

## Some Peculiarities of Mechanical Breakdown of Components in Mechanical Dispersion of Polymer Mixtures

N. K. BARAMBOIM, *Moscow Technological Institute of the  
Light Industry, Moscow, U.S.S.R.*

### Synopsis

This paper deals with the results of the experimental investigations of mechanical breakdown of individual polymers in mixtures with other polymers depending on different factors of mechanical treatment, polymer and mixture properties.

The peculiarities of mechanic breakdown of individual brittle and elastic polymers are sufficiently well investigated, and the general postulates relating to the mechanism and kinetics of the process have been outlined not only in original publications, but also in reviews.<sup>1-4</sup> Due to the expansion of the technological utilization of polymer mixtures, the researchers' interest has been directed of late to an evaluation of the mechanical breakdown of polymer components in mixtures in relation to the rheological properties of these components.

This paper presents the results of an investigation into the peculiarities of mechanical breakdown of two-component polymer mixtures in the brittle and molten state, as characterized in Table I.

The mixtures PS-PMMA, PS-PVA, and PMMA-PVA containing 0-100% of the components in the mixture were dispersed in steel vibration mills at a frequency of 50 c/s and temperatures of 220°, 260°, and 300°K, total duration up to 600 sec.

TABLE I  
Characterization of Polymers

Polymer	$\bar{M}_2$
1. Polystyrene emulsion (PS)	$2.8 \times 10^5$
2. Poly(methyl methacrylate) suspension (PMMA)	$4.06 \times 10^5$
3. Poly(vinyl acetate) beads (PVA)	$2.5 \times 10^5$
4. Polyethylene, high pressure (PEHP)	$2.5 \times 10^4$
5. Polypropylene, isotactic (PP)	$1.66 \times 10^5$
6. Polycapronamide (PA)	$2.24 \times 10^4$
7. Polyamide, mixture of 60% AG-salt, 40% caprolactam (PAAC 60/40)	$1.92 \times 10^4$

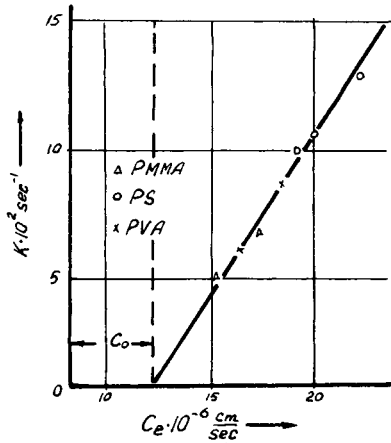


Fig. 1. Dependence of mechanical breakdown velocity constant  $K$  on velocity of sound wave propagation  $C_e$ .

The mixtures PEHP-PAAC 60/40 and PP-PA in the same proportions were processed in a laboratory extruder,  $D_{\text{serew}} = 40$  mm,  $L/D = 8$ , up to 10 cycles at  $450^\circ$  and  $485^\circ\text{K}$ , respectively. All mixtures contained acceptors guaranteeing linear breakdown. The phase structure of the mixture was assessed microscopically at a magnitude of  $10^3$ ; electromicroscopically, at  $10^5$ ; and by measuring the propagation velocity  $C_e$  of longitudinal sound waves, depending on the composition, on installation<sup>5</sup> with the observation of phase rotation.<sup>6</sup>

The molecular weight of the polymer components was determined in the process of breakdown viscosimetrically, after selective extraction, and the averaged breakdown velocity constant was calculated with the use of the Nairi computer according to the equation<sup>7</sup>

$$M_\tau = A \cdot e^{-k\tau} + M_\infty$$

where  $M_\tau$  = molecular weight at the moment  $\tau$ ,  $K$  = constant of destruction rate (speed),  $\tau$  = time of destruction, and  $M_\infty$  = top (limit) molecular weight attained at the result of destruction.

All mixtures, except PMMA-PVA, revealed distinct microheterogeneity by all the methods used, while the microscopically homogeneous mixture PMMA-PVA revealed ultramicroheterogeneity by the inversion of the relationship  $C_e = f$  (of the composition) at 25% PVA.<sup>8,9</sup> The experimental data presented in Figures 1-3 show certain peculiarities in the mechanical breakdown of components in polymer mixtures.

