

Polymers in wire and cables - past, present and future

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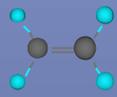
Thanks for the invitation. My perspective is materials science (polymer science and engineering). I am not an electrical engineer. In these days we all realise how difficult it is to tell about the future. I will, however, try to do so on the basis of trends within my discipline, also looking a little bit on the demands from the electrical engineers.

Outline of talk

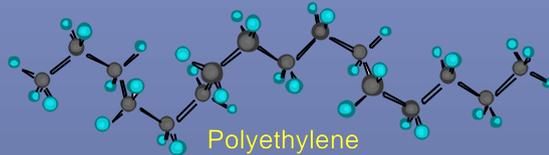
- What is a polymer and a polymeric material (small piece of chemistry and physics)
- Short polymer history (when and why it happened)
- Overall trends in past, present and future
- What will happen with PVC?
- Crosslinked (and thermoplastic) polyethylene: known trends (clean, efficient crosslinking, stable; possible: metallocene-catalysed polymers)
- Liquid-crystalline polymers?
- Polymer nanocomposites?
- Conclusions

I will start with presenting a little of chemistry and physics on polymers, continue with the history (a good tool to make a forecast) and current trends in polymer engineering. Then we will discuss PVC (the largest polymeric material used in wire and cable). The next most important material is PE and the possible trends including the possibilities with metallocene technology will be discussed. I will finally present some emerging materials that may find use in wire and cable technology.

What is a polymer?



Ethylene

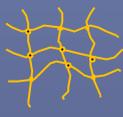


Polyethylene

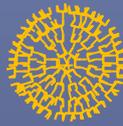
Molecular architectures



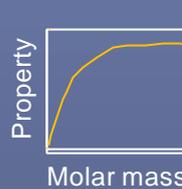
Thermoplastic



Rubber
Hot set



The struggle



A polymer is a compound consisting of many (that may be 100 000!) repeating units linked together by covalent bonds (example polyethylene).

Many different architectures can be made (linear, short-chain branched, etc).

Copolymers, having two or more repeating units are also made to achieve certain wanted properties.

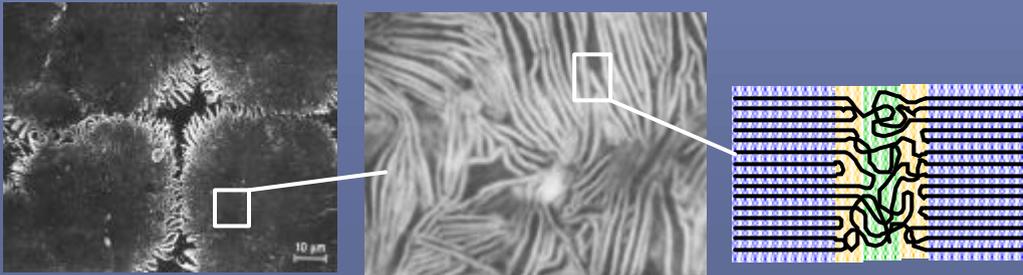
There is always a competition between the wish to have a material which is readily processed (low viscosity) and at the same time has excellent final properties (high strength for instance); see example.

What is a polymeric material?

Polymer(s) + Additives + Processing method



Polymeric materials,
i.e. plastics, rubbers, coatings, fibres



Structure hierarchy of polyethylene

Properties are determined by:

- the polymers used, it may be more than one, making polymer blends
- the additives, like antioxidants added in very small quantity to prolong life 50 fold; fillers, stabilizers, fibers, flame retardant substances, etc.
- the processing method used: A plastic bag is made of PE. Exactly the same material can be spun to a very stiff and strong fibre (almost as stiff as steel, 220 gpa!).

Polymeric materials find use as plastics, rubbers, coatings and fibres.

Structure can be complex and the properties are sensitively dependent on the morphology. So morphology control is vital for successful use of polymeric materials.

