

14 Mixing of Rubber without using a Mill or Internal Mixer

14.1 Masterbatch

The ultimate purpose of mixing rubber is to disperse filler into the rubber matrix. With carbon black the dispersion process may be stated as,

agglomerate → aggregate

100-10 μm → 100-10 nm

The process of carbon black manufacture may be stated as

primary particle → agglomerate (and pellet)

100-10 nm → 100-10 μm (and larger)

The question is whether or not the primary particles can be directly mixed into the rubber.

The size of latex particles of the emulsion-polymerised rubber is less than 100 nm. This size corresponds to the domain size of rubber after the mixing is completed. It follows that if the primary particles of carbon black are added to rubber latex, satisfactory mixing may be achieved [1]. This is easier said than done.

First of all, the primary particles of carbon black are small, being invisible or at best like smoke. There is a handling problem. If the particles are suspended in water, they tend to flocculate. When the aqueous suspension of carbon black is added to the rubber latex, the mixture tends to consist of flocculates of carbon black and flocculates of rubber particles. The latter flocculation occurs, because the latex contains a minimum amount of emulsifier and thus it has minimum colloidal stability. Any change of the condition tends to bring a loss of stability. Once the separate flocculates are formed, additional mixing is required for improving dispersion. However, this approach offers an opportunity for developing innovative mixing processes.

The main requirement is to keep the same kind of particles, i.e., carbon black - carbon black and rubber - rubber separate and for the different kinds of particles, i.e., carbon black - rubber to attract each other. For this purpose the carbon black particles may be given an electrostatic charge and the rubber particles given the opposite charge. The charging process may be done simultaneously with 'atomising' (mist formation) particles.

A similar process can be developed with silica fillers. The solution-polymerised rubber may be also atomised.

In a recent development by Cabot [2] a rubber latex and a carbon black slurry are co-coagulated in a continuous, rapid mixer with vigorous agitation. The process is particularly suited to NR latex, which has a delicate balance of stability, although in principle, it is applicable to any rubber latex. The advantages over dry mixing are demonstrated in several ways:

- (i) capability of dispersing a wider range of fillers including the high surface area/low structure carbon blacks which are very difficult to disperse
- (ii) improved macro-dispersion and micro-dispersion
- (iii) preservation of rubber MW, particularly for NR and resulting superior resistance to crack growth
- (iv) saving of mixing energy and improved cleanness.

The current method of preparing carbon black masterbatch is to grind the agglomerates first and then mix them into rubber. In this process the size of carbon black is much larger than that of the aggregates. Even so, a recent development of wet masterbatch resulted in savings of both mixing energy and better dispersion [3].

14.2 Continuous mixing

The mill mixing and the use of internal mixer have been the major modes of mixing of rubber. However, these methods are not without deficiencies. The mill mixing may be labour-intensive so that it is used when the cost of mixing is not a concern. Therefore, it tends to be used for research and development. In production, it is used when the cost, for other than mixing dominates or when there is a critical requirement for a good dispersion.

The internal mixer has been used for many years. Much experience has been accumulated to make optimal use of the mixer. Significant improvements have been made over the

years. However, there are many inherent deficiencies as discussed already. Major deficiencies are:

- (i) the non-uniformity of the contents resulting from the design of the machine and from the nature of the material;
- (ii) with a roll-mill (see section 11.2) after each passage, the material is completely removed and recharged. Therefore, mixing proceeds by a step-by-step improvement (see section 11.2). In the internal mixer the material is improved by passing through a gap and is then returned and diluted with unimproved material. This is not a very efficient process. This situation may be visualised by considering the chemical reaction of a reactant A changing to product B. The best efficiency may be obtained by removing B from the reacting system instead of returning and mixing with A:
- (iii) the optimal conditions required for incorporation and dispersion are very different. Trying to achieve the best result with the same machine for very different processes requires a compromise
- (iv) poor batch-to-batch reproducibility. Even with the same type machines, the mixing results are not necessarily the same
- (v) because the chamber volume is cubic and the cooling surface of the chamber is the square of the linear dimension of a machine, scale-up is difficult (see section 11.2). This is especially true, if one recognises the temperature sensitive nature of viscoelastic properties.

All of these deficiencies may be overcome by adopting continuous mixing. In addition there is no downtime for charging and discharging in the continuous operation so that the output rate can be improved.

Continuous mixing is not a new idea, but for many years there existed the Farrel continuous mixer, Figure 14.1 [4] and the Transfermix, Figure 14.2 [5]. In practice these machines have been used for improving dispersion of a compound containing incorporated fillers. Proposed in this section is a completely continuous operation from charging the formulation to discharging a well-mixed compound. In principle, a batch process may be translated into a continuous process, when every operational parameter of the former is known. However, between the batch mixing and continuous mixing of rubber there is a fundamental difference in the material transport. In the batch mixing the material is returned to the milling zone repeatedly. In the continuous mixer the material is moved forward, by conveying screws.