Individual components are subjected to mechanical breakdown at a velocity which is functionally connected with the propagation velocity of longitudinal sound waves  $C_e$  in the given component (Fig. 1),

$$K = (C_e - C_0) \tau g \alpha + K_0$$

where  $C_0$  = sound velocity at borderline of transition to highly elastic state ( $= 12.5 \times 10^6$  cm/sec);  $K_0$  = mechanical breakdown velocity constant at  $C_0$ ; and  $\alpha$  = inclination angle of straight line  $K = f(C_e)$ .

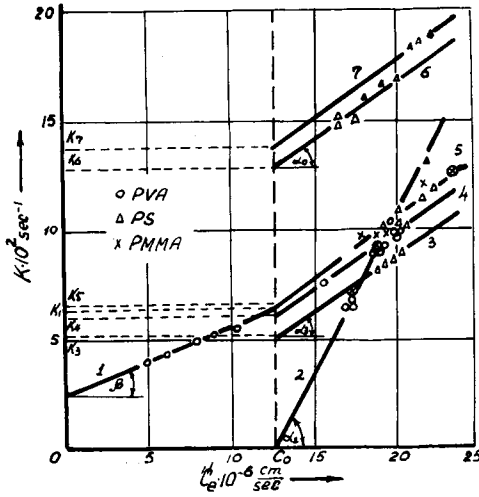


Fig. 2. Dependence of mechanical breakdown velocity constant  $K$  on velocity of sound wave propagation  $C_e$  in polymer mixtures: (1) PVA init. and PVA from mixtures at  $C_e < C_0$ ; (2) PS, PVA, PMMA init. and from mixtures at  $C_e > C_0$ ; (3) PS from 25:75 and 50:50 PS-PVA mixtures; (4) PVA from mixture of PS and PVA, and PS from 75:25 PS-PVA mixture; (5) PMMA from PS-PMMA mixture; (6) PS from 25:75 PS-PMMA mixture; (7) PS from 75:25 PS-PMMA mixture.

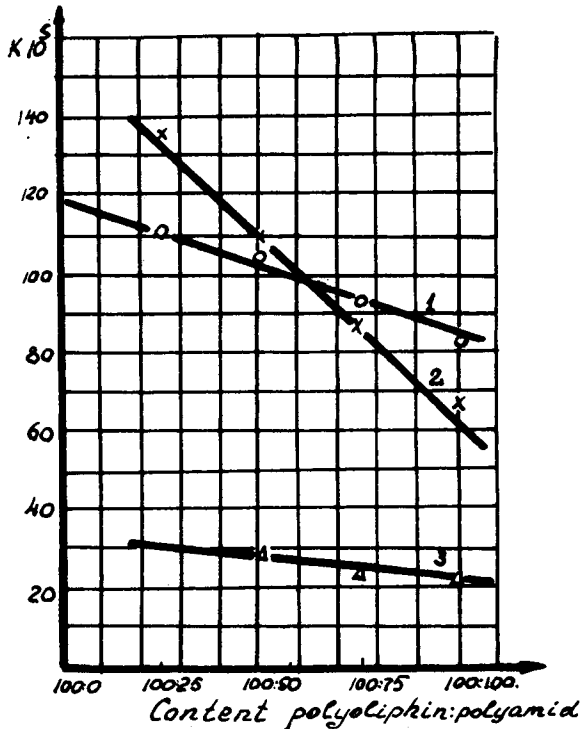


Fig. 3. Dependence of breakdown velocity constant on composition of polymer mixtures during melting: (1) PP; (2) PA in the PP mixture; (3) PAAC 60/40 in the mixture with PEHP.

In the mixtures, the components break down with a similar dependence on the acoustical properties of the mixture, but with account of the properties of the individual components. The latter is expressed in that  $K_0$ , at  $C_e = C_0$ , is different for the different polymers, and depends on the structure of the mixture and the size of the dispersed phase particles for one and the same polymer component (Fig. 2). If the mixture is ultramicroheterogeneous (PVA-PMM), with  $C_e > C_0$ , and the degree of dispersion of the components is typically colloidal, i.e., the mixture is a classical solid sol, then  $K_0 = 0$ , and the component breaks down at a velocity corresponding to the dispersion of the individual component. In the case of microheterogeneity of coarse mixture dispersion (all mixtures with polystyrene),  $K_0$  depends on the degree of fineness and type of dispersion.

