Aqueous Dispersions of Polyolefins

Rob Cotton, Charles F Diehl, Brad Moncla, Wenbin Liang, Miguel Prieto, Gary Strandburg,
Mark Vansumeren and Ronald Wevers*
The Dow Chemical Company

Speaker’s Name  Ronald Wevers
Position         New Business Development Engineer
Company         Dow Benelux B.V.
Address         Herbert H Dowweg 5
                 4530 AA Terneuzen
                 Netherlands
Telephone No.   +31 115673812
FAX No.         +31 115673219
EMAIL           rwevers@dow.com
Aqueous Dispersions of Polyolefins

Rob Cotton, Charles F Diehl, Brad Moncla, Wenbin Liang, Miguel Prieto, Gary Strandburg, Mark Vansumeren and Ronald Wevers*

The Dow Chemical Company

Abstract

Polyolefins are used extensively in many industries due to a combination of attractive attributes. To date, these attributes can only be incorporated into finished articles through conventional thermoplastic forming processes such as extrusion, thermoforming, injection molding, and blow molding. These so called high polymer polyolefins are high viscosity thermoplastic materials, which have not been available in a low viscosity aqueous environment.

To address this gap, a novel process has been developed to disperse conventional polyolefins in water. Dispersions of ethylene and propylene based resins have been produced at scale with high solids content and with submicron particle size. When applied to a substrate, these dispersions combine heat sealability, low temperature flexibility, and water and chemical resistance, adhesion to polar substrates and the ability to accept inorganic fillers. Polyolefin dispersions (PODs) can be applied via traditional low viscosity application techniques including printing operations such as rotogravure. This combination of properties makes these materials ideal for use as a laminating adhesive and as a heat sealable coating.
**Mechanical Dispersion of Polymers**

A mechanical dispersion technology has been developed to produce water-borne dispersions of polymers that cannot be made by emulsion polymerization. While the focus of this paper will be on mechanical dispersions of polyolefins, it is envisioned that commercially viable mechanical dispersions of other polymer types will be developed in the future. The advantage of the mechanical polyolefin dispersion technology is that there is no need to use a solvent and the dispersion is stable to high solids content.

Under the right processing conditions, the process produces high solids (40-55 wt %) dispersions with an average particle diameter of about 1 micron from olefin homopolymers and copolymers (see Figure 1). The dispersions typically have a viscosity of less than 500 cps at ambient temperature (USP Method 911) and pH ranges from 8.5 to 11.0 (USP Method 791).

*Figure 1. Example of particle size distribution of polyolefin dispersion.*

**Properties of Polyolefin Dispersions**

Mechanical polyolefin dispersions provide the properties of polyolefins in a water-based product that can be processed using many conventional low viscosity application techniques. Some of the attributes that polyolefins exhibit in end-use applications include:

- Water resistance
- Oil and grease resistance
- Heat sealability
- Range of hardness and melting point
- Recyclable
- Thermoformable / embossable
- Elasticity / low temperature flexibility
- Superior adhesion to polyolefin substrates
- Compliant for direct food contact
- Adhesion to polar substrates
- High coefficient of friction (anti-slip)
- “Consumer friendly” chemistry
- Non-allergenic
Many of the desirable attributes of polyolefin dispersions are driven by the semi-crystalline nature of the polymer. Figure 2 shows the crystalline structure of dried polyolefin dispersion that has not undergone film formation. Crystallinity provides structure for enhanced mechanical strength and flexibility. In addition, the crystalline structure is insensitive to the presence of water and oil and grease, providing good water and oil/grease barrier properties. Many emulsion polymers derive their strength from hydrogen and ionic bonding, which is susceptible to water and oils.

