

OCTOBER 2014

# RubberWorld<sup>125</sup> years

THE TECHNICAL SERVICE MAGAZINE FOR THE RUBBER INDUSTRY VOLUME 251, No. 1

## 125th Anniversary Issue

**RUBBER DIVISION MEETS IN NASHVILLE  
FOR INTERNATIONAL ELASTOMER CONFERENCE  
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**Reactive extrusion -  
opportunity for improved performance products**

by Paul Andersen, Coperion

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# Reactive extrusion: Opportunity for improved performance products and manufacturing productivity

by Paul Andersen, Coperion

The co-rotating twin-screw extruder is cost-effective to operate and has process flexibility. As such, it has become the most widely used piece of compounding equipment in the polymer industry. These characteristics have also enabled the twin-screw extruder to be successful in many other markets. These include, but are not limited to, such diverse processes as food, pharmaceuticals, bio-materials, energetics and chemicals. Additionally, application of the co-rotating twin-screw extruder in the polymer industry has been expanded beyond traditional compounding processes. Reactive extrusion/compounding for many polymerization reaction systems has been evaluated. Table 1 lists many, but not all, of them. While technically feasible, for most of the systems listed, the process was not commercialized. However, some have been very successfully commercialized. This raises the question: What makes some processes candidates for reactive extrusion, while others are left as laboratory curiosities? The reasons can be quite varied, but mainly there is one overarching advantage or shortfall, as will be discussed in the following sections.

## Suitability of twin-screw extruders for chemical reactions

The co-rotating twin-screw extruder has many characteristics that make it attractive for reactive processing. First, it can handle a wide range of viscosities. A typical chemical reaction starts with a blend of lower viscosity liquids and then, through reaction, produces a higher viscosity material. Stirred vessels can handle the initial low viscosity feedstock material, but will stall out when the material viscosity reaches a level much beyond the viscosity of heavy molasses.

Second, the extruder is a low internal volume high turnover device, whereas a stirred tank is a high volume low turnover apparatus. Therefore, the extruder needs to process smaller amounts of product over a shorter time period compared to an equivalent capacity stirred tank, which processes larger volumes of product, but over a longer time frame. Consequently, the extruder has a residence time measured in seconds or, at most, minutes, rather than in hours for most stirred tank reactions. This pro-

vides three additional advantages for the extrusion process:

- a) The lower internal volume of the extruder and higher surface to volume ratio provide more effective heat transfer to keep exothermic reactions under control.
- b) The extruder is more efficient at elimination of any reaction by-products due to greater surface regeneration capacity.
- c) The extruder has more efficient mixing to uniformly incorporate low percent components such as activators, cross-linking agents, etc. This is extremely critical for uniform product manufacturing. For example, if a crosslinking agent is not uniformly mixed into the rubber prior to initiating the reaction, the crosslink density will be higher for some rubber particles and lower in others. This results in inconsistent material performance.

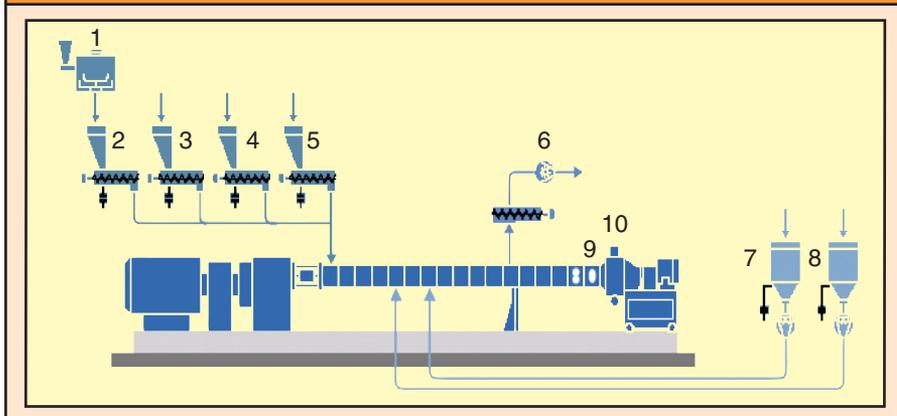
Third, mixing and compounding can be combined with the reaction. This is particularly advantageous in processes like dynamic vulcanization for TPV compounds.

