Kuraray Poval[™] for suspension PVC



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Introduction

Kuraray has much expertise in the use of polyvinyl alcohol (PVA or PVOH) based suspending agents for the needs of polyvinyl chloride (PVC) manufacturers. In this application, polyvinyl alcohol is used as a protective colloid for the polymerisation of vinyl chloride. Vinyl chloride monomer (VCM) is suspended in water by means of stirring, in combination with a suspending agent to allow the polymerisation reaction to proceed. The physical properties of the resulting PVC, including size, shape of the grains and bulk density, are directly related to the grain forming process during polymerisation. Kuraray's primary and secondary suspending agents allow precise control of the grain formation and its resulting structure and morphology. Furthermore, the surface activity can be widely tuned by selecting an appropriate combination of Kuraray's suspending agents. This diversity enables the PVC manufacturer to produce a very versatile range of PVC resins, varying in morphology and K value according to the intended end application

PVC resin can be used in many applications to replace such materials as wood, glass and some metals. Thanks to the economics, durability and self-extinguishing properties of PVC it can be used for water pipe, electrical cable and a variety of building products.

PVC also finds use in wallpaper and window profiles, agriculture and automotive parts, synthetic leather and film for packaging. Because of its use in many applications it is a material present in our everyday life. The majority of PVC resin is manufactured by the suspension polymerisation process. Polyvinyl alcohol is an essential part of this process as the main suspending agent.

Production of PVC resin

PVC can be manufactured in a number of ways from suspension polymerisation to emulsion polymerisation and bulk polymerisation, but the most popular is suspension polymerisation. PVC resin is manufactured with a mean grain size of around 150 μ m by adding water and suspending agent, polyvinyl alcohol (PVOH), into the reactor together with liquid VCM under pressure. This mixture is agitated to create fine droplets. To achieve PVC resin of this type it is required to control a number of parameters including particle size and morphology, which will influence bulk density and porosity and help processing of the PVC resin at a later stage.

Polyvinyl alcohol is an important additive as a suspending agent in this process to influence such properties as mentioned above to control PVC quality and technical performance.

Kuraray Poval[™] properties are mainly controlled by the degree of hydrolysis and degree of polymerisation as shown in Figure 1. For PVC suspension polymerisation the degree of hydrolysis and degree of polymerisation are important properties for surface activity and protective colloidability in the PVC polymerisation process.

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Figure 1. The role of polyvinyl alcohol for PVC polymerisation and PVC resin properties.

The role of polyvinyl alcohol for suspension polymerisation is different depending on the degree of conversion of VCM to PVC. The required properties of the polyvinyl alcohol for each stage (<0.1 % compared to 0.1 % to <30 % compared to >30 %) will be explained below.

Figure 2 shows the polymerisation mechanism starting with conversion <0.1 %, which is the stage where the initiator is dispersed throughout the VCM. The initiator and monomer will be mixed by the monomer droplet coalescence and dispersion caused by the agitation in the reactor. If this coalescence and dispersion process is poor, the achieved conversion of each droplet will be non-homogenous. Monomer droplets with high levels of initiator will have high conversion, which can lead to issues with fish eyes in thin film applications. To enhance this coalescence and dispersion behaviour a polyvinyl alcohol which has a higher surface activity and lower protective colloidability will be required. The most suitable Kuraray Poval[™] grades for the above process will be our L and LM grades.

As shown in Figure 2 on page 4, the next phase shows the conversion below 30 % which is the stage when the PVC primary particles are generated in the VCM droplets. Polymerisation occurs in each monomer droplet and the PVC primary parti-

cle around 1 μ m in size is precipitated in the monomer droplet as the PVC resin is not soluble in VCM. In this process it is said that primary particles agglomerate in the monomer droplet to form a network structure due to the frequent coalescence and dispersion of the monomer droplets. Because of this the internal structure of the PVC resin becomes more porous leading to benefits in porosity for easier absorbance of plasticiser and additives giving greater processability of the PVC resin.