Another attribute of crystalline structure is the presence of melting behavior. Most emulsion polymers are characterized by their glass transition temperature, $T_g$. Polyolefins have a glass transition temperature and a melting point, $T_m$, which is the temperature where regular packing of the crystal lattice disappears. The $T_g$ of polyolefins is typically below -20°C and is the reason for their excellent low temperature flexibility. The $T_m$ of polyolefins ranges from 40 to 160°C and is the more important thermal transition for most converting operations and end-use applications for PODs. The melting behavior of polyolefins is critical to providing the ability to heat seal, thermoform and emboss coatings made from PODs. The level of crystallinity can be tailored to adjust heat sealing temperatures as well as the hardness/modulus of the finished coating.

*Figure 2. Atomic force micrograph (AFM) of dried polyolefin dispersion showing crystalline structure.*

The low surface energy nature of polyolefins also plays an important role in the performance of polyolefin dispersions. Many polyolefins, especially the homopolymers of ethylene and propylene, are composed solely of carbon and hydrogen (see figure 3 below). The surfaces of articles produced from these polyolefins have low surface energy (often less than 34 dynes/cm) and are very difficult to adhere to. This often presents an issue
when building structures based on multiples layers that include polyolefins. The challenge is especially great when using traditional water-based dispersions as adhesives or coatings onto polyolefins. Most monomers used in emulsion polymerization are polar in nature and are not compatible with polyolefin surfaces. Polyolefin dispersions have the advantage of having the same chemical building blocks, or monomer units, as standard polyethylene and polypropylene polymers. This allows PODs to have excellent adhesion to substrates such as unprimed, untreated BOPP (biaxially oriented polypropylene) and HDPE (high density polyethylene). In addition to adhesion, the chemical nature of polyolefins allows PODs to be direct food contact compliant and non-allergenic.

*Figure 3. Chemical structure of homopolymer polyethylene and polypropylene.*

The low surface energy coatings possible from PODs are advantageous for adhesion to polyolefins, but this can be problematic for adhesion to paper, foil, and other polar surfaces. To balance the adhesion between polar and non-polar substrates, acid groups are incorporated into PODs. The carboxylate groups provide adhesion to metals and polar polymers such as polyamides. The acid groups also provide enhanced shear stability and compatibility with mineral fillers such as calcium carbonate and aluminum trihydrate.

Table 1 outlines examples of some of the developmental polyolefin compositions that have been produced. Ethylene and propylene copolymers have been widely investigated in the dispersion process. The melting point of the polyolefin copolymer can be varied by changing the ratio of the comonomers and is a key parameter that influences such properties as film formation and heat seal performance.

The addition of acid functionality is based on the desired properties of the end-use application. For example, in some applications it is desirable to blend the dispersion with fillers such as calcium carbonate. The ability to incorporate such fillers is particularly important for applications with textiles. In this case, we have found that incorporation of acid functionality in the dispersion formulation is desirable. The ability to incorporate such fillers is particularly important for applications such as carpet backing.
Table 1 – Examples of Developmental Polyolefin Dispersion Compositions

<table>
<thead>
<tr>
<th>Product Designation</th>
<th>Polymer Composition</th>
<th>Carboxylic Acid Content</th>
<th>Polymer Tm (°C)</th>
<th>Polymer Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dispersion A</td>
<td>Ethylene Copolymer</td>
<td>Yes</td>
<td>60</td>
<td>-55</td>
</tr>
<tr>
<td>Dispersion B</td>
<td>Ethylene Copolymer</td>
<td>Yes</td>
<td>116</td>
<td>-55</td>
</tr>
<tr>
<td>Dispersion C</td>
<td>Propylene Copolymer</td>
<td>Yes</td>
<td>85</td>
<td>-25</td>
</tr>
<tr>
<td>Dispersion D</td>
<td>Ethylene Copolymer</td>
<td>No</td>
<td>60</td>
<td>-55</td>
</tr>
<tr>
<td>Dispersion E</td>
<td>Propylene Copolymer</td>
<td>No</td>
<td>85</td>
<td>-25</td>
</tr>
</tbody>
</table>

Film Formation

One key difference to polyolefin dispersions, compared to conventional latexes produced via emulsion polymerization, is film formation. Many emulsion polymer latexes have film forming properties at or below room temperature (related to their low Tg). In order to achieve similar homogeneous film forming characteristics in polyolefin dispersions the semi-crystalline phases of these polyolefins need to be removed by temperatures above the melting point (Tm).

