Solvent Film Casting—A Versatile Technology for Specialty Films

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ABSTRACT

The oldest technology of plastic films manufacturing is attracting increasing interest. Specific requirements in the fields of optical, opto-electronic, electrical and other applications can only be met by this technology. In recent years, tremendous growth in new liquid crystal display applications has led to the development of new casting and coating technologies. The core competencies of cast film manufacturing include:

- Safe handling of organic solvents during dope making, casting, drying, coating and recovery
- Control of rheological processes and caster design
- Control of casting support surface
- Knowledge of drying processes to achieve high productivity and good surface quality
- Capability of combining process technologies such as dispersion, fine filtration, winding, slitting, handling in clean-room conditions etc.

The advantages of solvent cast technology include uniform thickness distribution, highest optical purity and extremely low haze. The optical orientation is virtually isotropic, and the resulting films have excellent flatness and dimensional stability. The cast film can be processed in-line with an optical coating design. An occasional drawback is the difficulty in finding an appropriate solvent for the casting process. Due to the rate of diffusion of the solvent during the drying step, a thickness of more than 200 mic is not favorable. As an example of applications, cellulose triacetate and polycarbonate cast films have been successfully used for various optical applications, e.g. protection of data storage disks and functional films in LC displays.

INTRODUCTION

The development of a continuous process to manufacture thin plastic films was closely linked to the emerging photographic industry starting from the end of the 19th century. In those times, no other technology was available for industrial film forming, and polymer science was also still in its infancy. Two different technologies have been developed: casting on wheels or large drums and casting onto endless flexible metal belts. Both are still in use today together with a third technology, casting onto moving plastic films. Since the development of extrusion technologies for the production of thermoplastic polymer films in the fifties, the importance of solvent casting methods has declined. Nowadays, solvent casting is a specific manufacturing method which is used for niche markets and films with high quality requirements, mainly for optical applications.

KEY ELEMENTS OF TECHNOLOGY

Polymer Solution Preparation

The first step in solvent cast film production is the preparation of a homogeneous polymer solution—also known as "dope"—in mixers. Due to large differences in viscosity, from pure solvents to highly viscous solutions, stirrer or paddle geometry has to be selected carefully. Heating/cooling management by thermal jackets and exhaust for solvent vapor is required. Some dissolution processes run at overpressure to ensure better or faster preparation. The next important process steps are de-aeration and filtration. De-aeration is needed to prevent the occurrence of air bubbles during the film formation process at higher temperatures. Discontinuous thermal or vacuum de-aeration and a continuous process are both possible.

One advantage of solvent casting is the possibility of fine filtration, even at the scale of microns. Filtration takes place in several consecutive steps. Frame and plate filters are widely used, the filter pads being made of textile or metal.

Raw Materials

Conditions to be met for the use of a specific combination of polymers and solvents are:

- The polymer must be soluble in a volatile solvent or water
- A stable solution with a minimum solid content ($\approx$ 10%) and a minimum viscosity ($\approx$ 1,500 mPa) should be formed.
- Formation of a homogeneous film and release from the casting support must be possible.

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Many process techniques are used to provide these properties:

- Co-solvent systems
- Dissolution under overpressure
- Use of specifically designed co-polymers
- Use of additives such as plasticizers, release agents etc.

In order to adjust specific properties of the finished films, soluble or insoluble substances can be added to the dope: dyestuff, pigments, antistatic compounds, antiblocking compounds, electrically conductive or thermally conductive substances, magnetic compounds etc. It is a major advantage of the solvent cast method that the level of solid contents can be set much higher than in an extrusion process, e.g. up to 95% by weight.

Casting Support
Many different materials have been used. Today, stainless steel, chromium-plated steel, polyester or PTFE are dominant. The release behavior of the semi-finished cast film from the support is pivotal for the entire process. For most cast film products, control of the surface finish of the support is crucial. The surface of the support is replicated by casting the liquid dope on it. Super-polished belts with extremely smooth surfaces are used to produce optical films. Defined matt finish is applied for films with structured surfaces. Extreme care is required to protect the surface against damage. Each defect at the surface of the support is replicated after one turn of the drum or belt.

Casting Machines
Belt machines use belts with dimensions of 1 to 2 m width and 10 to 120 m length. Drums diameters of drum machines can reach 8 meters. The air channel around the belt or drum prevents solvent vapor from escaping and directs heated drying air toward the film. Belt machines require guiding of the belt, which tends to shift from the supporting drums.