The picture shows solid state of PE. Leftside shows the spherulites, almost visible with the eye, this is via an optical microscope. Then, center, up in magnification by electron microscope, the crystals can be seen, surrounded by amorphous material. Further in detail, (right, a drawing!!) the laying of the molecules is sketched.

Properties very sensitively depend on this hierarchy of structures. Somebody has to study and to understand this to design the material to obtain the required properties.

Short polymer history



Before 1900, the polymers in use were from the nature (native polymers). These polymers were modified by some chemical reactions: vulcanisation (Goodyear); also the cellulose plastics.

The first wholly synthetic polymer was made by Leo Baekeland (Bakelite) from phenol and formaldehyde – a hot set - around 1905.

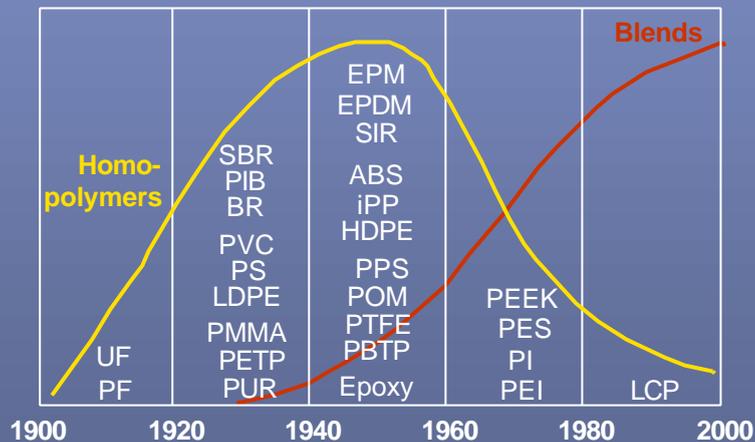
Synthetic rubber research in Germany and USA was early.

The polymer science was founded in the 1920s by the German chemist Hermann Staudinger. In the following decades a large number of the polymer used today were made for the first time. Polymer science developed strongly in the same time period.

Coordination polymerisation – a method to make regular polymers (linear PE, isotactic PP, etc.) came in the 1950s.

Since 1960s speciality polymers with high thermal stability (e.g. polyimide) and high stiffness and strength (Kevlar) have been made.

Introduction of new polymers



Introduction of new homopolymers (here indicated when they were first made) of general importance shows clear saturation; see peak in the 1950s.

New materials based on polymer blends (combining different homopolymers) is still growing.

The picture is not very true however. Exotic polymers is made extensively in the labs and occasionally find application in special fields such as photonics and medicine. Let us take another example, most relevant for you – PE (next slide)

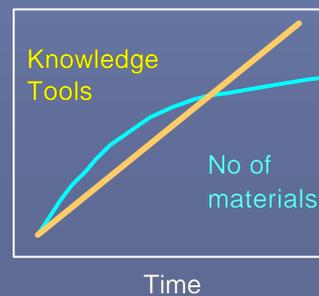
The polyethylene story



It is true that PE was first made in 1933 but as you see many important new versions of the same repeating unit has been made since. And in fact, as we stand here a new technology based on metallocenes (metal-organic compounds) is emerging.

Current overall trends

- More efficient use of current 100 000 materials (design, process simulation, materials selection, process control)
- Modification of existing materials by blending of different polymers, new additives (e.g. nanoparticles)
- Environmental aspects (think of freons, PVC)
- Very few real new polymers
- Polyolefins- single-site catalysts



More efficient use of existing materials, modification of existing materials by blending, adding new fillers, reactive processing in the extruder; environmental aspects; only a few new polymers; single-site technology.

The number of scientific papers produced in polymer science and engineering is still increasing so the knowledge and tools available for development work is increasing. It may be used also in this area of technology.

PVC - used in the future?

- Largest volume of all cable materials
- Excellent properties to a low price
- Environmental issues*
- Politics (similarities with nuclear power issue; myths)
- Conclusion: **Yes**; large efforts have resulted in major development of materials and more is to come (unbranched PVC and organic stabilisers).