Little to no film formation of the polyolefin dispersions occurs until all of the water is driven off, due to evaporative cooling. The coating must then be heated adequately above the crystalline melting point for the particles to melt and coalesce. For many existing converting processes and applications this does not present an obstacle, since in many cases the existing process already encompasses a drying step that operates at elevated temperatures.

Deformation of polyolefin dispersion particles and formation mechanisms of void-free film from discrete particles were investigated in situ using hot-stage tapping-mode atomic force microscopy (TMAFM)\(^1\). Figure 4 shows the TMAFM topography images of an ethylene copolymer film cast from Dispersion D, which has a crystalline peak melting point of about 60 °C. Spherical particles with clear boundaries can be observed. The size of the spherical particles ranges from 0.1 to 3 µm. The unique advantage of TMAFM with hot stage capability is that it allows the monitoring of the particle deformation and inter-particle coalescence processes in real time at the same location.

In order to examine the particle deformation with increasing temperature, a series of TMAFM topography images associated with film formation at elevated temperature are shown in Figure 4. Essentially no coalescence occurs at temperatures below 50°C. The particles maintain their shape even up to 60°C. At 70°C, the particles start to deform and a low level of particle coalescence is reached. At 78°C, individual particles
essentially disappear with few residual particles still recognizable. The particles become exceedingly diffuse when the temperature is over 80°C.

*Figure 4. A series of TMAFM topographic images of ethylene copolymer dispersion film at elevated temperature. (Reprinted with permission from Reference 1)*

Under the appropriate drying conditions, the polyolefin dispersions produce films with excellent mechanical properties. Figure 5 shows the stress-strain curve for a relatively thick (10 mil) film cast from a dispersion of ethylene-octene copolymer, when dried under different conditions. These thick films were dried in a standard forced-air convection oven. Excellent quality films and foams have been produced in continuous processes at conventional processing speeds.
Conversion Options for Polyolefin Dispersions

Polyolefin dispersions have been processed using many of the traditional converting processes employed with emulsion polymers. As shown in Figure 6, PODs can be (1) air-frothed to produce a foam or foamed backing on various substrates, (2) spray-dried to produce a very fine powder, (3) applied as a very thin coating on a variety of substrates using processes such as roll coating, gravure, spray-coating, and others processes, (4) used to impregnate porous substrates such as woven and non-woven fabrics, etc.

![Figure 6. Conversion options for polyolefin dispersions.](image)

It is also within the capability of this process to disperse compounded blends of polymer(s) with plasticizers, fillers, tackifiers, pigments, stabilizers, and other common thermoplastic compound ingredients. For example high solids, water-based dispersions of hot melt adhesive (HMA) compounds have been
successfully produced in this process. These HMA...and antioxidants. Pigmented polyolefin powder coating formulations have also been dispersed as a precursor to spray drying to produce fine powders.

**Adhesive Lamination and Heat Sealable Coatings**

Polyolefins are widely used in the packaging industry as coatings on polymer films and aluminum foil. Typically, polyolefins are applied in the melt phase using processes such as extrusion coating, coextrusion, or extrusion lamination. Often these polyolefin coatings provide a sealant layer or function as a laminating adhesive. The availability of a water-based polyolefin dispersion allows converters to apply these sealant and adhesive layers using conventional water-based application techniques such as flexographic printing. This can provide advantages such as the ability to apply a much thinner coating than can be achieved with melt processing techniques, the ability to coat at significantly higher line speeds, the ability to coat in a pattern, the ability to apply very low melting point polyolefins with low heat seal initiation temperature, as well as the ability to apply a polyolefin coating at low temperatures. Applying polyolefins at traditionally high melt processing temperatures can sometimes have detrimental effects on the substrate being coated.