Angle  $\alpha$ , probably, depends on the interaction energy of the components at the phase-to-phase borderline, on the adhesion of the components or, in other words, on the magnitude of the free energy at the phase-to-phase borderline.

On the whole, two cases are distinguished: for the mixture of components which are comparatively close in their chemical nature, for example, for PVA-PMMA mixtures, where adhesion is great and  $\Delta F$  is low,  $\alpha$  is the same for the individual components (Fig. 2); and for mixtures with a different nature (all mixtures with polystyrene),  $\alpha$  differs sharply from the  $\alpha$  which corresponds to the individual components but changes very little in relation to the composition of the mixture. These regularities are typical for mixtures and individual components in cases of brittle breakdown in the process of mechanical dispersion. With transition to a highly elastic breakdown at  $C_e < C_0$ , the general character of the relationship is preserved, but angle  $\alpha$  (Fig. 2) is much smaller and the general kinetic curve shows a clear bend at the point corresponding to  $C_e = C_0$ . PVA breaks down in this way both individually and in mixtures at 300°K (higher than the  $T_c$  for this polymer). A somewhat similar picture is observed in the mechanical breakdown of mixtures during screw processing of melts. The dependence of the breakdown velocity constant on the composition of the mixture of molten components, presented in Fig. 3, can be described by an elementary straight line equation

$$K = K_0 - Bn$$

where  $K_0$  is the constant for the individually processed polymer and  $n$  is the weight fraction of the mixture component, less brittle in the given circumstances.

Naturally, the mechanical breakdown velocity constant drops along with the lowering of the macroviscosity of the melt, but this is reflected differently on each of the components, depending on their nature. For example, for the PP-PA mixture, where PA is the less brittle component during treatment at 485°K, its breakdown velocity increases along with the reduction of its content in the mixture down to the magnitude which is markedly higher than the breakdown velocity during individual treatment under the

given conditions. In the same direction, the breakdown velocity of a more brittle component of the mixture (PP) increases only till the velocity corresponding to individual processing. These regularities, naturally, are valid for linear breakdown in the presence of inhibitors, i.e., practically for all technically stabilized polymers.

Experimental determination of kinetic equation constants of mechanical breakdown of mixtures makes it possible to calculate the breakdown transformations of their components in a broad range of compositions. In the absence of inhibitors, which is not typical for technical polymers, the possible formation of copolymer products may complicate considerably these elementary regularities.

### References

1. N. K. Baramboim, *Mechanochemistry of High-Molecular Compounds*, Khimia, Moscow, 1971; N. K. Baramboim, *Mechanochemistry of Polymers*, W. P. Watson, Ed., McLaren & Sons, LTO, London.
2. W. F. Watson, in *Chemical Reactions of Polymers*, E. M. Peltes, Ed., Interscience, New York, 1964.
3. A. A. Berlin, *ДАН СССР*, **110**,(3), 401 (1956).
4. P. Yu. Butyagin, *ДАН СССР*, **140**(1), 145 (1961).
5. Yu. V. Zelenov, G. M. Bartenev, and G. K. Demidov, *Zavodskaya Laboratoria* (Factory Laboratory), **29**, 7 (1963).
6. H. Kowai and J. Ogawa, *Kobunski*, **12**, 10 (1963).
7. N. K. Baramboim, *ДАН СССР*, **114**(3), 568 (1957).
8. L. M. Polukhinia and N. K. Baramboim, *Polym. Mech.*, **4**, 744 (1969).
9. L. M. Polukhinia and N. K. Baramboim, *High-Molecular Compounds*, **11**(6), 441 (1969).
10. N. K. Baramboim and V. F. Rakityanski, *High-Molecular Compounds*, **6**(9), 662 (1971).
11. N. K. Baramboim and V. F. Rakityanski, *Plastics*, **11**, 34 (1971).

Received July 6, 1973

Revised February 20, 1974