Die or Spreader or Caster
Using solvent cast manufacturing, thickness distributions can be set much narrower than in other methods. The spreader has a crucial role in providing a homogeneous thickness profile. A great deal of theoretical work has been done to calculate ideal hydrodynamic profiles for dies. In solvent casting, laminar flow governs the process, resulting in films with low intrinsic orientation and low thickness variation. Slot dies and doctor blade dies can be used as well, depending on dope viscosity, film thickness and process rate.

The Drying Steps
In many cases, at least two drying steps are required. Firstly, on the support the solvent evaporates at one open surface up to the point where it is sufficiently stable to be stripped off. During this first step, most of the solvent is removed and directed to the recovery system. After strip-off, the film is dried from both sides by heated air jets in floater dryers or in cabinets with many rollers to reduce the residual solvent as far as necessary. In many polymer-solvent systems, the glass transition temperature rises and the diffusion coefficient drops sharply with reduced residual solvent. Long drying passes and higher temperatures are therefore supplied, with film lengths of up to 1,000m and temperatures of 100 °C or more.

The solvent diffusion coefficient of a given combination of materials is the crucial parameter which governs the rate of production. A typical rate is 5 to 60 m/min, corresponding to an area of about 500 to 6,000 square meters/h.

In-line coating of dried or semi-dried film with solvent-based or water-based coating solutions has been standard in the photographic film industry for many years. Gelatin subbing, antistatic, slip agent, colored layers, hard coat, diffusion barriers, optically active layers and magnetically active layers can be applied.

Solvent Recovery and Handling
Solvent casting cannot be mastered without detailed know-how and experience in handling organic solvents. One of the most widely used solvents is methylene chloride. There are many restrictions and low limits for workplace air, exhaust air, wastewater pollution etc. The existing standard in industry contains safety equipment such as extra-tight fittings, seals, double-shell tanks, explosion-proof equipment, automated in-line measurement of exhaust air and workplace air, solvent detectors for wastewater etc.

Recovery Processes
Several recovery processes or combustion processes exist: adsorption to active carbon, absorption in liquids, condensation, membrane process, thermal oxidation, catalytic oxidation, “biofilter.” Most commonly, industry uses the discontinuous adsorption process with active carbon, for several reasons; a wide range of feed solvent concentrations in air can be used, recovery of many different solvents is possible. The reduction of solvent concentration in the exhaust air to a very low ppm is feasible. Long lifetime of active carbon and equipment is another advantage. Other processes such as condensation by cooling or absorption in liquids are in use for specific cases.

Thermal or catalytic combustion is a method for complex mixtures of solvents if distillation of the recovered mixture is too expensive, or in order to be more flexible in lines with changing solvents and products.

PRODUCTS AND MARKETS

Principal Advantages of Solvent Cast Films

- Homogeneous thickness distribution
- Highest optical purity, free of gels, specks, excellent transparency, low haze
- Isotropic orientation, low optical retardation, excellent flatness
- Surface structure can be adjusted easily: high-gloss or matt or specially structured
- Processing of thermally and mechanically sensitive components is feasible
- Possibility of production of high-temperature-resistant films from non-melting but soluble raw materials

Due to low diffusion coefficients, films with thicknesses above 200 mic cannot be easily produced. Lamination of two or four thinner films is possible. Another drawback is the higher cost of solvent cast film production compared to extrusion processes caused by higher energy consumption for the solvent recovery.

Photographic Applications

The largest quantities of solvent cast films are used in photographic products. A photographic film base made from cellulose triacetate is used for the manufacturing of consumer products such as miniature film (135 format), roll film and disposable or single-use cameras. Other photographic products such as X-ray film, microfilm and movies mainly use polyester films made by other processes. Advantages of cellulose triacetate base films are absence of optical defects, good adhesion to photosensitive layers in dry state and during the wet processing steps, excellent flatness during and after processing and no cold creeping. Photographic film base is slightly gray-colored for antihalation purposes and is used in thicknesses between 100 and 190 mic. World production amounts to about 500 million square meters/year. This matured market is stable.

LCD Applications

Cellulose triacetate, polyvinyl alcohol and other cast films are used for providing different functions of a liquid crystal display.