**Paper Coating**

Oil/grease and water resistance are key properties of paper and carton board that can be improved with the right choice of coating. High levels of oil and grease resistance (OGR) are often needed for demanding packaging applications such as pet food bags, pizza boxes, hamburger wrappers, and the like. Fluoropolymer based coatings provide excellent OGR, but have come under increasing regulatory pressure. This has led converters to search for alternative water-based OGR coatings. Polyolefins are widely used for paper coating, but are typically applied as a thermoplastic melt using extrusion coating techniques. The availability of water-based polyolefin dispersions provides an excellent alternative with good OGR performance and economics.

**Paper Oil and Grease Resistance Examples**

Water-based polyolefin coatings were made on paper to evaluate the oil and grease resistance of the coating. The dispersion was applied onto the rough side of a Fraser base stock having a basis weight of 59 g/m² using wound rods. A coating weight of 8.9 g (dry) /m² was used. The drying of the dispersion coating onto the paper substrate was performed at 149°C for 5 min. using a convection oven.
OGR was determined by performing a hot oil evaluation. A drop of oil was placed on each sample and the drops were examined at various time intervals to determine the degree to which the oil penetrated to the back side of the sample. Test oils consisted of sesame, vegetable, canola, olive, peanut, corn, and oleic acid. The oils were preheated to 60°C in an oven. A 6 × 7 inch coated sheet was taped onto a PLEXIGLAS® acrylic sheet. A drop of oil was then placed on the sample surface and the time recorded. Samples were then rated on a pass to fail scale, immediately without oil wipe-off. This is the immediate or “I” reading on the test chart.

The pass to fail scale is rated as follows:

P = Pass, i.e. no staining noted on front-side or backside

LS = Lightly Saturated, i.e. stain not through to backside of paper

HS = Highly Saturated, i.e. spreading stain through to backside of paper

S = for complete saturation of the fiber network

A# = Number of pinholes noted in the field of the drop

M = Multiple pinholes in the field of the oil drop

The samples were rated again after one hour at ambient conditions. This reading is indicated as “I” (1 hour) on the test chart. The treated samples were then placed in a 60°C oven overnight. After 20 to 24 hours in the oven, the samples were taken out and the oils wiped off the surface. The back side of the samples were observed through the PLEXIGLAS® acrylic sheet. Staining through to the backside is more easily observed with back lighting. Alternatively, the samples were removed completely from the PLEXIGLAS® acrylic sheet. The total amount of time from initial to final reading was recorded to the nearest 0.5 hour. Hot oil test results are shown in Table 2.

<table>
<thead>
<tr>
<th>Oil Type</th>
<th>Corn</th>
<th>Sesame</th>
<th>Vegetable</th>
<th>Olive</th>
<th>Peanut</th>
<th>Canola</th>
<th>Oleic</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Exposure (HR)</strong></td>
<td>I</td>
<td>1</td>
<td>24</td>
<td>I</td>
<td>1</td>
<td>24</td>
<td>I</td>
</tr>
<tr>
<td>Polyolefin Dispersion D</td>
<td>P</td>
<td>P</td>
<td>HS</td>
<td>P</td>
<td>A1</td>
<td>HS</td>
<td>P</td>
</tr>
<tr>
<td>Polyolefin Dispersion A</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>Styrene/Butyl Acrylate Latex</td>
<td>P</td>
<td>A1</td>
<td>HS</td>
<td>P</td>
<td>P</td>
<td>HS</td>
<td>P</td>
</tr>
</tbody>
</table>

Table 2. Hot Oil Evaluation for Coated Paper Samples
Polyolefin Dispersion A showed superior performance when compared to a commercially available styrene-butyl acrylate latex formulation. It is also interesting to note that the carboxylated POD (Dispersion A), performed significantly better than the acid-free dispersion (Dispersion D).

The polyolefin dispersion can be applied to paper using conventional processes for water based coatings, including various spraying techniques. In addition, the dispersion can be printed onto a paper web, such as by gravure printing, roll coating, etc.