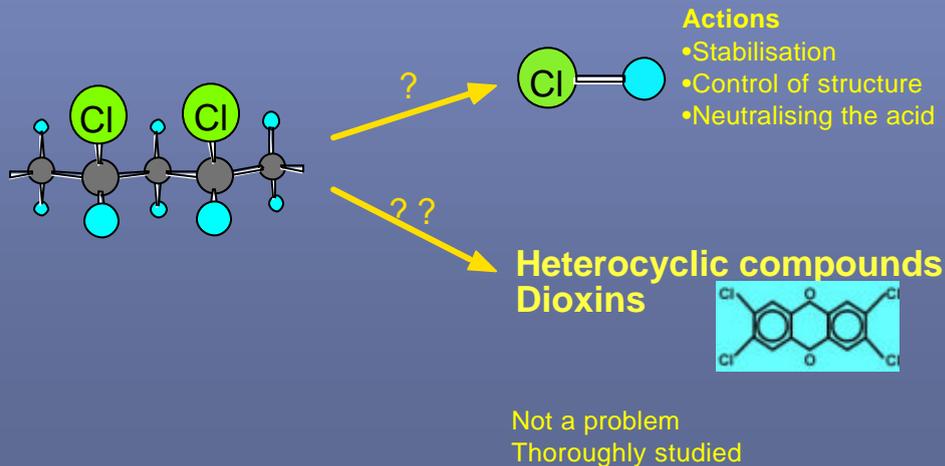
* Acknowledge.: Dr. Lena Lundberg
PVC Forum
Plastics & Chemicals Federation, Sweden

PVC is the dominant polymeric material in wire&cable. It has excellent overall properties and a low price. On the negative side - the environmental problems, which I will return to.

I think it is fair to state that the environmental issue is partly political. Some Nordic countries are militant and the wire&cable business should be PVC-free in a couple of years.

My conclusion is that PVC will be used, most of all perhaps because of its good overall properties and secondly (perhaps as important) because of the development of the material driven by environmental concerns. PVC replacement will occur in some Nordic countries.

Degradation of PVC



At moderate temperatures: formation of hydrochloric acid. Avoided (at low temperatures) by stabilisers; these being one environmental problem. Other means to reduce the tendency for degradation is by control of chain structure.

At high temperatures (incineration): risk of formation of certain heterocyclic compounds (dioxin). This has been very thoroughly studied and the consensus among scientists is that these substances are formed to some extent **independent** of the presence of PVC.

Stabilisation of PVC

- **Traditional** (and some still in use): Pb, Cd; not wanted
- **First major step:** Ca/Zn (much less toxic)
- **Final major step:** Organic stabilisers (only small amounts of Na); still expensive. **Problem is technically solved.**
- Chemical structure less susceptible to degradation



Branched - sensitive
Radical polymerisation



Linear-less sensitive
Anionic polymerisation

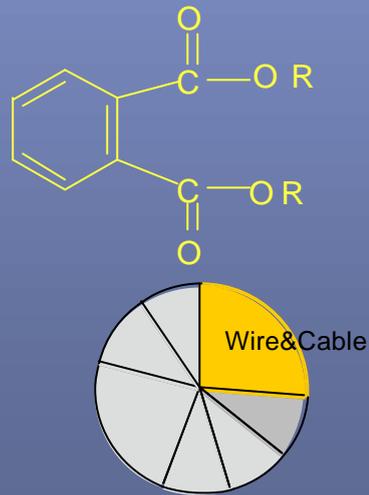
Traditionally made with metal compounds (lead and cadmium) but already calcium-zinc compounds in use are of much lower toxicity.

Wholly organic stabilisers have been developed but they are still expensive (not really on the market). The problem is technically solved.

PVC produced by radical polymerisation is branched and these branches are sensitising the material for degradation. Linear PVC (without the branches) of greater stability has been made on labs already. Such materials would need much lower concentrations of stabiliser.