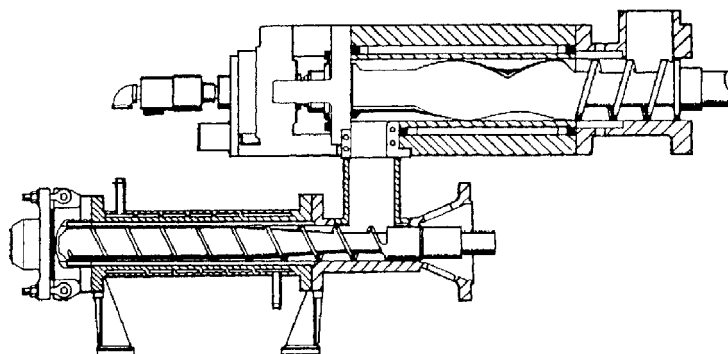


Figure 14.1 Farrel continuous mixer.

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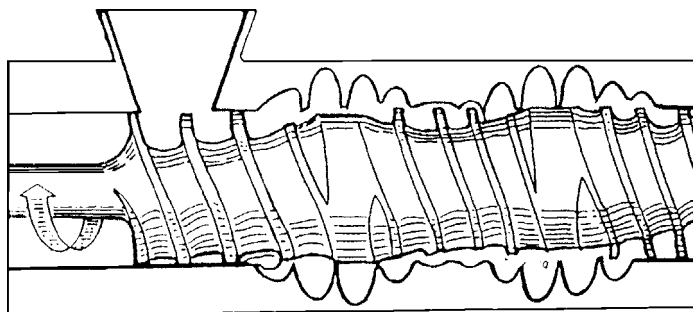


Figure 14.2 Transfermix screw and barrel.

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As a first approach a cylindrical barrel rather than the complicated barrel of Transfermix may be chosen. With a single screw extruder a filled channel is required in order to create pressure necessary for feeding material to a mixing zone. This leads to excessive temperature rise. With a twin-screw a starved condition may be used to move the material forward with a minimum of temperature rise. A successful example of the continuous mixing of EPDM with a Werner & Pfleiderer twin screw extruder was described by Tyler [6].

There is a twin-screw mixer-pelletiser for mixing polyolefins and carbon black, see Figure 14.3 [7]. It has a large size and the output rate is comparable to that for the largest batch internal mixer for rubber.

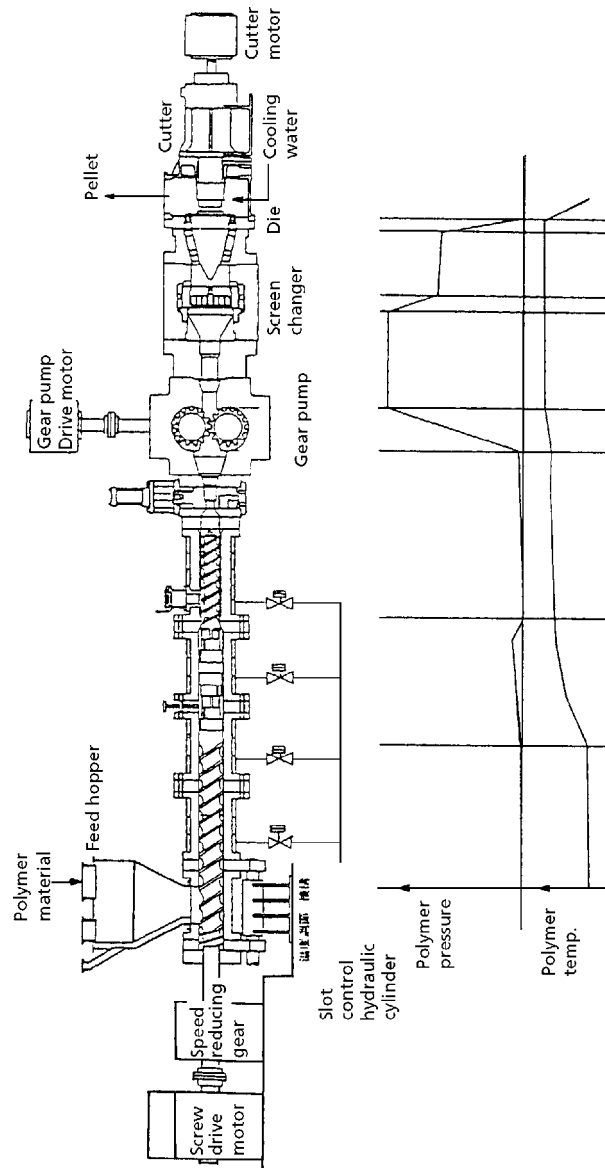


Figure 14.3 JSW CMP Pelletiser.