**Paper Moisture Vapor Transmission Rate Examples**

The water resistance / absorption of PODs were measured using a Cobb test in accordance with ASTM D3285-93 with an exposure time of 2 minutes. The test involves a known volume of water (100 ml) being poured onto a specific area of the board’s surface (100 cm²). Dispersion coatings were applied on kraft paper using a #3 rod and then dried at 120°C. The moisture vapor transmission rates and water resistance of the coated paper samples were then measured and compared to uncoated kraft paper. The board is weighed before and after the exposure and the difference between the two can then be expressed as the weight per unit area of water absorbed in that given time; the lower the Cobb value, the better the result.

The moisture vapor transmission rate (MVTR) was measured using ASTM E96-80 dish test. The test measures the transmission of moisture from a wet chamber through a test specimen (sheet) and into a dry chamber containing a desiccant. The MVTR experiments performed were performed at room temperature with a wet chamber relative humidity of 70%.

Table 3 shows the MVTR and water resistance via Cobb test for both coated and uncoated samples. In contrast to the OGR, these data show that the acid-free polyolefin dispersions are preferred for water resistance. Blends of acid functionalized and non-acid functionalized formulations can be used to achieve a very desirable balance of both OGR and water resistance in the same polyolefin dispersion coating formulation.

<table>
<thead>
<tr>
<th>Dispersion</th>
<th>% Solids</th>
<th>Ambient Brookfield Visc (cP)</th>
<th>pH</th>
<th>Cobb 120 (g/sqm/120 sec)</th>
<th>MVTR (g/sqm/24hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyolefin Dispersion E</td>
<td>50%</td>
<td>56</td>
<td>12</td>
<td>1</td>
<td>40</td>
</tr>
<tr>
<td>Polyolefin Dispersion B</td>
<td>44%</td>
<td>510</td>
<td>11</td>
<td>7</td>
<td>420</td>
</tr>
<tr>
<td>None</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>28</td>
<td>950</td>
</tr>
</tbody>
</table>
Frothed Foams and Coatings

Frothed foams can be readily made from polyolefin dispersions, thereby producing structures that are vastly different from foams available from extrusion based foam processes. Figure 7, illustrates the lab-scale converting process for producing air-frothed foams from PODs. Continuous foaming on a larger scale has been conducted using readily available equipment employed for froth foaming of conventional latexes. Novel formulation and process technology has been developed in order to balance the foaming and drying processes. Achieving this without encountering foam collapse or surface cracking is the key to preparing foams from polyolefin dispersions.

These novel foams have the following features:

- Open-cell structure
- High moisture adsorption and “wicking”
- Low compression set at ambient temperature
- High elasticity
- Very soft, luxuriant feel
- Biocompatibility
- Excellent adhesion to polyolefins and other substrates
- High filler loading capability
- Recyclability
- Embossability

*Figure 7. Process for producing frothed foams from polyolefin dispersions.*
Foams can be foamed directly onto a variety of substrates such as textiles and fabrics, non-wovens, carpet, paper, metal, plastic films, etc. A scanning electron microscope picture of frothed polyolefin foam is shown in Figure 8.

Figure 8. Frothed foam produced from polyolefin dispersion.

Summary
Thermoplastics, including polyolefins, have many desirable properties in end-use applications. However, extrusion is typically the only viable method for converting these materials into a finished good. A proprietary process has been developed for mechanically dispersing a wide range of polyolefins to produce high solids content polyolefin dispersions with an average particle size of approximately 1 micron. These dispersions can be employed in conventional converting processes typically used for emulsion polymer latexes, including: spraying, froth foaming, roll coating, gravure printing, dipping, impregnation, etc. The polyolefin dispersions offer a unique combination of characteristics not found in typical emulsion polymers. These attributes create significant opportunities for innovation by formulaters and converters.

1 Li, Jing, Liang, Wenbin, Chum, Steve. In Situ Monitoring of Dispersion Film Formation Using Tapping Mode Atomic Force Microscopy, MRS 2004 Fall Meeting Proceeding: Vol. 838E O10.19