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Forty years of NAD microgels as rheology control agents

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ABSTRACT

Today, the major environmental concern of the coating industry is the emission of volatile organic compounds (VOCs). One of the main objectives of paint manufacturers is to reduce the level of VOCs in their products in order to comply with increasingly strict environmental legislation while improving the final coating properties. The preparation of solventborne coatings with High Solids is one of the approach to lower the VOC. Although High Solids coatings have lower levels of solvents than do conventional coatings, the final film after curing may have disadvantages in terms of appearance and performance. Rheological additives such as microgels are the key to overcome most of these disadvantages by insuring excellent flow and leveling while at the same time providing good sag resistance even during baking.

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1. Introduction

Non-aqueous polymer dispersions are certainly not new, having been described in the literature as early as 1970s. For example, Barrett [1] has described the theoretical aspects of non-aqueous dispersion, design, synthesis, properties and use. Non-aqueous dispersions (NAD) typically consist of dispersions of addition polymers in a relatively non-polar non-aqueous liquid containing a steric stabilizing agent which has dual affinity to both the dispersing and the dispersed media. The micron- or submicron-size dispersed polymer particles which are produced by non-aqueous dispersion polymerization are insoluble in the organic non-aqueous medium and they are stabilized with a polymeric dispersant.

Sometimes, the polymeric microparticles produced by NAD techniques may be internally crosslinked. In this case, the stable colloidal dispersion of polymeric gels in non-aqueous medium is usually called "non-aqueous microgels" or briefly "microgels", and these crosslinked microparticles find use as rheology control agents in coating compositions, particularly for automobile coatings. Automotive OEM coatings are applied using automatic electrostatic spray equipment and then baked after a flash-off time. The viscosity of the paint must be low enough to promote atomization during application, and on application, the viscosity must increase rapidly to prevent sagging of the paint. To prevent sagging in High Solids coatings (which have low MW resins), the coating formulations must be shear thinning with a yield stress. The common method to accomplish this is the addition of microgels. They do not increase the high shear viscosity of the coating significantly, which is critical for achieving good atomization during spray application. In High Solids coatings under low shear conditions, the microgels can flocculate (either by bridging or depletion flocculation) forming a three dimensional network, trapping liquid, and effectively increasing the viscosity. The presence of the microgels reduces the tendency of High Solids coatings to sag during flash-off time by increasing the rate of viscosity build after application and raising the ultimate level of low shear viscosity. It also reduces sag in the oven during the bake cycle (hot sag) by flattening the viscosity-temperature curve for the paint. When the coating includes metallic pigments, microgel has a beneficial effect on the alignment of the metallic pigment. It retards popping in high film build by keeping the film open for evaporation of the volatiles easily and it improves transport efficiency in spray applied coatings.

All these effects have the end result of producing a glamour finish that is more attractive and is substantially free of defects. Although, this was discovered and disclosed by PPG Industries Inc., about 40 years ago in 1975 [2], the stabilizer used to prepare these microgels was based on poly(12-hydroxystearic acid) stearate and was first developed by Imperial Chemical Industries, Ltd. (ICI) [3]. Since then various methods of their synthesis which are based on dispersion polymerization processes came forth from different industrial laboratories [4–15]. Although, Funke [16,17] was the one who first suggested to use microgels prepared via emulsion polymerization in organic coatings, the first patent application was made by Cook Paint and Varnish Co., in 1979 [6] to use acrylic microgels in aqueous and non-aqueous media as paint constituents. In this article a brief description of non-aqueous and aqueous processes to prepare non-polar microgels and their limitations are discussed.

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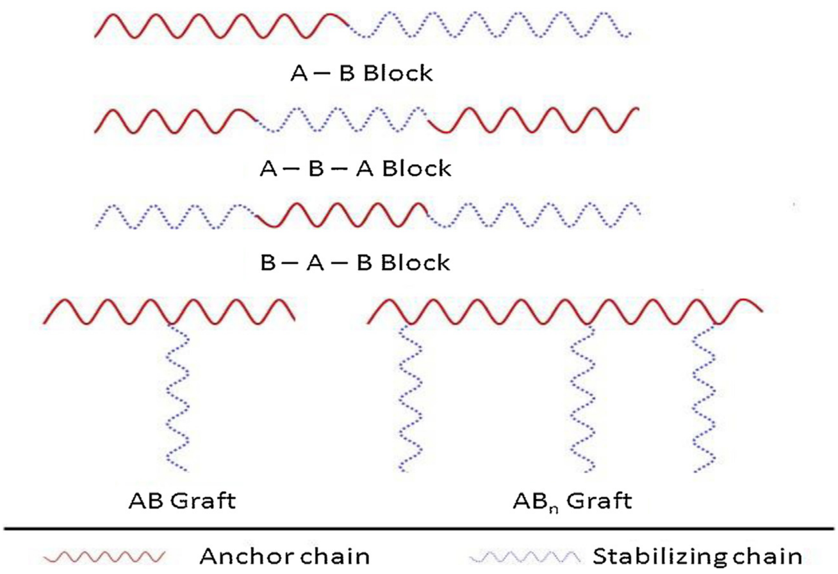

Fig. 1. Configurations of block and graft copolymers.

