BULLETIN VC-5672

extrusion

with ashland binders

background

Extrusion is a manufacturing process used to create products of defined and consistent cross-section. Material is pushed through a die, flowing around the supports and fusing together to create the desired shape (figure 1). An advantage of this manufacturing process is its ability to create consistent complex structures. Materials used can be powdered solids, inorganic, like ceramic oxides, concrete, clay, metal powders or even graphite. As only compressive and shear stresses are applied the resulting products can have excellent surface appearances.

figure 1: schematic of the extrusion process

The process may be continuous (continuous flow of material) or semi-continuous (batch-process). The extrusion can be done with the material at different temperatures. The products of extrusion are generally called "extrudates" (figure 2).

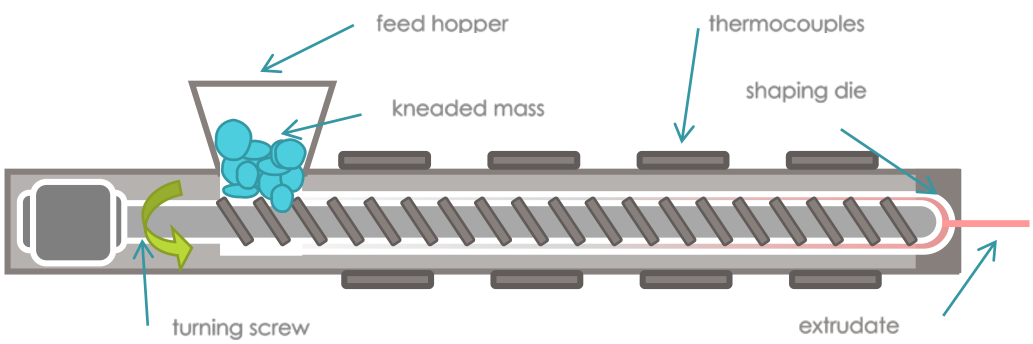

figure 2: schematic of an extruder

critical steps in the extrusion process

- plastification – liquid is added to the dry mix
- material is fed into temperature-controlled extruder
- plastified mass is pushed (screw / ram) through a die to shape the material
- drying – liquid is removed giving dried green body
- burning / sintering – binders are burnt-out

role of a binder

The main purpose of the binder is to provide green strength so the body will simply maintain its shape until it is sintered. (Some ceramists and powder metallurgists use the word binder to mean all of the organics present in the green body, including the plasticizer, lubricant, etc.)

component	wt%
base material depending on end-product properties	**~85**
binder	**~2-3**
solid lubricants, flocculants, dispersants	**~1**
plasticizers (glycerol, EG, DEG, TEG)	**~1**
liquids (water, light oils, organic co-solvents)	**~10**
sum	**100**

In many cases, the green ceramic body must be machined, inspected, stored, and placed onto setters for firing. To avoid any damage or shape deterioration considerable strength would then have to be provided by the binder. The more sophisticated the shape or the higher the surface area is, the more strength is needed.

Also, as the body dries during the initial stages of firing, it will weaken and gravity might be sufficient to deform it, particularly if there is vibration from kiln car motion or fans.

needs of a binder

purity

- low insoluble particle content to avoid defects and poor surface quality of the extruded ceramic
- low salt / impurity content

performance

- pressure during extrusion process should not be too high
- self-lubrication / ratio between binder viscosity and liquid phase
- robust temperature window / higher gel point

wet green strength

- after extrusion stability to maintain the shape of the extruded ceramic
- use binders offering high gel strength for more complex ceramics

dry / sintering strength

- extruded material should be free of cracks
- sufficient water retention

recommended products

Culminal™ is a trademark of Ashland LLC for a line of cellulose ether products. The abbreviation MC, MHPC, MHEC identifies the type of cellulose ether, its "chemistry" (figure 3). The last two-digit numbers can be read as viscosity value (first digit) followed by the number of zeros (second digit). The viscosity of the product is given in millipascal-seconds (mPa·s), measured at 2% concentration (bone-dry) in water at 20°C using the appropriate Brookfield® RVT viscometer spindle set at 20rpm, where millipascal-seconds is equivalent to centipoise. The remaining number(s) in front represent the chemistry designation as the percentage amount of the second substituent.