Fourth, the reaction can take place without solvents or other non-contributory ingredients. This reduces the post-reaction

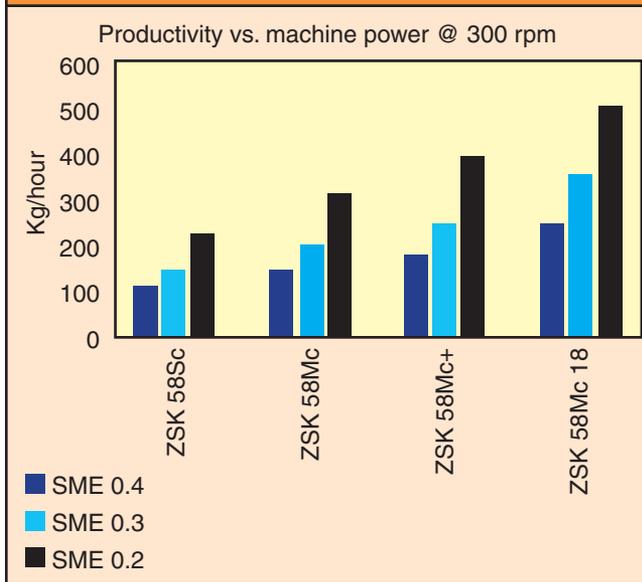
**Table 1 - reactive extrusion systems**

Product	Feed product	Type of reaction
TPV: (PP/EPDM)	Crosslink agent	Free radical
Graft copolymer: PP-g-MA	MA + peroxide	Free radical
PMMA (polymethyl-methacrylate)	Methacrylic ester	Free radical (chain termination)
TPE (thermoplastic polyurethane)	Polyols, isocyanate	Polyaddition
Polyamide 6	Caprolactam	Ionic polymerization
Polyarylate	Bisphenol A, phthalic acid	Polycondensation
POM (polyoxymethylene)	Trioxane, comonomer	Ionic polymerization
SMAC (styrene-MaH copolymer)	Styrene, maleic anhydride	Polyaddition

**Figure 1 - typical set-up for TP-V 1) rubber grinder, 2) EPDM, 3) PP, 4) filler, 5) additives, 6) vacuum with side stuffer, 7) plasticizer, crosslinker, 8) plasticizer alternative, 9) gear pump (optional), screen changer, 10) underwater pelletizer**



**Figure 2 - productivity improvement with increased machine torque capacity**



process and avoids expensive vacuum systems and separation of volatiles and contaminants.

Fifth, more uniform product is based on continuous operation with some controlled back-mixing based on screw configuration.

Sixth, the extruder provides a flexible system for barrel and screw element configuration, as well as operating conditions. This permits customization of feed introduction sequencing, residence time and residence time distribution.

As with all systems, there are some shortcomings for the reactive extruder. First, total residence time for reaction is typically limited to the 1 to 3 minute range due to restrictions on machine length, as well as process economics. For example, a 14 barrel 56 to 1 length to diameter ratio (L/D) ZSK 125 Mv (outer diameter/inner diameter = 1.8) has an internal volume of approximately 70 liters. If the entire machine is full, then at three minutes residence time, the rate would be about 1,400 liters/hour, or 1,400 kg/hour for a product with a density of 1. At a more typical degree of fill of 50%, the rate would be 700 liters/hour. In comparison, material compounded in this same machine would typically have a residence time of 20 seconds or even less with a corresponding rate of 6,300 liters/hour.

Second, free radicals terminate more quickly as the reaction proceeds and the viscosity increases. This tends to result in lower molecular weight tails being produced toward the end of the reaction.

Third, scale up from laboratory extruder to production unit can be heat transfer limited for highly exothermic reactions. The volume inside an extruder of constant l/d scales as the ratio of the diameter cubed, whereas the surface area for heat transfer scales as the ratio of the diameter squared.