Plasticizers

- Added to make the plastic soft, reduction of T_g
- Migration
- Phthalates
- Extensively studied
- DEHP (Di-2-ethylhexyl phthalate); previously used; Class 2 reproduction toxic; no environmental hazard.
- DIDP (Di-isodecyl phthalate); now used in cables; no hazards; **Problem solved.**



Source: ECPI

Added to make the stiff PVC soft by reduction of the glass temperature.

Migration is the problem from material perspective (embrittlement) and environmental point of view.

The effect on animals and human being has been extensively studied.

DEHP (used a lot in previous times) has no environmental hazard but is class 2 on reproduction toxicity. DIDP which is used in cables has no such hazards.

Can PVC be replaced?

- It will happen soon in Sweden and Denmark.
- Polyethylene seems to be a good candidate because possibility to control flexibility, low dielectric constant and low price.
- Flame retardant properties can be obtained by adding inorganic fillers and silicone elastomer to copolymers of ethylene.
- At high temperatures: silicone elastomer forms a tight inorganic/organic glass. The inorganic filler is however needed!

Can soft PVC be replaced (Sweden and Denmark)?

Polyethylene of low crystallinity can mimic PVC in some respects but not in all.

Flame-retardant recipes have been made. Polyethylene (copolymer) with inorganic filler (calcium-based) and silicon elastomer is one option. The silicon elastomer forms a tight glassy layer structure at high temperatures.

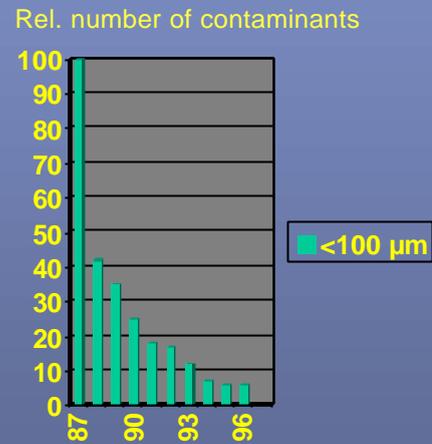
Crosslinked polyethylene-trends

- Cleaner
- Faster crosslinking (production)
- Thermally more stable
- Single-site catalyst technology; multistep?

Three different lines: cleaner, faster and thermally more stable.
In addition - the emerging single-site technology.

Cleaner

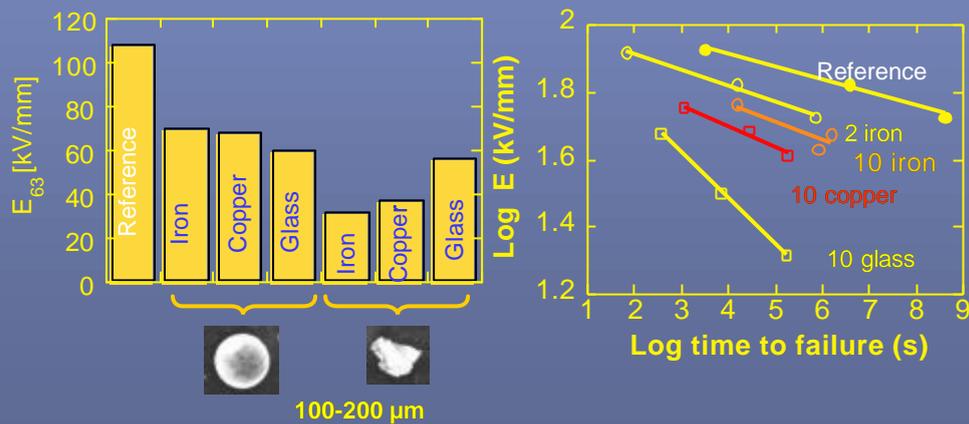
- Impurities are sites for enhanced electric field
- Impurities are always present
- Reduction of frequency of impurities reduce the risk of early failure
- New production technology (combining process steps)- fewer contaminants



Source: W. Raymaekers,
ICF Conference, 1998.