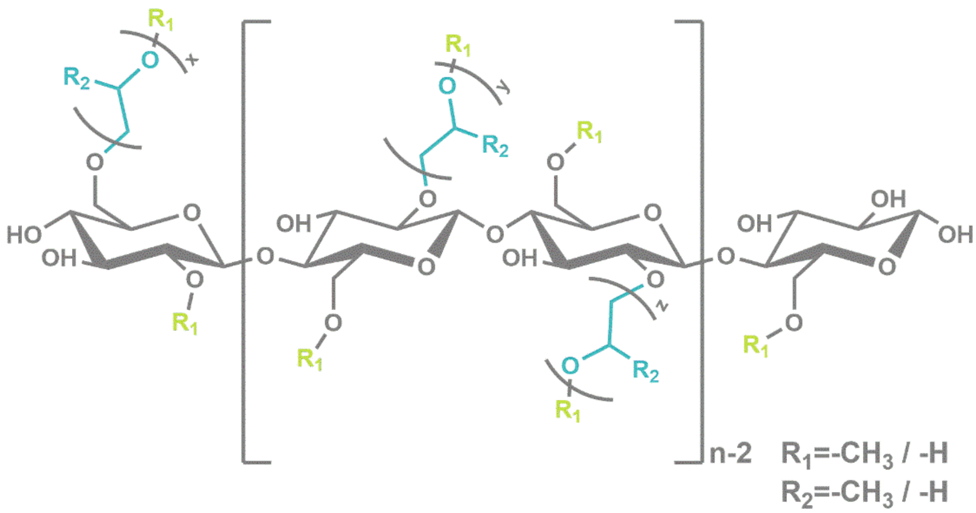

figure 3: chemical structure of MC-derivative
(pure MC x/y/z =0 / R_1=-CH_3; MHPC x/y/z ≠0 R_2= -CH_3; MHEC x/y/z ≠0 R_2= -H)

product	chemistry	viscosity level	application benefits
Culminal™ MC 014	A-type	10.000mPas	o providing ultra-high green strength o high purity (very low insoluble particles) o reduced sodium levels **special shape requirements**
Culminal™ MHPC 814	E-type	10.000mPas	o providing high green strength o high purity (very low insoluble particles) o reduced sodium levels **carrier / ultra-thin wall applications**
Culminal™ MHPC 724		20.000mPas	
Culminal™ MHPC 1014	K-type	10.000mPas	o optimized for higher processing temperatures o low amount of insoluble particles o reduced sodium levels o increased extrusion speed **carrier & filter systems**
Culminal™ MHPC 1034		30.000mPas	
Culminal™ MHEC 644	E-type	40.000mPas	o universal binder / use level reduction o optimized for higher extrusion temperatures **regular shapes** **bed topping media** **catalyst support media** **carrier & filter systems**

ashland product benefits

characteristics	unit	specifications
moisture	[%]	5.0 max
viscosity **(2% aqueous Brookfield® viscometer RV20/20rpm@20°C)**	[mPas]	viscosity designation ± 15%
substitution profile	[%]	A 1st subst. 27.5-31.5 E 1st subst. 28-31 / 2nd subst. 7-12 K 1st subst. 19-24 / 2nd subst. 7-12
bulk density	[g/l]	200-500
sodium chloride content	[%]	1.0 max
PSD (retained on 63µm / 125µm)	[%]	0-40 / 0-8

typical addition levels

1-5 wt% in formulation

gelling behavior

The chemical substitution has a significant impact on the properties of cellulose ethers in highly concentrated suspension systems. A method to describe the temperature dependence on the functionality is the phenomenon of thermal gelation (figure 4). When aqueous solutions are heated, they gel at temperatures that are specific for each product type. These thermogels are completely reversible, meaning that they will liquefy again upon cooling. A theory is that this effect is primarily caused by the hydrophobic association of the substituents along the molecular chains. The hydration of the molecules under standard conditions reduces the polymer-polymer interaction, only slight entanglements are happening. When temperature increases, the motion of the molecules increases and they lose their water of hydration, seen by a decrease in viscosity. Furthermore, a continues dehydration leads to an increased hydrophobic-hydrophobic interaction and increased association of the polymers. The resulting inter-molecular network structure or gel leads to a sharp rise in viscosity finally in shrinking as a result of the complete loss of hydrated water molecules.

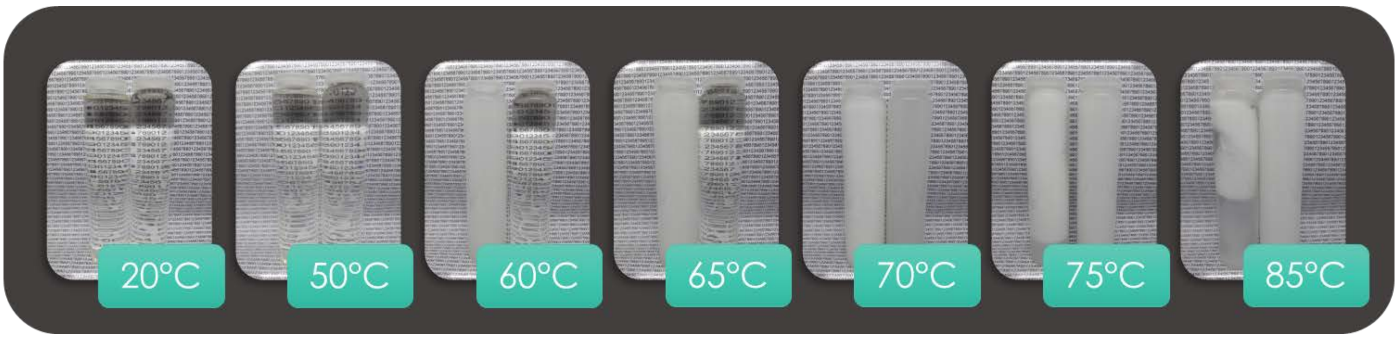

figure 4: thermal gelling effect of 2% aqueous solutions of E (left) and K(right) -type binder