The physical principle of LCD requires two polarizers on both sides of the LC layer, enclosed between two glass plates. For the polarizer, two layers of cellulose triacetate films are needed to protect the polarizing layer made from a stretched polyvinyl alcohol film. The unique combination of properties requires the use of solvent cast cellulose triacetate films for this purpose.

- Absence of optical defects due to the solvent cast production process
- High transparency, low haze
- Excellent thickness distribution
- Long-term stability against light and UV radiation
- Extremely low birefringence
- Good adhesion of the finished product for long-term use
- Reasonable price of the raw materials

The market volume of cellulose triacetate films for LCD polarizers is growing rapidly. An estimate is about 80 million square meters for the year 2001.

Another example of optical components in the rapidly growing field of LCD which require cast film technology is the polyvinyl alcohol film cast from aqueous solutions. The estimated volume is about 10 million square meters/year.

Polycarbonate cast films are used for special optical functions in LC displays as compensation or retardation layers. This functional film corrects the color image, enhances the contrast of the display and improves the viewing angle. This speciality film is produced at the scale of several hundreds of metric tons per year.

Other retardation or compensation films are based on new classes of polymers cast from solutions or have been manufactured by combinations of cast films with coatings. There are several products under development.

For the last decade, researchers have been looking for materials for the “LCD plastic cell.” The glass protecting the LC layer is replaced by polymer films. In addition to the optical requirements mentioned above for polarizer protection film, properties required:

- High temperature stability
- Extremely smooth surface
- Sufficient mechanical stability
- Adhesion to barrier layers

The optical requirement can obviously only be met with films made by solvent cast methods. Candidates for LCD plastic cells include films of polycarbonates, polyether sulphone, polyarylates and cyclic polyolefins.

Electrical and Electronic Applications

Other advantages of cast film technology are important for applications of this type.

Processing of highly purified and filtered polymers with high bulk resistivity and low dissipation factor. Long-term high-temperature stability of the electrical properties is achievable only by polymers with high or no melting temperatures. Thermoplastic manufacturing methods are often not feasible for the production of these films.

Typical products are base materials for flexible printed circuits, insulation films, wrappings, capacitors etc.

Polymers such as polycarbonates, polyimide (KAPTON and others), polyetherimide (ULTEM), polyarylates etc. are used for these purposes. Consumption of this type of films is growing together with the electronic industry and the development of new electronic devices with stricter requirements. Expected sales for just one type of polyimide films (KAPTON) for 2001 are about 2,200 metric tons/year with high added value.

High-Temperature Applications

Some of the high-temperature applications are identical to the list given above for electrical/electronic use. Depending on the temperature requirements and chemical nature of the polymer, cast film techniques can be used for the field of release films. Polyimides and cellulose triacetate are typical raw materials.

Another emerging area is the application of high-temperature resistive films for LCD, as mentioned above, and as substrate materials for OLED displays. Feasible trial films have been made on the basis of polyether sulphone, polycarbonate, cyclic polyolefins, polyarylates and polyimides.

Diverse Applications

There are various film applications which require specific advantages of the solvent cast film process.

- Very high load of fillers or functional compounds
- Homogeneous thickness distribution
- Gauges of 100 mic or below
- Low shrinkage

The products have a variety of specific properties: high electrical or thermal conductivity, high magnetic coercivity, conductivity of protons for fuel cell membranes, substrate for diagnostic films with a defined optical remission, highly filled films for tamper-proof labels, weather-proof labels etc.

Acoustic membranes produced from solvent cast films have to meet the requirements:

- Very thin gauges and matt surface
- Isotropic mechanical properties before and after thermoforming
- Long term stability under mechanical stress

These membranes are used in normal sized and miniature loudspeakers, e.g. for mobile phones. Typical raw materials are polycarbonate and polyetherimide.

To achieve a controlled pore structure, another inherent advantage of solvent casting is used: solubility or partial solubility in solvents and in-line precipitation and extraction processes

Products based on proprietary processes have been used for diuresis membranes, desalination membranes, wastewater purification and other membrane processes for many years. Cellulose derivatives, polysulphones and polyimides have been used for these purposes.

SUMMARY

Solvent cast technology was developed a hundred years ago to produce thin plastic films. Now, this technique is used in markets with high quality requirements for specialty films such as photographic film base, flexible printed circuits, insulation films, high temperature resistive films, fuel cell membranes, separation membranes, loudspeaker membranes, electrical conductive films etc. In recent years, the progress made in flat panel display applications has incited the development of new film materials and improved processes for the solvent casting technology.