Can **Aliphatic Polyesters** Mimic LDPEs?

New polymerisation methods are emerging to make high molecular weight, linear aliphatic polyesters having 'long' aliphatic chains. Aliphatic polyesters will certainly expand the scope of new materials for new or specialised applications, suggests Dr. S. Sivaram.

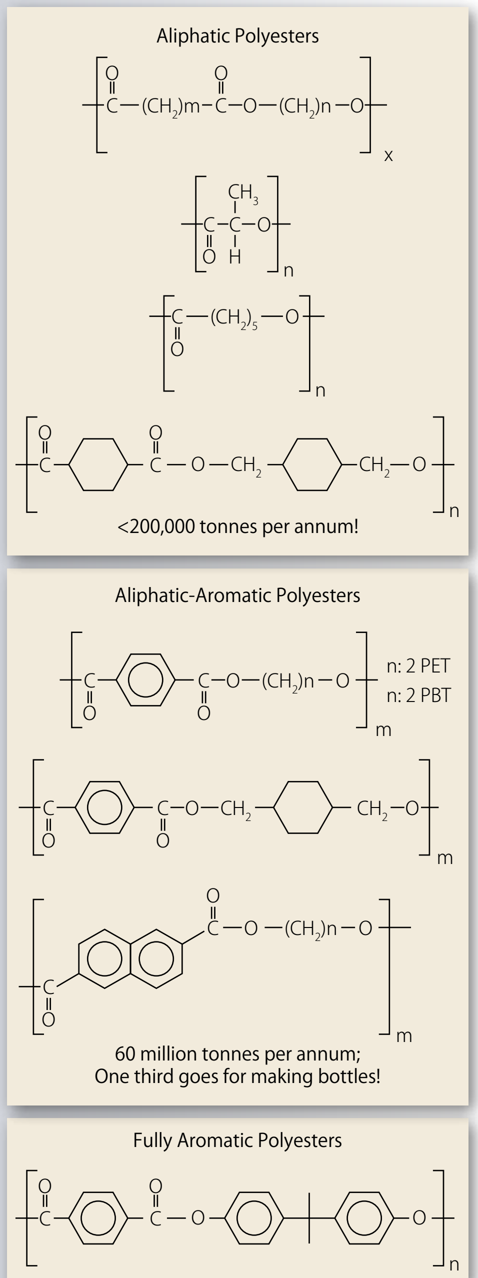
Dr. S. Sivaram
Former Director, CSIR-NCL
Polymers and Advanced Materials Laboratory
National Chemical Laboratory
Pune

Most widely used class of polymers, such as polyolefin, possess an aliphatic backbone structure, that is, only aliphatic carbon atoms linked to each other in a repetitive fashion with no heteroatoms. The useful properties of polyolefin result from the aliphatic nature of the chain, such as, crystallinity, hydrophobicity, chemical inertness and processability. However, carbon – carbon bonds are very strong and cannot be easily degraded. While this is responsible for the durability of polyolefin, they are also the cause for concern as they persist in the environment. As consumption gallops, civic society is increasingly concerned about the fate of plastics in the environment. Citizens seek magical solutions, of a material, which has all the attractive properties of a polyolefin, yet which will disappear safely in the environment, leaving no trace or any toxic residues.

Structure Driven Performance

Polyesters and polyamides, made by the condensation of aliphatic diacids with aliphatic diols or diamines, are also aliphatic. However, in the most commonly used materials of this class, the aliphatic chains are relatively short, typically six atoms or shorter linear carbon chains, --$(CH_2)_n$--. In such cases, the properties of the polymers are controlled by the heteroatom, namely the ester or the amide bond. The best examples of this are nylons (6, 6, 6, 11 etc.)

Fully aliphatic polyesters have one major advantage. They are hydrolytically degradable. Poly (lactic acids) is a class of fully aliphatic polyesters, with one carbon atom separated by an ester group. Poly (lactic acids) are the most studied aliphatic polyesters since they fulfill a unique set of attributes; they are based on bio-renewable monomers, are bio-degradable, bio-compatible and can be degraded under composting conditions to innocuous residues. While they meet all the criteria for a sustainable material, the properties of such polymers are limiting and cannot meet all the diverse applications of a polymer, such as, low-density



General Classes of Polyesters

polyethylene. Nevertheless, poly (lactic acid) markets are growing steadily and are likely to be the largest volume, economically viable, bio-based polymer.

It was realised very early that useful properties could be realised in polyesters with short aliphatic chains only if aromatic repeat units are introduced in the chain. This led to the discovery of poly (ethylene terephthalate), made by the condensation of terepthalic acid with ethylene glycol. The usefulness of PET is evidenced today by the fact that over sixty million tonnes of the polymers are consumed in a variety of applications. But, the introduction of the aromatic group results in poor degradability of the polymer under hydrolytic or composting conditions.