purity

Due to the nature of cellulose, all entangled and associated chains need to be "unzipped" prior to the reactive substitution process. Caustic is used to break the hydrogen bonding and separate the chains (figure 5). The longer the unzipping time is, the better the accessibility will be for the reactants. On the other hand, the high concentration of alkaline can destroy the molecular chains and therefore a balance has to be found.

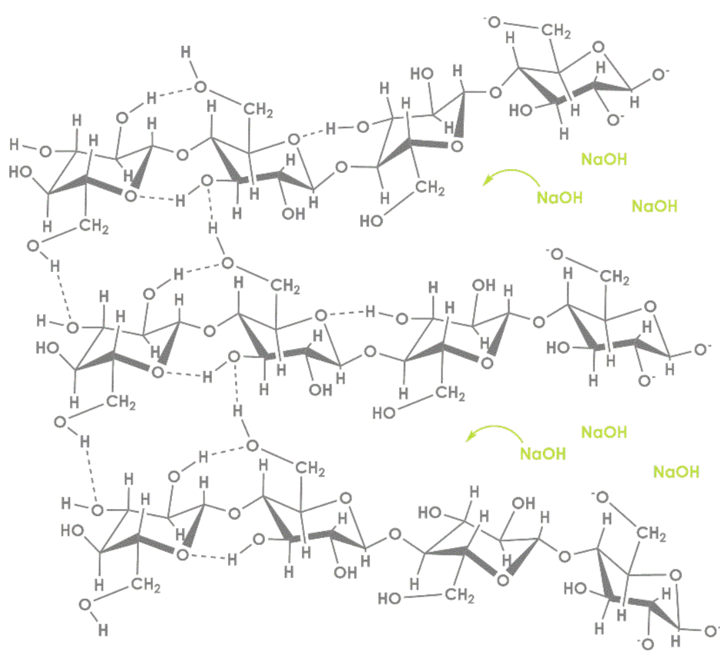

figure 5: unzipping of cellulose chains

Ashland
always solving

The remaining aggregates lead to a certain amount of unreacted or half-reacted moieties that stay insoluble in an aqueous environment. This leads to swollen particles or fiber-like structures that can cause defects in the final extrudate. To quantify the amount of insoluble particle, we specify for some products the so-called fiber count. For this, we use the Coulter Counter instrument.

The Coulter Principle has become the accepted "Reference Method" throughout the world for particle size analysis and is the recommended limit test for particulate matter in large-volume parenteral solutions. The Coulter principle was named for its inventor, Wallace H. Coulter.

The Coulter method of sizing and counting particles is based on measurable changes in electrical impedance produced by nonconductive particles suspended in an electrolyte. A small opening (aperture) between electrodes is the sensing zone through which suspended particles pass. In the sensing zone, each particle displaces its own volume of electrolyte. Volume displaced is measured as a voltage pulse; the height of each pulse being proportional to the volume of the particle (figure 6). The quantity of suspension drawn through the aperture is precisely controlled to allow the system to count and size particles for an exact reproducible volume. Several thousand particles per second are individually counted and sized with great accuracy. This method is independent of particle shape, color and density.

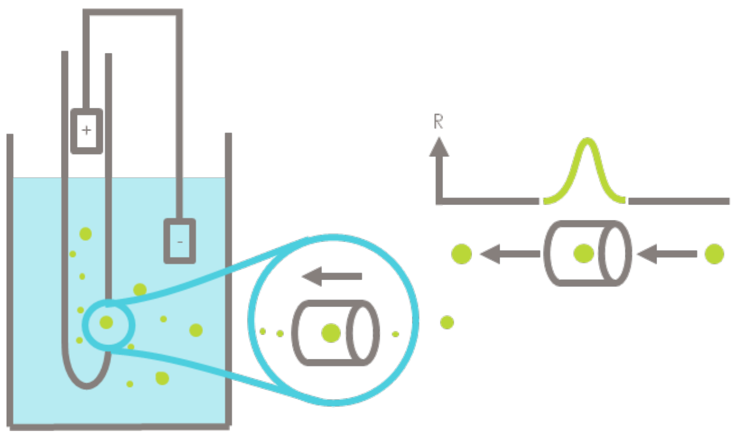

figure 6: the coulter principle

product safety

Read and understand the Safety Data Sheet before using this product.