## Reaction mechanisms

*Free radical: R-O-O-R → RO·*

The most common free radical reactive extrusion processes are dynamic vulcanization, short chain or single molecule grafting and vis-breaking polypropylene. Long chain molecules have been polymerized on small scale extruders to produce polymers, as in the case of PMMA, and they have been grafted onto a rubber backbone, as is the case of SAN polymerized in the presence of EPDM to produce an ABS type of product with a saturated elastomeric backbone.

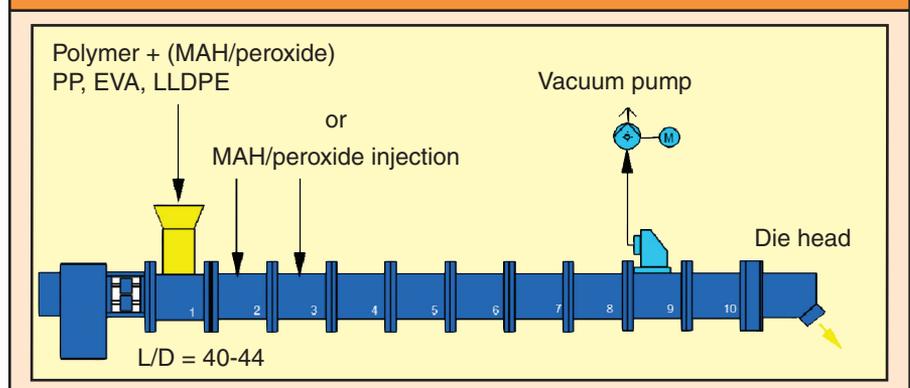
*Dynamic vulcanization: TP-V*

Figure 1 illustrates a typical set-up for an EPDM/PP based TP-V. The PP, EPDM and any small amount of filler are fed at the beginning of the extruder. The PP and EPDM are melt/mixed in the first few barrels. Depending on the ratio of the components, the EPDM is the continuous phase or the EPDM/PP form an interpenetrating network (IPN) of two co-continuous phases. Once the crosslinking agent is introduced downstream, it is mixed into the EPDM/PP blend and starts to crosslink the EPDM. As the EPDM continues to be crosslinked while undergoing high shear “dynamic” processing, the system transforms from one where the EPDM is the continuous or co-continuous phase to one where the PP is the continuous matrix surrounding the crosslinked EPDM.

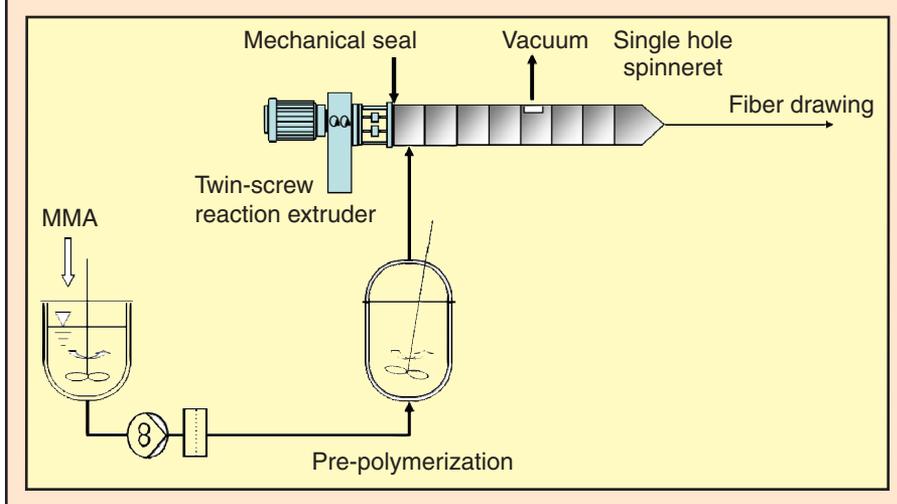
One of the key productivity advantages of the reactive extrusion process for TP-V is that it does not produce just one product, but a family of products. The ratio of EPDM to PP in the formulation is easily modified to influence the product elasticity and hardness. Additionally, heat distortion temperature (HDT) and hardness of the product are influenced by the percent of the crosslinking agent added and amount of plasticizing oil introduced with the crosslinking agent. If the EPDM is too lightly crosslinked, the rubber will maintain more elasticity and therefore have a lower heat distortion temperature.