Poly (Lactic Acid)s: An Aliphatic Polyester from the Most Simple AB Monomer

- Insoluble in water, moisture and grease resistant
- Biodegradable and compostable
- Clarity and gloss similar to PET
- Requires 20 to 50% less fossil fuels to produce than PET
- CO_2 emissions down by 60% (0.75 kg of CO_2 per kg v/s 3.4 for PET

The question that is, therefore, relevant to ask is whether a compromise solution is possible, of a material, which has the desirable properties of LDPE, yet can be easily disposed off in the environment. Some early answers to this question are now emerging from academic research laboratories[1,2]. Recent reports show that higher melting points and crystallisation abilities can be achieved in aliphatic polyesters provided 'long' aliphatic carbon chains can be incorporated. In this context, 'long' means aliphatic chains consisting of fourteen carbon atoms or longer.

The Chemistry

Wallace Carothers studied polyesters with 'long' linear aliphatic repeat units in the early thirties. In his pioneering studies, he established the relationship between monomer chain length and crystalline melting points. He was unable to make significant progress because of non-availability of 'long' chain bi-functional monomers in adequate purity and the inadequacy of classical polycondensation methods to make 'long' chain aliphatic polyesters. Classical polycondensation reaction is an equilibrium process, which requires removal of the by-product from the reaction zone to generate polyesters of adequate molecular weights. When short chain diols (e.g. ethylene glycol) is used, this is easy to accomplish. However, 'long' chain diols are not sufficiently volatile at temperatures typically used for polymerisation.

Advances in chemistry have resulted in solutions to these impediments. Larger number of 'long' chain aliphatic monomers in adequate purity is

PACKAGING DOESN'T HAVE TO BE SO RIGID

PacXpert™ Packaging Technology, winner of the 2015 Plasticon Award for "Best Innovative Finished Product", has changed the packaging game.

This innovative technology enables the transition from larger, traditional, rigid containers to flexible packaging with sustainability benefits and convenience. The distinctive flexible stand-up pouch is durable, lightweight, and cost effective.

That's how science and humanity come together to create solutions for human progress. **That's Dow.**

Learn more about Dow Packaging.

becoming increasingly available from both, naturally occurring resources and synthetic processes. These include processes such as ozonolysis of long chain unsaturated fatty acids, enzymatic conversion of terminal methyl group in fatty acids and metal catalysed isomerisation-alkoxycarbonylation of unsaturated fatty acids.

Concurrently, new polymerisation methods are emerging to make high molecular weight, linear aliphatic polyesters having 'long' aliphatic chains. These include ring opening polymerisation method for cyclic esters containing 'long' aliphatic chains (ROP), acyclic diene metathesis polymerisation (ADMET), catalytic dehydrogenation polymerisation of long chain diols and enzyme-catalysed polymerisation.

Increasing data on the physical, chemical and mechanical properties of 'long' chain aliphatic polyesters are now becoming available. Crystalline melting points of these polymers depend not only on the number of carbon atoms, but also on whether this number is odd or even. A polyester containing twenty-three aliphatic carbon atoms between an ester group has a crystalline melting point of 108^{0}C, similar to LDPE. It can be inferred from theory that further increasing the chain length of the aliphatic repeat units, the crystalline melting points should approach that of HDPE. Whether this is possible in practice, is an open question. The crystal structure of 'long' chain aliphatic polyesters is 'PE like' where the hydrocarbon segment crystallises in an all-trans zigzag conformation. ROP of polypentadecalactone (a cyclic ester containing fifteen aliphatic carbon atoms) yields polyester, which shows a deformation behaviour similar to HDPE. These polyesters show 650% elongation at break and 16 MPa stress at break, comparable to HDPE.

In conclusion, emerging science is unfolding what is doable. None of these solutions, however, hold any immediate promise of replacing the versatile polyolefin. This may well be impossible. However, aliphatic polyesters will certainly expand the scope of new materials for new or specialised applications.

References

1. Long Chain Aliphatic Polymers to Bridge the Gap Between Semicrystalline Polyolefin and Traditional Polycondensates, F. Stempfle, P. Ortmann and S.Mecking, Chem. Rev., 2016; DOI: 10.1021/acs.chemrev.5b00705.
2. Mimicking Linear Low Density Polyethylenes Using Modified Polymacrolactones, M.P.F. Pepels, R.A.C. Koeken, S.J.J. van der Linden, A. Heise and R. Duchateau, Macromolecules, 2015, 48, 4779.