Polyvinyl Chloride (PVC)

**Advanced and Sustainable Properties for the Construction, Automotive and Consumer Goods Industry**

PVC stands out for its great versatility, but users’ requirements are also rising. It is therefore increasingly important to carefully select, develop and match all the formulation components. With its voluntary commitment, VinylPlus, PVC has gained a good reputation as the pioneer of a circular economy in the plastics field.

Worldwide PVC demand in 2016 was 41.5 million t (source: IHS) and was therefore narrowly 2% above 2015. Since 2011, it has increased by 2.7% per year (CAGR). For coming years, an annual growth of the order of 3% is expected. Global demand for PVC is primarily determined by construction activities. Since construction activity in Europe is still well below historic levels, and also lagging behind the global average, growth was primarily driven by countries and regions such as North America, India, Asia and Turkey. However, the BRIC states – the growth engine of the recent past – have weakened somewhat in an international comparison.

Globally, the most important applications for PVC are, practically unchanged, pipes and fittings (44%), profiles and tubes (17%), film and sheet (18%) and cables (8%). The specialties segment paste PVC has a share of 6% (Fig. 1). The world’s biggest market for PVC, at 46%, is North East Asia, followed by North America with 13% and Western and Central Europe with 12% together (Fig. 2).

**Changes among Manufacturers, Capacities and Demand**

While trade in commodity PVC, which makes up 92% of the total amount, is still a relatively “regional” business because of the high transport costs, PVC specialties, which, in total, only have a share of 8%, are marketed globally. In the gross consideration, global PVC trade in 2016 held a share of 9 million t, or 22% (source: IHS). The biggest net exporter was North America, followed by North East Asia and Western Europe. The customer regions were India, followed by the Middle East, Africa, South America, South East Asia and CIS.

Global plastics production for PVC in 2016 was about 55 million t (source: IHS). Almost half of this was accounted for by China. The capacity growth since 2011, averaging at 2% annually, can also be al-
most entirely attributed to China. Figure 3 shows the production capacities of the ten world’s biggest PVC manufacturers. Shin-Etsu Chemical, Tokyo, Japan, and Formosa Plastics Group, Taipei, Taiwan, still hold first and second place. The new number three is the US Westlake Chemical, after the purchase of Vinnolit in 2014 and the US competitor Axiall in 2016. Following in fourth to sixth place are Inovyn, which was formed from the PVC activities of Ieneo and Solvay in 2015, and ChemChina (China National Chemical Corporation) and Mexichem, of Mexico, after the acquisition of Vestolit in 2014. The regional distribution of the headquarters of the biggest manufacturers also reflects the importance of the regional markets: six companies in the top ten originate from Asia, three still from North America and only one from Europe. The picture looks entirely different for manufacturers of PVC specialties, with the Europeans Vin- nolit (Westlake), Inovyn, Vestolit (Mexichem) and Kem One among the ten leading suppliers.

The capacity utilization of PVC manufacturers in the European Economic Area (EEA) rose by three base points compared to the previous year; it was about 87% in 2016. The excess capacity here is about 1.8 million t of PVC, so that about 20% of production was exported in 2016. The demand from 2014 to 2016 in the EEA rose by 14% p.a. on average. Consequently, exports are declining again. The imports, on the other hand, reached a new record in 2016: almost 400,000 t were imported into the EEA. That corresponds to about 8% of demand. In the past, imports were at a relatively low level of between 3 and 4%. In 2016, the market for S-PVC grew by 1.7% in the EEA compared to 2015. Nevertheless, the demand is still well below that of 2010, and still below the value at the nadir of the financial and economic crisis in 2009. The area of rigid profiles remains the biggest market segment at 1.3 million t. There has not been so much movement in paste PVC. This market segment has stagnated since 2011.