On the contrary if coalescence and dispersion are not efficient during this stage the primary particle will not have a network structure in the monomer droplet and the PVC resin will become less porous, which would lead to a resin of poor processability. To enhance this coalescence and dispersion behaviour a polyvinyl alcohol which has a higher surface activity and lower protective colloidability will be required. The most suitable Kuraray Poval[™] grades for the above process will be our L and LM grades.



The final phase for conversion above 30 % which is the stage when the PVC resin particles will be formed by the agglomeration of primary particles, coalescence and dispersion of monomer droplets will not occur due to the increase of conversion. The protective colloidability of the polyvinyl alcohol can control this agglomeration process. Lower protective colloidability can lead to too much agglomeration and generate large particles and the polymerisation will become unstable. Higher protective colloidability leads to more balanced agglomeration and polymerisation will be stable.

For this stage a polyvinyl alcohol with higher protective colloidability will be required. The most suitable Kuraray Poval™ grades for the above process will be products with a degree of hydrolysis of 80 mol% or higher and our L grades. High protective colloidability polyvinyl alcohols which are required for stability in the polymerisation process are called primary suspending agents. On the other hand higher surface activity polyvinyl alcohols which are required for greater porosity generation in the polymerisation process are called secondary suspending agents.

The required performance of a polyvinyl alcohol as a suspending agent will be different for each polymerisation stage but in the actual process each polyvinyl alcohol is added into the reactor at the same time, at the beginning of the process. It is important to design the recipe using a combination of suitable polyvinyl alcohols for each part of the polymerisation process taking into account the attributes of the equipment being used in terms of agitation, baffles, jacket or condenser cooling and reactor size and geometry.



Figure 2. The polymerisation mechanism

Surface activity	Protective Colloidability
High = small monomer droplets	High = less agglomeration
Low = large monomer droplets	Low = more agglomeration



Kuraray Poval[™] grade list for PVC suspension polymerisation

Primary Suspending Agents

5.0 - 7.0
5.0 - 7.0
5.0 - 7.0
5.0 - 7.0
5.0 - 7.0
5.0 - 7.0
5.0 - 7.0
5.0 - 7.0
5.0 - 7.0
5.0 - 7.0
5.0 - 7.0
5.0 - 7.0
5.0 - 7.0
5.0 - 7.0

(1) of a 4 % aqueous solution at 20 °C DIN 53015 / ISO 15023-2 (2) after 3 hours drying at 105 °C DIN 53189 / ISO 15023-2 (3) calculated as Na₂O

Secondary Suspending Agents

Kuraray Poval™	Viscosity ⁽¹⁾ [mPa•s]	Degree of hydrolysis [mol%]	Non-volatile ⁽²⁾ content [%]	Ash ⁽³⁾ content [%]	рН
LM-10HD	4.5 - 5.7	38.0 - 42.0	98.5 ± 1.5	≤ 0.6	NA
LM-20	3.0 - 4.0	38.0 - 42.0	98.5 ± 1.5	≤ 1.0	NA
LM-30	9.3 - 10.3(4)	45.0 - 51.0	98.5 ± 1.5	≤ 0.6	NA

(1) of a 4 % methanol / water (1/1) solution at 20 °C DIN 53015 / ISO 15023-2 (3) calculated as Na₂O (4) of a 10 % methanol / water (1/1) solution at 20 °C

(2) after 3 hours drying at 105 $^{\circ}\mathrm{C}$ DIN 53189 / ISO 15023-2

Characteristics of Kuraray Poval[™] for PVC suspension polymerisation

Kuraray Poval[™] grades with a degree of hydrolysis of 80 mol%

These grades have a high degree of hydrolysis and a high degree of polymerisation among our primary suspending agents. With these grades suspension polymerisation can be carried out in a stable manner, especially for the combination with a secondary suspending agent. It is possible to stabilise the PVC resin particle size.

