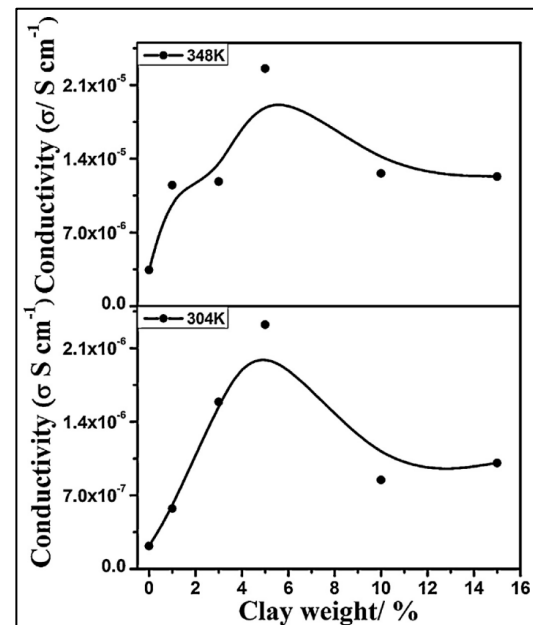

Figure 11. Dc-conductivity of PEG-PU/PMMA-LiClO$_4$/MMT composite with clay content [43]

4.6. Conductivity

Ionic conductivity increases up to 5 wt% MMT content, then it decreases (Figure 11.) [43]. In solid polymer-salt-clay electrolytes, ionic transport is associated with the segmental motions [44]. The intercalated MMT structure is more favorable for high conductivity, while exfoliated MMT can be used for low permittivity ion conducting electrolytes [5, 45]. Also proton conductivity increases adding montmorillonite [30].

4.7. Synergistic with other additives

Montmorillonite is often used with other additives, e.g. flame retardant, carbon nanotube, graphene, silver to reach the synergetic effect. Addition of secondary filler can provide additional functionalities to the matrix [24]. For instance, MMT improves the compatibility between the polymer and alumina trihydrate (flame retarder), so the flammability is ameliorated [46]. Moreover the antibacterial effect of silver (Ag) containing film can be improved [47]. The same way, electrical, barrier or mechanical properties can be modified by synergetic effect [11, 48].

In Figure 12. the voltage amplitude is shown in function of time. Sepiolite and montmorillonite was added to low density polyethylene (LDPE). The overall clay content was 5 wt%. The lifetime of the nanocomposites increases with clay content. Moreover with the use of more types of clay (with the same overall clay content) higher values are shown [11].
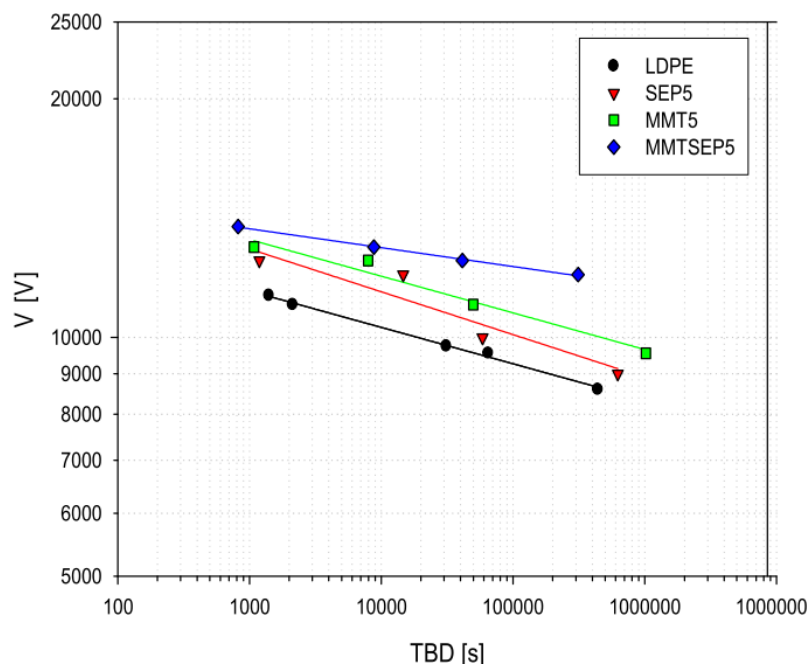
Figure 12. The lifetime diagrams of LDPE/clay composites [11]

5. Conclusion
Clay particles, like MMT, can improve thermal, mechanical, rheological, barrier properties and conductivity, although the structure of the platelets greatly influences their behaviour. Moreover, nucleating and synergetic effect can occur, which also improve the properties. The evaluated papers provide a solid foundation for the investigations. In conclusion, 3-5 wt% additive is enough for the modification, above this percentage the structure of MMT can transform. The most used polymers are polyamide (PA) and polypropylene (PP).

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