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Because rubber has a much higher viscosity and elastic modulus than those of polyolefins, this machine is not immediately usable for rubber. However, it may be taken as the starting point of the idea and necessary modifications will be discussed next. One significant difference between this machine and other plastic-extruders is the placement of a gear-pump between the die and the screw-head.

The characteristics of the use of the gear pump are:

- (i) improved efficiency of increasing pressure for overcoming the die resistance. In the conventional screw extruder, the metering zone is used for this purpose but the reverse flows, i.e., pressure flow and leakage flow reduce the efficiency
- (ii) the gear pump maintains a steady output rate through the die. With a screw pump, the pressure level and the output rate are affected by the property of material. Therefore, the material non-uniformity disturbs a steady operation
- (iii) With a gear pump taking care of the extrusion through the die, the screw section can be dedicated to mixing.

In developing successful continuous mixing it is important to design a steady process from the beginning to end. This means a strict feed control is a must. One approach is to use a premixed formulation with powdered or pelletised rubber. Maintaining a steady rate of feeding requires a feeding device.

In feeding a bale of rubber a conical extruder may be used for masticating and feeding. However, because the conical extruder is operated with a periodic feeding of bales, it may affect the stability of feeding. If this is the case, mastication may be performed with an extruder and a steady feed achieved with use of a gear pump.

In the incorporation stage, three changes must be brought about, i.e., comminution-lamination, imparting a tacky surface and compaction. When the powdered or pelletised rubber is used, all three must occur. This may require a powerful kneading gear. Pre-masticated rubber it is already in the form of supermolecular flow units which have tackiness, and a relatively mild kneading gear may be sufficient.

The continuous dispersion has already been demonstrated with the Farrel continuum mixer and the Transfermix. There is no need for a feasibility study. The temperature-rise during incorporation should be kept to a minimum. Otherwise the temperature-control during dispersion becomes difficult. The temperature-control by cooling is difficult for the following reasons; for better cooling the channel must be shallow. The shallow passage requires a higher rate of the material transport; otherwise, the output rate is sacrificed.

The high rate contributes to a temperature-rise. Therefore, cooling may not be effective. The distributive mixing is achieved by a rigorous control of feeding of additives. However, non-uniformity can arise within a volume at the feed-port. The volume of the material corresponding to that of the feed-port may be homogenised for example, with the Rapra CTM, see Figure 12.7 [5].

14.3 Handling of new material

This book is about mixing of rubber in traditional rubber processing. In recent years many new materials have been introduced into the field of rubber processing. They are plastic-rubber blends, block or graft copolymers consisting of plastic and rubber segments, soft-rubbers containing large amount of liquid and rubber compounds containing fibrous fillers. The mixing of these materials is not covered in this book. Nevertheless a few comments are in order.

First, mixing of these materials may be very different from what has been described so far. For example, the internal mixer described here is primarily a tangential type. For many of the new materials an intermeshing type may offer an advantage. Also, use of a twin-screw and continuous mixing may be a preferred choice.

Increasing uses of office machines, money-changers, computer-related equipment and medical equipment require relatively small volumes but require a large variety of rubber products each having unique properties. The rubber materials for these applications may be very different from those discussed in this book. However, with understanding of what is different in new materials through characterisation [8, 9 and 10], an insight may be gained for choosing proper mixing operations.

References

1. N. Nakajima, *Journal of the Society of the Rubber Industry, Japan*, 1994, **67**, 3, 163.
2. N. Tokita, M. J. Wang, B. Chung and K. Mahmud, *Journal of the Society of the Rubber Industry, Japan*, 1998, **71**, 9, 522.
3. K. Sone, *Journal of the Society of the Rubber Industry, Japan*, 1998, **71**, 6, 308.
4. *Advances in Polymer Technology*, 1984, **3/4**, front cover.

5. P. S. Johnson, *Rubber Chemistry and Technology*, 1983, **56**, 3, 575.
6. R. C. Tyler, D. W. Tredinnick and F. R. Burbank, Presented at the 148th Meeting of the ACS Rubber Division, Cleveland, OH, Fall 1995, Paper No.61.
7. M. Mizuguchi, S. Ogoshi and Y. Mizutani, *Japan Steel Works Technical Review*, 1990, 14, 76.
8. N. Nakajima, R. Babrowicz and E. R. Harrell, *Journal of Applied Polymer Science*, 1992, **44**, 8, 1437.
9. N. Nakajima, *Rubber Chemistry and Technology*, 1996, **69**, 1, 73.
10. N. Nakajima, *Rubber World*, 1996, **215**, 3, 33.