Kuraray Poval™ L grades

These grades have a low degree of hydrolysis and low degree of polymerisation among our primary suspending agents. Compared to our grades with a degree of hydrolysis at 80 mol% they can reduce the polyvinyl alcohol use in the recipe. They can also control the PVC particle size easily by adjusting the amount used. They can provide good porosity PVC resin maintaining good bulk density. Plasticiser absorbance speed, fish eye level and residual VCM level will be improved leading to a good balance of properties for the PVC resin produced. These grades also provide a narrow PVC resin particle size distribution and improved morphology giving more spherical particles leading to better processability.

Kuraray Poval[™] grades with a degree of hydrolysis of 88 mol% to 95 mol%

These grades have a high degree of hydrolysis and a high degree of polymerisation among our primary suspending agents. Combining these grades with grades of hydrolysis at 80 mol% it is possible to obtain high bulk density PVC resin. Kuraray Poval™ 55-95 can also be used in recipes to increase the bulk density of the PVC resin.

Kuraray Poval[™] LM grades

Kuraray Poval[™] LM grades are secondary suspending agent products with a degree of hydrolysis below 50 mol%. They provide high porosity and excellent plasticiser absorption for PVC resins whilst maintaining good bulk density. The products are supplied as solid dry powders but can be dispersed in water without the need for organic solvents.



Figure 3. Viscosity of aqueous PVOH solutions at 20 °C vs. concentration.



Figure 4. Viscosity of aqueous PVOH solutions at 20 °C vs. concentration.



Figure 5. Viscosity of aqueous PVOH solutions at 20 °C vs. concentration.



Figure 7. Viscosity of PVOH solutions in water / methanol (1:1) at 20 °C vs. concentration.



Figure 6. Viscosity of aqueous PVOH solutions at 20 °C vs. concentration.



Kuraray Poval[™] solution preparation

Method 1

Kuraray Poval[™] L grades are partially hydrolyzed polyvinyl alcohols varying in their degree of hydrolysis from 69.5 - 73.5 mol%. As such they are cold water soluble and solutions can be made either in cold water or in hot water.

Kuraray Poval[™] is slowly added to a stirred tank of cold water to avoid lump formation. The product can be passed through a coarse mesh (10 mesh) to catch any extraneous items that may fall into the solution mixer. After adding all the L-grade, the mixture is heated up to 70 - 80 °C with agitation. There should be sufficient agitation in the mixer for efficient dissolution but not too intense to cause foam build up at the surface. Mix for 2 hours or until the solution is homogenous. The solution is then cooled to below the cloud point to obtain a clear solution. The solution concentration can then be checked and adjusted if necessary. Before pumping to the charge vessel or reactor the solution is passed through a 200 micron filter as a final "cleaning process". L-grades exhibit a cloud point and the prepared solutions have to be stored below the product's cloud point to avoid separation during storage.

Method 2

Kuraray Poval[™] 80 mol% hydrolysis grades are partially hydrolysed polyvinyl alcohols varying in their degree of hydrolysis from 76.5 - 81.0 mol%. For these grades it is recommended to utilize hot water to prepare solutions.

Kuraray PovalTM is slowly added to a stirred tank of cold water to avoid lump formation. The product can be passed through a coarse mesh (10 mesh) to catch any extraneous items that may fall into the solution mixer. After adding all the Kuraray PovalTM, the mixture is heated up to 80 - 90 °C with agitation. There should be sufficient agitation in the mixer for efficient dissolution but not too intense to cause foam build up at the surface. Mix for 2 hours or until the solution is homogenous. The solution is then cooled to below the cloud point to obtain a clear solution. The solution concentration can then be checked and adjusted if necessary. Before pumping to the charge vessel or reactor the solution is passed through a 200 micron filter as a final "cleaning process".