Impurities enhance the electric field at its site and cause early failure. There is an ongoing trend that larger impurities are less frequent by new processing technology.

AC breakdown strength- inclusions in XLPE



Ref. S. T. Hagen, Ph. D. Thesis,
University of Trondheim (1993)

Breakdown strength is very strongly decreased in the presence of impurities. The data are from Rogowski objects with added particle inclusions.

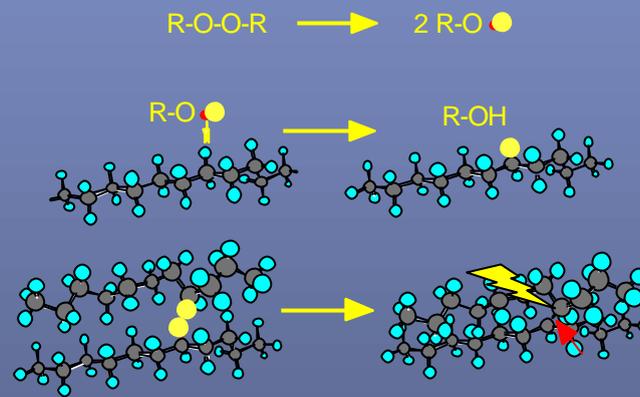
Note that the negative effect of the inclusions is very strong at low electric fields (i.e. the long-term performance is much influenced).

Faster

- Faster vulcanisation means faster production
- Conventional XLPE systems; one crosslink per peroxide molecule
- Polyethylenes with reactive sites (unsaturation); more than one crosslink per peroxide molecule (higher gel content) or
- the same degree of crosslinking at shorter time
- High pressure PE's with diene as comonomer

Faster vulcanisation can be achieved by adding reactive sites onto the polymer chains, basically by using the same technology as is done for making the raw material for conventional XLPE.

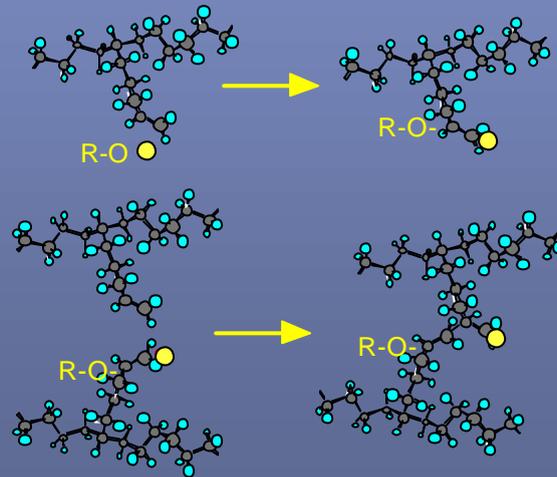
Peroxide crosslinking



One peroxide molecule yields one crosslink

Conventional peroxide crosslinking schematic representation.
Essence: one peroxide molecule gives one crosslink.

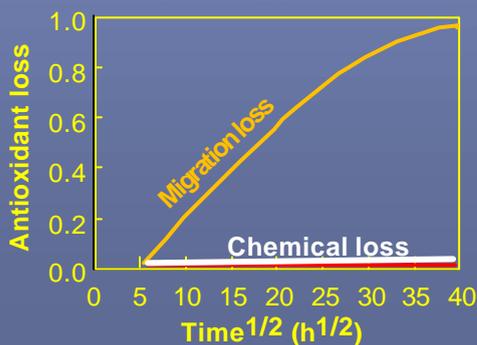
Additional reactions in copolymers with diene monomer



With diene units additional reactions are possible and the actually one peroxide molecule may give more than one crosslink.