2. Synthesis of microgels by non-aqueous dispersion (NAD) polymerization

The polymeric microparticles are produced by NAD techniques in the presence of linear polymers, block polymers, and macromonomers. In the NAD process, the monomer(s), a non-aqueous solvent, an oil-soluble initiator, and a stabilizer (to protect the resulting particles from flocculation, sometimes referred to as "protective colloid") are added to the reaction mixture. Typically, non-aqueous dispersions are prepared by the free radical addition polymerization of ethylenically unsaturated monomers in a hydrocarbon rich dispersing medium. The polymerization is carried out in the presence of a steric stabilizer, a portion of which is soluble in the dispersing medium and a portion of which is associated with the dispersed phase; the dispersed phase is insoluble in the dispersing medium. The steric stabilizer can be physically or chemically bound to the dispersed phase. The most successful stabilizers used in NAD are block and graft copolymers. These copolymers are assembled in a variety of ways to provide the molecule with an "anchor chain" and a "stabilizing chain". The anchor chain should be sufficiently insoluble in the medium and has a strong affinity to the polymer particles produced. In contrast, the stabilizing chain should be sufficiently soluble in the medium and strongly solvated by molecules of the medium to provide effective steric stabilization. The length of the anchor and stabilizing chains has to be carefully adjusted to ensure strong adsorption (by multipoint attachment of the anchor chain to the particle surface) and a sufficiently "thick" layer of the stabilizing chain that prevents close approach of the particles to a distance where the van der Waals attraction becomes strong. The successful stabilizers used in NAD polymerization are block and graft copolymers, which are assembled in a variety ways, as illustrated in Fig. 1.

The portion of the steric stabilizer that is soluble in the dispersing medium is typically an aliphatic polyester such as poly(12-hydroxystearic acid) stearate which can be converted to a macromonomer by reaction of the terminal carboxylic acid group with the epoxy group of glycidyl methacrylate. The macromonomer can be used directly as a stabilizer, in which case it will copolymerize with the monomers that form the dispersed phase, or it can be copolymerized with acrylic monomers in solution to form a comb polymer having aliphatic side chains that are soluble in the continuous phase and a polar acrylic backbone that is insoluble in the continuous phase. Alternatively, the soluble portion of the steric stabilizer can be derived from a macromonomer produced from aliphatic acrylic monomer such as ethylhexyl methacrylate or lauryl methacrylate. There are several drawbacks with non-aqueous dispersions produced using these types of stabilizers due to the large difference in polarity, compatibility and solubility characteristics between the stabilizer and the dispersed polymer. The non-aqueous dispersions can become unstable if polar solvents are added, because the stabilizing segment becomes less soluble as the polarity of the continuous phase increases. If the non-aqueous dispersions are used in coatings, any fraction of the steric stabilizer that does not remain associated with the dispersed polymer during film formation may become incompatible. It may form a film at the interface between the substrate and other coating layers, leading to loss of adhesion, or it may form regions of high concentration within the coating leading to defects such as craters. Non-aqueous dispersions that are not as dependent on the solubility difference between the stabilizer and the dispersed phase are desirable. It is essential to choose the right block or graft copolymer, which should have a strong anchor chain A and good stabilizing chain B, as shown schematically in Fig. 1.

Typical preformed graft stabilizers based on poly(12-hydroxystearic acid) stearate are simple to prepare and effective in NAD polymerization. Commercial 12-hydroxystearic acid contains 15–18% stearic acids, which limits the molecular weight during polymerization to an average of 1,500–2,000. This oligomer may be converted to a "macromonomer" by reacting the carboxylic group with glycidyl methacrylate. The macromonomer is then copolymerized with an equal weight of methyl methacrylate or similar monomer to give a "comb" graft copolymer with an average molecular weight of 10,000–20,000. The graft copolymer contains on average 5–10 poly(12-hydroxystearic acid) chains pendant from a polymeric anchor backbone of poly(methyl methacrylate). The synthesis of the comb-like grafted polymeric stabilizer starting with a mixture of 12-hydroxystearic acid and stearic acid and having pendant polymerizable carbon–carbon double bonds is schematized in Fig. 2. This graft copolymer can stabilize particles formed using various monomers such as methyl methacrylate and ethyl acrylate.

The major limitation of the monomer composition is that the polymer produced should be insoluble in the medium used. Two main criteria must be considered in the process of dispersion polymerization: (i) the insolubility of the polymer formed in the continuous phase and (ii) the solubility of the monomer and

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