Method 3

Kuraray Poval[™] 88 mol% and 95 mol% hydrolysis grades are partially hydrolyzed polyvinyl alcohols varying in their degree of hydrolysis from 87.0 - 96.0 mol%. As such they are only completely soluble in hot water and solutions can only be made utilizing hot water.

The Kuraray Poval[™] is slowly added to a stirred tank of cold water to avoid lump formation. The product can be passed through a coarse mesh (10 mesh) to catch any extraneous items that may fall into the solution mixer. After adding all the Kuraray Poval[™], the mixture is heated up to 90 - 95 °C with agitation. There should be sufficient agitation in the mixer for efficient dissolution but not too intense to cause foam build up at the surface. Mix for 2 hours or until the solution is homogenous. The solution is then cooled to room temperature. The solution concentration can then be checked and adjusted if necessary. Before pumping to the charge vessel or reactor the solution is passed through a 200 micron filter as a final "cleaning process".

Method 5

Kuraray Poval[™] LM-30 is slowly added to a stirred tank of a mixture of cold water and methanol or ethanol (50:50 mix) passing through a coarse mesh (10 mesh) to catch any extraneous items that may fall into the solution mixer. There should be sufficient agitation in the mixer for efficient dissolution but not too intense to cause foam build up at the surface. Mix for 4 hours or until the solution is homogenous. The solution concentration can then be checked and adjusted if necessary. Solutions of Kuraray Poval[™] LM-30 should be charged through the VCM charge line or a dedicated line due to their low solubility in water.

Kuraray Poval™	Method	Recommended concentration
L-8	1	4 - 6 %
L-9	1	4 - 6 %
L-9P	1	4 - 6 %
L-9-78	2	4 - 6 %
L-10	1	4 - 6 %
L-11	1	4 - 6 %
L-508W	1	4 - 6 %
32-80	2	4 - 5 %
35-80	2	4 - 5 %

Method 4

Kuraray Poval[™] LM grades are solid products and are classed as low hydrolysis polyvinyl alcohols varying in their degree of hydrolysis from 40.0 - 50.0 mol%. As such they are not fully water soluble but can be easily dispersed into water.

The Kuraray Poval[™] LM grade is slowly added to a stirred tank of cold water to avoid lump formation. The product can be passed through a coarse mesh (10 mesh) to catch any extraneous items that may fall into the dispersion mixer. There should be sufficient agitation in the mixer for efficient dissolution but not too intense to cause foam build up at the surface. Mix for 1-2 hours or until the dispersion is homogenous. The solution concentration can then be checked and adjusted if necessary. For storage of LM-grade aqueous dispersion, solid content should be less than 5 % and the temperature below 40 °C.



Kuraray Poval™	Method	Recommended concentration
40-80E	2	4 - 5 %
48-80	2	4 - 5 %
44-88	3	4 - 5 %
49-88	3	4 - 5 %
55-95	3	4 - 5 %
LM-10HD	4	2 - 4 %
LM-20	4	3 - 7 %
LM-30	5	3 - 7 %

Cloud point

The cloud point is the temperature at which a solution of polyvinyl alcohol starts to phase separate into lower and higher concentration phases and the solution gets turbid because of the difference in refractive index of the two phases. Low hydrolysis polyvinyl alcohols are more hydrophobic and exhibit cloud points at lower temperatures. As the degree of hydrolysis of a polyvinyl alcohol increases the product becomes less hydrophobic and more hydrophyllic so their cloud points tend to be at higher temperatures. Detailed below are the cloud points of some of our different hydrolysis grades. When the solution is stored above its cloud point without agitation sedimentation of the higher concentration phase happens. Generally aqueous solutions of primary suspending agents have cloud points as shown in the following graph. So the solution of DH 80 mol% grade should be stored below 45 °C and DH 72 mol% grades (L-grades) should be stored below 25-30 °C to avoid sedimentation issues.