**Differences in the Polymerization of Vinyl Chloride Monomers**

In the industrial polymerization of vinyl chloride monomer, three basic processes are used to generate PVC. Over 91% of global production capacity is accounted for by the discontinuous suspension process (source: IHS), in which vinyl chloride, water, protective colloids and organic peroxides are polymerized under pressure and stirring. The specific stirring conditions and protective colloids are used to control the grain size and porosity, and the polymerization temperature to control the K value. Almost 7% of capacity is based on the discontinuous or continuous emulsion process, including the discontinuous microsuspension process. Here, the end product properties are fundamentally determined by the emulsifier systems used and the particle size distribution. The bulk process has a share of less than 2%.

**Thermoplastic Applications**

Standard PVC grades for thermoplastic processing are generally based on the suspension process (S-PVC). The K values start at 57 and extend up to 73, covering almost all large-volume applications. The lower K values 57 to 60 are used for hard films and thin-wall profiles, as well as for injection molding; the higher K values are used in the pipe and profiles segments, which still dominate the thermoplastic applications in terms of volume. K values of 70 and higher with corresponding grain morphology for absorbing plasticizers are mainly used in flexible products. Because of the increasing cost pressure in all these applications, processors try to use ever higher quantities of fillers or recycle. However, there are qualitative limits to the use of fillers, which affect the mechanical end product properties and welding or the conveying properties of the dry blend.

The aforementioned standard grades are complemented with higher polymeric products with K values of about 80, which are particularly used in the flexible PVC area, if high mechanical specifications are required. Examples of this are hoses and cables. In the cable industry, the trend towards e-mobility is setting new challenges, since the number of electrical cables in the vehicle is growing strongly, but it must be reconciled with demands for weight reduction and space saving (Fig.4). A step further is taken by special products with K values of 93 to 100, which are mainly used for dynamic window seals. Special grades are suitable for absorbing particularly large quantities of plasticizer of 180 parts and more, which allow Shore A hardness of 35 and below to be achieved.

For special requirements, a large assortment of new long-chain or polymeric plasticizers is now available, with relatively low migration. This can be further...
reduced by the use of suitable two-phase graft copolymers based on butyl acrylate and vinyl chloride. Since these products have their own soft phase, they have a lower plasticizer requirement per se, which is even more effectively bound in the polymer matrix. As a result very high quality, durable flexible PVC products are obtained, with tactile properties similar to natural rubber, but which are superior as regards their weathering resistance, processing characteristics and the possibilities for pigmentation. These graft copolymers are enhanced versions of PVC additives that were originally developed for the impact modification of rigid profiles. The soft acrylate phase absorbs the impact energy in the hard PVC matrix and converts it into heat. These impact modifiers are currently used as a 50% concentrate or, with approximately 7% acrylate, as base resin, usually for window profile applications. These applications have the common feature that, due to the very uniform phase distribution and the absence of inactive sheathing of the soft phase, they are highly effective and have very good processing properties.

**Revival of Vinyl Records**

Along with graft copolymers, copolymers of vinyl acetate are also widely used. The commercial standard contains 11% vinyl acetate with a K value of 57 and is mainly used in rigid film production, usually as a blend with S-PVC and emulsion PVC (E-PVC). Such statistical copolymers act by largely suppressing the formation of crystallites, thereby improving the flow behavior of the melt and the thermoformability. In addition, the acetate content improves compatibility with other polymers, which in turn improves the printing and lamination properties. The applications are just as varied, ranging from pharmaceutical films through credit cards to flooring. In the latter case, higher acetate-containing copolymers are used, which usually have lower K values. These variants are also used in formulations for vinyl records, which have seen a revival in recent years and are regaining markets that were thought to have been lost. In the pressing of records, the outstanding low-temperature flow behavior of this variant is exploited to neatly reproduce the fine structures of the sound tracks.

In classical PVC flooring, vinyl acetate copolymers and E-PVC in particular support the high filler loading. The designer vinyl flooring segment has developed rapidly, usually in the form of luxury vinyl tiles (Fig. 5). These very natural-looking wood, stone or metal effect finishes are used in both professional and private surroundings. Until now, there has been no standard construction for this development. The common feature of most products is a highly filled PVC base layer and a transparent PVC topcoat, which allows the photorealistic reproduction of natural materials in combination with printing and embossing techniques.