More stable

- Higher power ($P=UI$) means higher temperature and shorter lifetime
- More stable materials are needed
- Antioxidant technology (problem with vulcanisation)
- Migration of antioxidants - controlling factor (pipe studies)



- Extend lifetime by adding a barrier
- Barrier reduces AO migration
- Barrier reduces transport of O_2 , H_2O

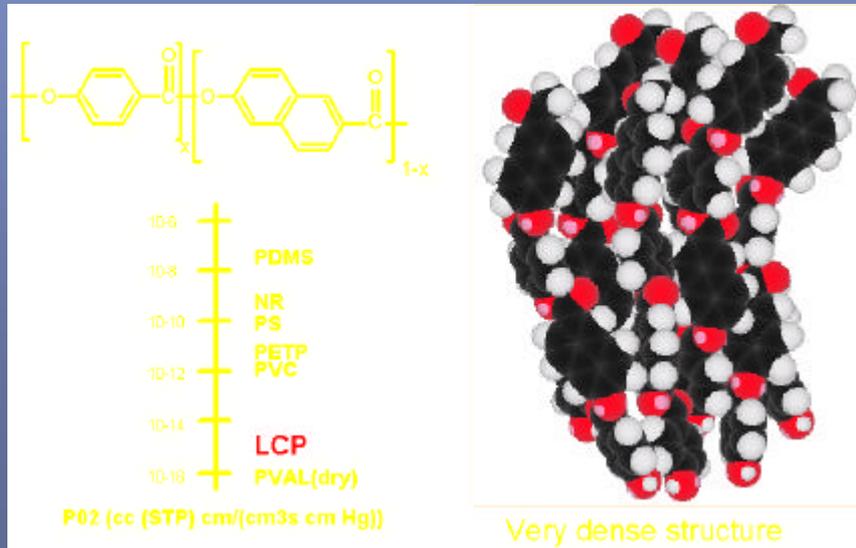
Higher power means higher temperatures and a shorter expected lifetime.

Lifetime may be extended by use of emerging new antioxidant technology but it is more difficult than for thermoplastic materials; remember that vulcanisation is also a radical-driven process. Very effective antioxidants will stop the vulcanisation process before it even started.

My own experience in the plastic pipe field suggests also another strategy. In hot-water pipes the lifetime is controlled by the migration loss of the antioxidants. So by introducing a barrier it would be possible to extend the lifetime (or increase the service temperature at constant lifetime).

Are there such polymeric materials?

Liquid crystalline (LC) polymers



Liquid crystalline polymers are among the best barrier polymers and they are completely tight to larger molecules (such as antioxidants). They would reduce the oxygen content and they would very efficiently block migration of the antioxidant system.

LC polymers-features

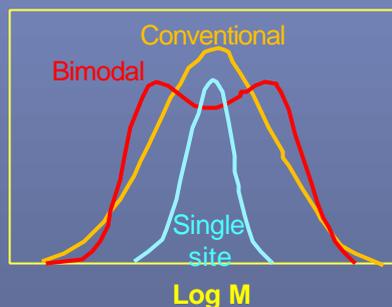
- The best polymer barrier: low oxygen permeability evn in wet conditions
- Completely tight to larger molecules (including antioxidants)
- Low viscosity (but high melting point)
- Flame retardent
- Great dimensional stability
- High price
- Coextrusion with commodity polymers - (soon) possible

LC polymers are extremely good barriers, of low viscosity but very high melting point (220-300°C), flame-retardant (because they contain aromatic groups), great dimensional stability, high price.

Co-extrusion with commodity polymers such as polyethylene will be possible.

The new tools

- **Bimodal materials:** excellent tool to control processability and solid-state properties (fracture toughness).
- **Jacketing materials** with superior properties (very low shrinkage).
- **Single site technology** provides a new dimension: extreme control of MWD and comonomer distribution and it tolerates dienes (fast crosslinking).
- **Combination:** Single site and bimodal technology: exciting changes may occur

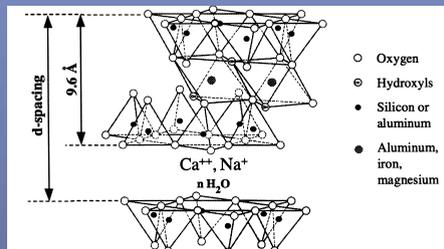


Bimodal materials using new polymerisation technology provide new possibilities for control of rheological properties and solid state properties; good example in cable technology: jacketing materials with low shrinkage.