Another productivity advantage for TP-V reactive extrusion is the advent of higher torque extruders. When compared to non-crosslinked TPO materials, the TP-V process requires significantly more specific mechanical energy (SME). As an example, a typical range of SME for TP-O recipes would be between 0.10 Kw-h/Kg and 0.17 Kw-h/Kg. The lower SME

**Figure 3 - schematic of process configuration for grafting MAH onto a polyolefin polymer**



**Figure 4 - polymethyl-methacrylate PMMA for optical fibers**



doubled from 130 kg/hour (286 lbs./hour) for the ZSK 58 SuperCompounder (Sc) generation of the 1980s to 270 kg/hour (594 lbs./hr.) for the ZSK 58 Mega-Compounder Mc18 of today.

*Grafting: XX-g-MAH*

Figure 3 illustrates a typical set-up for grafting maleic anhydride (MAH) on polyolefins such as PP, LLDPE or EVA.

The key requirements for this process are:

1) An extruder system with high torque. Just as with TP-V products, these base materials can be very high viscosity. Therefore the process requires high specific mechanical energy and would be less economical on a lower powered system. For example, a 92 mm high torque extruder operating at 600 rpm would produce between 2,400 and 3,400 kg/hour, depending upon polymer type and viscosity.

2) Efficient mixing of a small amount of reactant assures uniform grafting onto the matrix molecules.

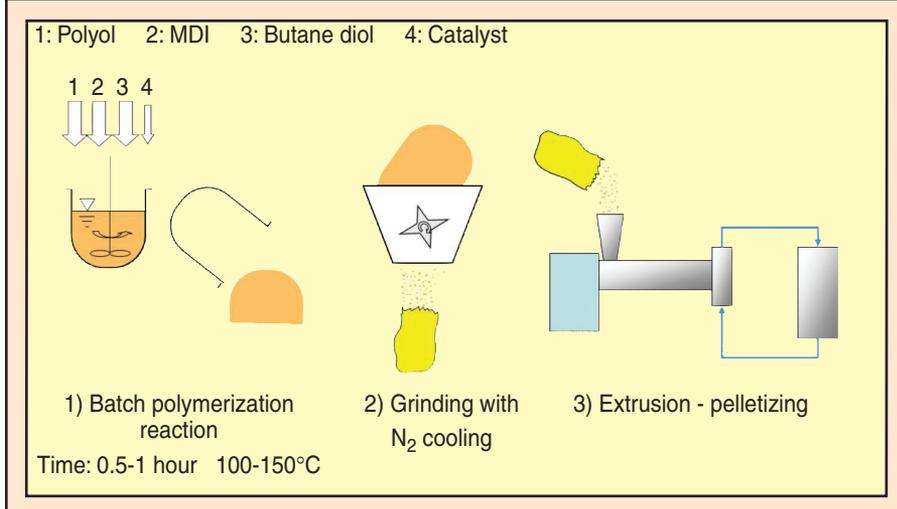
3) Overall residence time needs to be less than one minute for good economics and to avoid gel formation.

4) Narrow residence time distribution (RTD) avoids gel formation.

*Long chain polymerization: Polymethyl-methacrylate (PMMA)*

Figure 4 shows a set-up for polymerization of PMMA optical fibers. There are several key elements for this process. The first is to have a secure mechanical

**Figure 5 - history 1 - stirred vessel batch process**



would be for higher oil and filler content formulations. On the other hand, a typical range of SME for TP-V formulations would be 0.16 Kw-h/Kg to 0.4 Kw/Kg. In general, they require a greater SME than TP-O materials due to the longer and more intense mixing process length required for crosslinking and dispersing the EPDM. For example, a 90 durometer A formulation may require between 0.33 Kw-h/kg and 0.40 Kw-h/kg, while one 64 durometer A hardness TP-V might require an SME of between 0.28 Kw-h/kg and 0.34 Kw-h/kg, and a different formulation with a 67 durometer A product might require an SME of only 0.18 Kw-h/kg and 0.20 Kw-h/kg. The higher SME for similar durometer A formulations would correspond with recipes with less oil and higher viscosity (molecular weight) EPDM and PP.