Besides the aforementioned main applications, a range of PVC products make an important contribution to PVC processing as additives. Thanks to its very fine, compact particle structure, emulsion PVC as a blend component in a proportion of 10 to 30% can increase the bulk density of S-PVC, and is therefore used as a highly compatible processing aid. The advantages are very rapid gelling and uniform energy input into the melt, and therefore a uniform melt flow in the extruder, or kneading on the calender. End products with low fish-eye count can be produced; the emulsifiers contained additionally act as release agents and improve the end product properties, such as gloss and antistatic. In this manner, the use of further gelling and flow aids can be minimized, and unattractive side effects, such as the formation of deposits are avoided.

Suitable E-PVC grades in the K values 60 to 70 are available on the market and are fitting for rigid and soft applications. In thermoplastic processes, pure E-PVC is practically only used for adhesive tape production: in the highly specialized Luviherm process, E-PVC with K values between 78 and 80 can be calendared to form very thin, high-strength adhesive tape films.

Crosslinked PVC is used for controlling the surface properties of end products. Fine, non-gelling particles in low concentrations on the surface of the final part act as spacers, reducing the adhesion forces, for example between film layers. In higher concentrations, these products lead to fine, satin surfaces or, with appropriate product design, also to tactile rough structures. Last but not least, bulk PVC
should also be mentioned, which although a niche product, is relevant in applications in which transparency and low moisture absorption play a role.

PVC for Paste Processing

The majority of PVC for paste processing ("paste PVC") is manufactured by emulsion or microsuspension polymerization. A small proportion is based on special suspension processes. The powdery PVC is dispersed in liquid organic plasticizers for processing, and thus compounded into plastisols ("pastes"). The liquid plastisols can subsequently be coated on carrier materials in various technical processes, for example by means of doctor blades or dip baths. The carriers (substrates) include special papers, textile fabrics, nonwovens and many others. The high-quality end products (often also multilayer) that can be produced in this way extend from flooring, artificial leather through tarpaulins to modern designer wallpapers (Title figure). In automotive applications, PVC pastes are used, e.g., as compounds for underbody coating and body seals. In this way, high-quality, low-emission, flexible and long-term durable car interior trim materials can be achieved. Rotary casting can be used for complex hollow articles such as balls and dolls’ heads, but also buoys and fenders. The huge variety of products is the result of a wide variety of material constructions (e.g. multilayer structures), the type of
Fig. 6. PVC in the car interior must meet high requirements (© Benecke)

coating technology and the plastisol formulations to be processed. The material itself, the paste PVC, plays a central role in determining the end product properties to be adjusted.

Besides the main components of PVC and plasticizer, the paste formulations also include many other ingredients. Thus, special thermal stabilizers are used to prevent thermal damage due to the high temperatures occurring in the production process. Fillers such as chalk are incorporated, mainly to reduce costs. To meet particularly high requirements for fire behavior, special flame retardant additives are often used. Anchoring to the carrier materials can be significantly increased with adhesion promoters, usually based on isocyanates. Additives such as UV stabilizers or biocides to prevent microbial degradation are other formulation components that are widely used. Pigments are added to adjust the desired color and opacity. If necessary, rheology modifiers, wetting agents or diluents can also be used to precisely adjust the processing viscosity. These paste formulations are continually adapted.

An important development is the increased use of alternative plasticizer types. In the case of general purpose phthalate plasticizers – against the background of European chemical legislation (REACH) – there has been a trend in recent years toward the use of non-classified, longer chain variants, such as DINP/DIDP. Moreover, alternative systems such as cyclohexanoates (e.g. DINCH), terephthalates (DOTP) and special citrates are increasingly being used. This applies in particular to sensitive applications, such as children’s toys or in food contact, but is also to be found more and more in areas such as flooring or wallcovering. However, changing over is not a recipe for sure-fire success and topics such as, e.g., plasticizer migration or substrate anchorage require careful matching of the formulation components in order to ensure compatibility.

