Breakthrough in additives for polymer systems

Taking oligomers to another level

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TWI provides industry with engineering solutions in welding, joining and surfacing through information; advice and technology transfer; consultancy and project support; contract R&D; training and qualification; and personal membership. It is the only single source of expertise in every aspect of joining technology for engineering materials

Formulators facing the constant demand from end-users for improvements in performance are faced with the challenge of squeezing the most value out of each component in the systems they produce. The ability of a formulator to differentiate their products is limited since most have access to the same raw ingredients. Recent research at TWI may solve the problem

Most polymer systems are complex blends of ingredients, each selected to impart a particular property or confer a specific characteristic. Acrylate based UV curable coatings provide a good model system to consider. Most coatings consist of an oligomer, one or more monomers and other additives such as surfactants and matting agents. The formulator has a wide range of oligomers and monomers to choose from to achieve the characteristics desired in the final coating. Selection of the oligomer is critical since this ingredient has a major impact on the final system performance, particularly influencing properties including:

- Scratch resistance
- Abrasion resistance
- Chemical resistance
- Gloss
- Adhesion

There are many oligomers available which belong to a smaller number of classes which include:

- Urethane acrylates
- Polyester acrylates
- Epoxy acrylates
- Amine modified acrylates

Whilst there are significant differences in performance between the oligomer classes, there are smaller differences between materials within a given class. Oligomers within these classes are widely available commercially and whilst new additions to the classes are constantly being brought out they often only offer a small incremental property improvement.

One of the most cherished properties from an end-user perspective is that of abrasion resistance. This is particularly true of clear coats which have multiple application areas such as protective coatings for transparent plastics like polycarbonate or poly(methyl methacrylate). It is generally believed that purely organic systems are unlikely to yield coatings with the required performance to allow, for example, plastic glazing solutions for automotive windscreens, or more durable display windows for mobile phones.

Over the last ten to fifteen years there has been considerable research and development activity on the incorporation of inorganic (ceramic) components into coating formulations. Most of this activity has focused on very fine ceramic particulates and has concentrated on increasing the ceramic loading and reducing the agglomeration of the particulates.

This approach has yielded significant improvements in certain performance characteristics, but has the disadvantage of an increase in viscosity as the ceramic loading increases as well as requiring high performance mixing to achieve the highest levels of homogeneity. Alternative approaches have included the development of interpenetrating organic and inorganic networks, although few commercial products have resulted.

TWI has been investigating this area for a number of years for Member companies who would like coatings that are liquid and readily processable using standard facilities, yet give excellent performance once cured. The conclusion of this work is that rather than focus on a coating (and by implication a specific formulation) the question relates to the components used within formulations.

To incorporate high levels of ceramic into a blend of oligomers and monomers requires the ceramic to be available in a similar form and with a similar chemical functionality. There are few molecular structures that possess these characteristics but one family of materials that do are the silsesquioxanes. When considered structurally these materials are intermediate between silicones (normally linear polymers) and glass.

Silsesquioxanes are usually described as either cage (Fig 1) or ladder structures (Fig 2).

Cage structures are well defined and can contain a number of silicon atoms and certain configurations are favoured due to steric considerations.

Ladder structures are more like conventional organic polymers and oligomers in the sense that they may possess a molecular weight distribution related to chain length. However, they differ from conventional polymers or oligomers since the backbone is based on siloxane bonds (silicon-oxygen) rather than carbon. In addition, rather than having a single chain of carbon atoms bonded together, or a single polymer chain based on siloxanes as in the silicones, ladder silsesquioxanes have a double backbone consisting of siloxane chains.

The organic groups attached to the silsesquioxane have a significant effect on the properties of the material. For example, an eight membered cage structure with eight vinyl groups attached (one to each silicon atom) is solid, whilst one with eight octyl groups is liquid. Silsesquioxanes with reactive ligands attached can therefore be an attractive route for the incorporation of ceramic constituents into organic resins.

Silisesquioxanes should simply be considered as another class of oligomer available to the formulator. Since these materials are not widely used, familiarity with them is low and so it is worth considering some of the advantages they may bring and consequently some of the areas that may result in significant rather than incremental property improvement.

The most obvious difference between silsesquioxanes and conventional organic oligomers is that of functionality. A simple eight-membered cage structure with eight propylmethacrylate ligands will have a molecular weight of 1432; this structure will of course be octa-functional. This means that this silsesquioxane will have a significant effect on the cross-link density in any formulation into which it is incorporated.

However, this is only one structural consideration. Not only does the silsesquioxane have eight potential sites for cross-linking, it also possesses pre-formed siloxane bonds producing inorganic connectivity within the matrix as a whole.

The importance of this is still not yet clear but since the siloxane bonds are already formed they will not undergo any significant change during processing and so reduced shrinkage may be a result. This in itself is an important consideration since most existing additives which increase the hardness of the system have the drawback of increasing shrinkage. This example pre-supposes that the methacrylate silsesquioxane and an acrylate resin system are compatible. Work in our laboratory has shown significant levels of compatibility between functionally similar systems indicating that silsesquioxanes have a significant potential for incorporation in acrylate and methacrylate systems.

Since the core of the silsesquioxanes is a ceramic the effect of incorporating these species into resins will be a reduction in the amount of combustible material within the system. Whilst this effect may be negligible at low loading levels, the ability to incorporate high levels due to the inherent compatibility suggests that enhanced fire and flame retardency are likely advantages.

The inherent connectivity of the ceramic component will have an effect on the overall stiffness of the resultant material. This is likely to be enhanced due to the lower rotational potential of the bond compared to a carbon-carbon bond and due to the higher connectivity compared to a carbon based oligomer/polymer. The connectivity of the siloxane component and the potential for higher overall cross-link densities of resins containing high functionality silsesquioxanes also suggests that materials with significantly reduced permeabilities may be possible. Low permeability could be translated into a coating with high barrier properties for use in displays or packaging.

Considering the functional groups that can be located on a silsesquioxane suggests a number of potential end uses . So far the discussion has focused on acrylate based systems for coatings. If the silsesquioxane has an epoxy functionality, incorporation into epoxy based adhesives is possible. This gives the potential for low viscosity/high stiffness adhesives, or adhesives with reduced sensitivity to moisture ingress/degradation. Alternatively, silsesquioxanes could be used to incorporate mixed functionalities into formulations, perhaps giving rise to mixed cure systems with high cross-link density and low surface energy by the use of a fluorocarbon ligand.

TWI's Vitolane™ is a technology for the manufacture of silsesquioxanes by building the functionality into the structure, as opposed to grafting onto a pre-defined structure.

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