Typically an SME of 0.4 Kw-h/kg would limit the productivity of the manufacturing to such an extent that it would not be economical to produce. However, with the latest high torque extruder designs, this can be significantly mitigated. Figure 2 shows that potential productivity has been more than

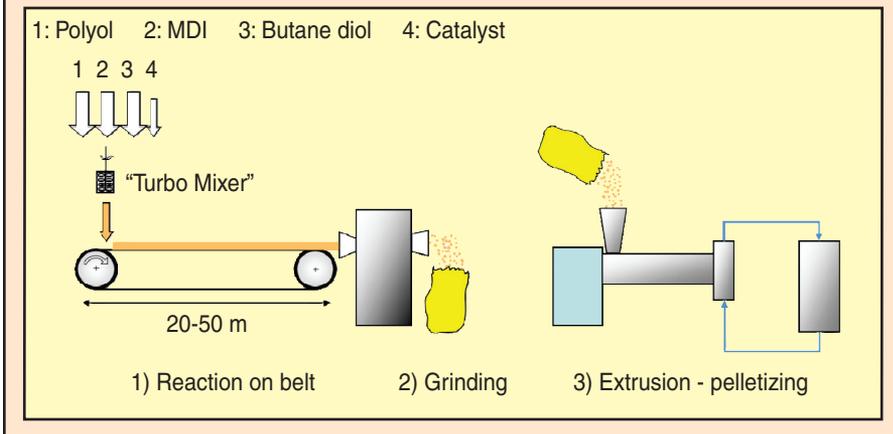
seal between the first barrel and the lantern of the extruder to contain the monomer and vapors. The second is to have conveying elements specifically designed for forwarding low viscosity "syrup." The next is to have good devolatilization to remove residual monomer.

The drawback for this and other long chain reactive extrusion polymerization processes is chain termination. As the reaction proceeds, viscosity increases and the growing chains terminate more readily because it is increasingly difficult for

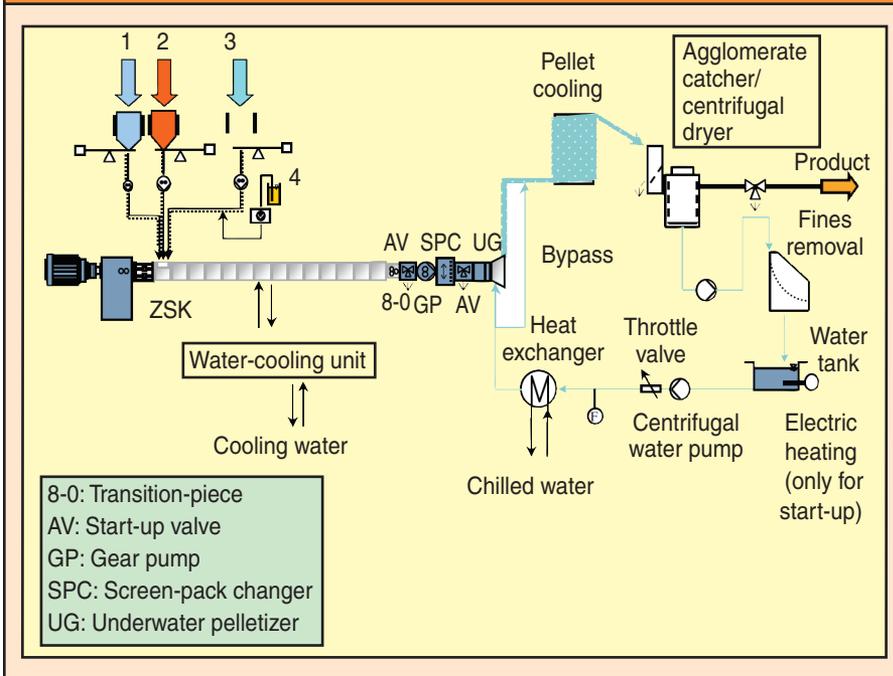
**Table 2 - TPU formulation variations**