Cloud point was measured by UV/Vis spectroscopy at 660 nm with a heating rate of 1 K/min. The cloud point is defined as the temperature at which the transmission of the solution drops below 85 %.



Figure 8. Cloud points of aqueous Kuraray Poval[™] solutions vs. concentration.



Foaming

There are two types of foam that can be generated when using polyvinyl alcohol in suspension polymerisation.

The first is the production of wet foam when polyvinyl alcohol solutions are made. Polyvinyl alcohols by their nature are used to alter the surface tension of water and reactor contents so it is no surprise that they foam when being made into solution with possibly fast agitation. It is also possible to get wet foam during the beginning of the PVC polymerisation as the polyvinyl alcohol is dispersed in the water VCM mixture. The other type of foam is dry foam (or still could be classed as wet foam)! As suspension reactions progress they generate heat which causes VCM to boil. The VCM gas bubbles rise to the surface of the reactor either to cool in the space above or via a condenser. As reactions run more quickly due to faster initiators more heat needs to be removed from the reactor and the use of condensers becomes the norm. The boiling VCM droplets rise to the surface of the reactor and can at-

Handling and storage

Kuraray Poval[™] is an industrial chemical and as such when handling the necessary personal protective equipment (PPE) should be used for handling a fine powder. Care should be taken when discharging from plastic packaging as static charges can be generated. It is recommended that packaging and equipment is earthed to prevent static build up.

Kuraray Poval[™] should be stored in clean dry conditions and not exposed to water or high humidity for long periods of time. Kuraray Poval[™] solutions should be stored below their cloud points in clean vessels with gentle agitation or circulation pumps. They should be protected from biological attack by micro organisms.

∋ For more detailed information please refer to our Kuraray Poval[™] handling brochure which is available upon request. tach themselves to PVC resin particles. At the same time the PVC resin slurry increases in viscosity so it becomes more difficult for the VCM droplets to be released from the slurry which looks like a foam / cream at the top of the reactor contents. To reduce the generation of foam you need good end to end agitation and a good vortex at the top to try and wet out the PVC slurry. You can increase the water / monomer ratio to reduce the slurry viscosity. An injection of water will also reduce the viscosity and also help cooling. The last option is to use an antifoam. This can be a proprietary antifoam or polyvinyl alcohol. The decision on what to use would be based on performance vs cost as antifoams are more effective but are considerably more expensive than polyvinyl alcohols. If a polyvinyl alcohol is to be used it is better to use one of high molecular weight and of high degree of hydrolysis.

Safety

Kuraray Poval $\ensuremath{^{\text{\tiny M}}}$ is not classified as hazardous to health and is not classified as dangerous for transport.

G For more detailed information please refer to our product safety data sheets.

Descriptions are based on materials, information and data available at this moment, and we do not guarantee it although we are accurate. The notes are intended for ordinary handling and do not necessarily conform to all situations, uses, and usage. Therefore please set and use safe management and use conditions as these are at the responsibility of the user.



Adding value to your products – worldwide

KURARAY POVAL[™], EXCEVAL[™], ELVANOL[™], and MOWIFLEX[™] are the trademarks for polyvinyl alcohols (PVOH) made by Kuraray. Their key characteristics — outstanding film-forming properties and high binding strength — add real value to your products. Our polymers are water-soluble, highly reactive, crosslinkable and foamable. They have high pigment binding capacity, protective colloid characteristics and thickening effects. The physical and chemical properties of KURARAY POVAL[™] make it ideal for a wide variety of applications, ranging from adhesives through paper and ceramics to packaging films. Many of our polymers are food contact-approved and thus suitable for food applications.

Kuraray produces its wide range of KURARAY POVAL[™] grades in Japan, Singapore, Germany and the USA. Kuraray's global production and service network make us your partner of choice for innovative high-quality PVOH resins.

Kuraray Poval[™]

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