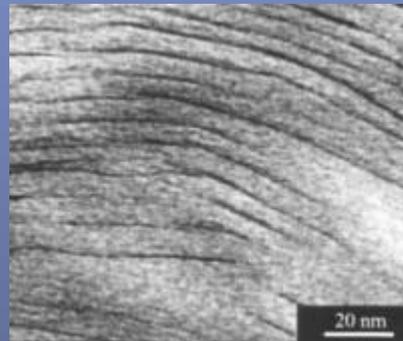
Single-site (metallocene) technology can be used to control molecular weight, degree of branching and these catalysts tolerate dienes (for fast crosslinking).

Combination of single-site and bimodal technologies – sounds exciting!!

Nanocomposites

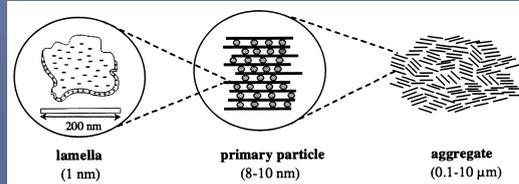


Montmorillonite From Hoffman et al. (1933)



Montmorillonite/epoxy

Kornmann et al (2001)

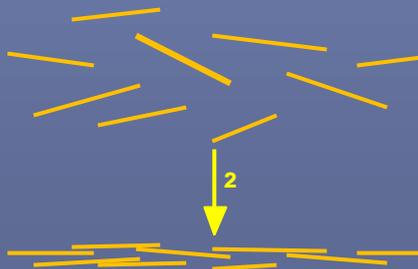
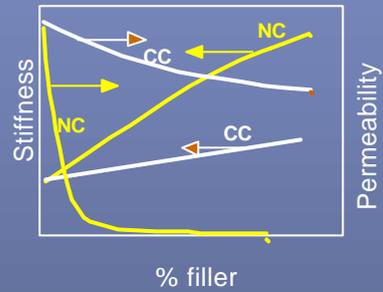


From Akelah et al. (1994)

Nanocomposites are polymers filled with nano-sized particle fillers. Montmorillonite is one example. These clays are made organo-philic by substitution of the positive ions with similar alkylammonium ions. They were first invented by Toyota (Nylon-6 with Montmorillonite).

Why nanocomposites?

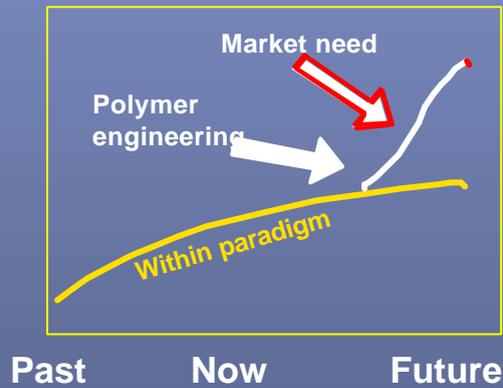
- Pronounced increase in stiffness and barrier properties
- Better fracture toughness
- Higher heat distortion temperature
- Flame retardancy: very significant decrease in heat release rate



They will provide stiffness and strength, higher distortion temperature, higher barrier properties and flame retardancy.

Electrical and magnetic properties are less well known.

Conclusions



Will something dramatic happen in the nearest five to ten years?

I am sure that ongoing improvements will make your life a little bit easier to live.

The PVC problem is technically more or less solved but it may be that politics interfere and that it has to be replaced with polyethylene (which seems possible).

Single-site technology may provide some more radical (positive) change to your polyethylene materials.

I also would like to say that it is only through the combined efforts of specialists in different fields (I represent only one of them) that significant changes can be made.