	PO	MDI	BDO
Adhesives	85-90%	5-10%	0-2%
Soft grades TPU durometer 70-95 A	50-75%	20-45%	3-12%
Rigid grades TPU durometer 50-75 D	35-55%	35-50%	10-15%
Catalyst: 0.05-0.2%			

**Figure 6 - history 2 - semi-continuous belt process**



**Figure 7 - TPU polymerization line 1) polyol, 2) MDI, 3) butane diol (most typical), 4) catalyst**



the free radical end to “find” monomer to continue the reaction. The result can be production of a significant number of low molecular weight chains that reduce polymer viscosity or cause a reduction in physical properties. This is more problematic with long chain polymerization free radical extrusion because it typically operates at higher temperatures to speed up the reaction to compensate for the shorter residence time.

#### **Polyaddition: (A+B)<sub>n</sub>**

Polyurethane and SMA (styrene maleic anhydride copolymer) are the most prevalent addition polymers.

#### *Block copolymer: TPU*

Most TPE based elastomers are compounded with additional ingredients to provide hardness, softness, stiffness, etc. TPU

products are customized during polymerization. To control stiffness, the MDI to polyol ratio is modified. Table 2 shows three variations of TPU from very soft adhesive grades to rigid grades. For each increase in stiffness, the relative amount of MDI is increased with respect to the polyol. For UV resistance formulators, the aliphatic hard segment, TDI, is used, rather than the more typical aromatic MDI. For hydrocarbon resistance, the polyol is typically polyester based, while for a moist environment, a polyether polyol would be chosen.

A look back to the historical development of the TPU process provides an excellent roadmap to illustrate the advantages of the reactive extrusion. The original process was a batch polymerization, as illustrated in figure 5. It depicts the three required steps, including polymerization in a kettle, grinding, melting and pelletizing. The process took an hour or so from start to finish. The next step forward was the semi-continuous belt process (figure 6). This required a significant amount of floor space, as well as multiple steps. The next progression was the continuous in-line reactive extrusion process (figure 7).

Successful polymerization of TPU places several stringent requirements on a twin-screw extruder, as shown below.

- Precise feeding of liquid raw materials
- Required residence time of between 1 and 3 minutes
- Narrow residence time to avoid reduced reactions
- Good homogenization of the reactants
- Removal of any heat of reaction energy through barrel cooling
- Pelletizing sticky and elastic product

- Crystallization of the product in post-reaction device

Referring again to figure 7, the first bullet point is easily addressed with a well-designed liquid loss-in-weight feed system. Narrow residence time, good homogenization of reactants and removal of heat can be accomplished with screw design and efficient barrel tempering. An underwater pelletizer will cut sticking and elastic materials, and a long tempered water transfer line will provide post-reaction finishing.

The more challenging requirement is residence time. As noted previously, a residence time of 1 to 3 minutes can have a significant negative impact on production rates. A typical compounded TP-O has a residence time of 10 to 20 seconds. The longer TP-V process section approaches a minute residence time. Therefore, a high internal, lower shear design twin-screw is optimal for this polymerization process. With a

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twin-screw is optimal for this polymerization process. With a 1.8 OD/ID ratio (ZSK Mv geometry), there is 30% more free volume than the typical high torque compounding unit.

### **Summary**

The modular co-rotating twin-screw extruder provides flexibility for reactive extrusion. It provides good heat transfer, efficient mixing, and with the right screw design, either a narrow residence time distribution or a broader one for improved

back-mixing and homogenization. The high torque (power) systems are appropriate for materials such as TP-V and MAH grafted LLDPE that require a significant amount of specific mechanical energy. High free volume systems are appropriate for materials such as TPU that require longer residence time for completion of the reaction.

This article was originally presented at SPE's Thermoplastic Elastomers 11th Topical Conference in September 2014.

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