New Regulations, Many Adaptations

Because of the stricture regulatory environment, thermal stabilizers (and their formulations and application forms) have also been completely revised and some important components have been replaced by others. The leading manufacturers have reached a good level here through intensive research and development. Nevertheless, it is increasingly important to select PVC products with good inherent stability.

Focus has also shifted to the volatile components of the plastisol formulations. That is particularly true of products such as flooring, wallcovering or artificial leather, which are used in interiors. A trend here is the reduced use of volatile organic compounds, such as solvents. The resulting processing disadvantages can be compensated, for example, with special PVC grades with especially low intrinsic viscosity. To meet the extremely high requirements for applications in car interiors (Fig. 6), new PVC grades, developed especially for this application, with low emissions and very good thermomechanical foam stability have been developed for modern processing techniques.

REACH has also targeted the foam blowing agent ADC (azodicarbonamide). This is currently used for almost all foamed products of paste PVC. Even if it is not currently subject to authorization, processors are eagerly searching for alternatives. Since other blowing agents do not generally offer the desired performance, attention is increasingly turning to the process of mechanical foaming by beating in air. Here too, it should be considered that these blowing agent-free foams require a basic PVC with significantly different properties than those foamed with chemical blowing agents.

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A key environmental and cost issue is saving energy during processing. This may be achieved, in particular, with shorter residence times or lower temperatures in the gelling oven. Both can be achieved by the addition of special fast-gelling co-polymers, which can considerably speed up gelling thanks to the co-monomer content in the PVC molecular chain.

To sum up, it can be stated that, with new PVC grades and advanced additives, higher requirements, especially in the fields of health and environmental protection, can be met. To maintain and develop the high technical level of the paste PVC products, however, under these premises the careful selection and matching of all formulation components will increase in importance and it will be necessary to develop ever more effective PVC grades.

**PVC and Sustainability**

Along with more advanced products and processes from the individual companies, societal expectations and legal requirements, VinylPlus is one of the most important drivers for the sustainable development of the material PVC. It is backed up by a voluntary commitment by the European PVC industry (www.vinylplus.eu). At the top of the political agenda is the step-by-step transition to a circular economy. PVC has gained a reputation as a pioneer here. In 2016, a total of 569,000 t of PVC was recycled within the scope of VinylPlus, 40% of which was plasticized PVC. Since 2000 – when the predecessor program Vinyl 2010 started – it has totaled 3.6 million t (source: VinylPlus). The reachability of the recycling aims must be supported by suitable regulation and, if necessary, trackability of recyclates. A major challenge here is to achieve the future recycling of PVC with legacy additives that are no longer used in the EU, such as cadmium and lead stabilizers, or short-chain phthalate plasticizers. The complete abandonment of lead-based stabilizers in primary goods was achieved in the EU in late 2015 (source: ESPA). The trend to alternative (non-phthalate) plasticizers is continuing: by 2025, a global growth rate (CAGR) of 5.9% p.a. is predicted (source: Research and Markets).

For the first time, VinylPlus has assigned the successes achieved to the sustainable development goals of the United Nations Agenda 2030. This comprised the over 30 concrete targets of the VinylPlus program in the five areas of circular economy, emission reduction, sustainable use of additives, energy and raw materials efficiency and developing sustainability awareness.

The switch of chlorine production in the EU from the mercury to the energy efficient and environmentally friendly membrane process, which was driven by members of the European chemical association Euro Chlor as part of their voluntary commitment, is forging ahead. At the end of 2016, the market share of the mercury process in Europe had declined to below 20% (source: Euro Chlor). By the end of 2017, this, too, is history: the Chloralkali conclusions about the best available technology of the EU commission require the abandonment of mercury technology by the end of 2017.

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