Mastication of Rubber. VII. Mechanical Degradation of Polymers During Mastication

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Many polymers which are not rubbery at ordinary temperatures become so within a range of higher temperatures, for instance, polystyrene at 120–160°C. Incorporation of suitable amounts of liquids produces rubberlike properties at lower ranges of temperature, which may extend to room temperature and below. Deforming forces can then readily be imposed on the polymers; indeed, mastication, milling, extruding, and molding processes depend on deformation in this state.

It was reported in Parts I[1] and III[2] of this series that the long-chain molecules of rubbers can be homolytically ruptured to free radicals by the deforming forces imposed during mastication. The possibility then arises that degradation occurring during the processing of plastics when in a rubbery state is also explicable by a mechanicochemical mechanism. The present report is concerned with the testing of this hypothesis for the degradation on mastication of polystyrene, polymethylmethacrylate, polyvinyl acetate, cellulose acetate, and polyvinyl choride while in a rubbery state brought about by raising the temperature or by adding solvents. (A preliminary note has been published.[3])

EXPERIMENTAL MATERIALS AND METHODS

Polymers

Polystyrene samples numbered PS1 and PS2 were prepared by emulsion polymerization by the Distillers Co. Ltd. PS3 was a molded sheet also obtained from the Distillers Co. Ltd. PS4 was prepared from PS2 by adding methanol to a 2.5% solution in benzene under reflux until the onset of precipitation, cooling slowly to room temperature, redissolving the precipitate in methyl ethyl ketone, and pouring into 1.5 vols. methanol. The flocculent precipitate was dried on a vacuum hot-plate

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at 60°C. to yield 60% of the original weight of the polymer. Polystyrene PS5 was prepared from PS2 by extraction in a Soxhlet apparatus with hot methanol followed by 60/80°- petroleum ether for periods of 18 hr. and finally drying at 60°C. under vacuum.

The polymethyl methacrylate PMMA1 was a disintegrated sheet of Perspex from I.C.I. Ltd. PMMA2 was obtained from PMMA1 similarly to PS4 from PS2. Cellulose acetate was a commercial product of Lansil Ltd. Polyvinyl acetate PVA1 and PVA2 were Gelva 25 and 15 grades, respectively, of the Shawinigan Co., and polyvinyl chloride was Corvic DR of I.C.I. Ltd.

Plasticization of the Polymers

The required volume of liquid was dripped on 3 g. powdered polymer in a shallow weighing bottle and left overnight for swelling into the polymer. Homogeneity of the swollen mass was attained during the early stages of mastication.

Heating to Rubberlike State

The polymer (11 g.) was placed in the masticator. Air was flushed out by a brisk stream of nitrogen, the masticating assembly immersed in its thermostat at the temperature of the ensuing mastication for 15 min. with occasional slow turning of the rotor to mix gently and heat the polymer uniformly. The masticator was then operated for 15 sec. to give a homogeneous, rubbery mass and a sample of ca. 0.2 g. abstracted. The viscosity of this sample was taken as the initial value for the particular run.

Mastication Procedure

The one-rotor machine employed for mastications at moderate temperatures has been described.[4] A plough-shaped rotor,[5] rotating at 120 rpm was usually employed. The swollen sample was inserted into the masticator, air flushed out by nitrogen, the chamber volume set to a volume
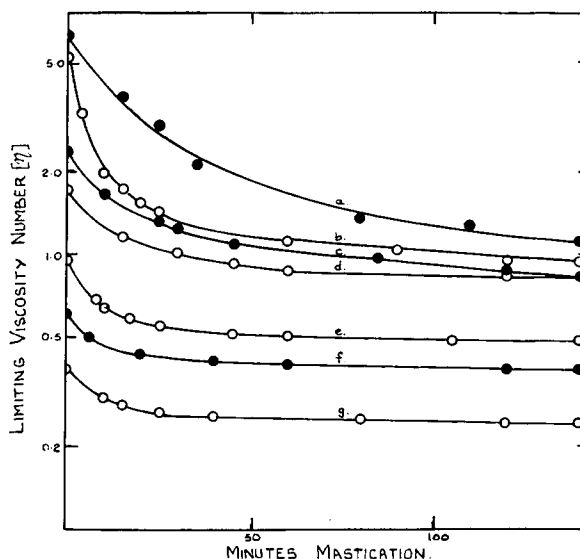
Fig. 1. The mechanical degradation of high polymers.

Curve	Polymer	% benzene	Temp., °C.	Scroll design	Rotor speed, rpm	% radical acceptor	Masticator model ref.
a	PMMA2	Nil	185	Spiral	140	1.0[a]	6
b	PMMA1	16	12	Plough	120	0.1[b]	5
c	CA	25[c]	12	"	120	0.1[b]	5
d	PS2	Nil	130	"	140	1.0[a]	6
e	PS1	16	12	"	120	0.1[b]	5
f	PVA1	Nil	90	"	140	1.0[a]	6
g	PVA2	16	12	"	120	0.1[b]	5

[a] Thio-β-naphthol.
[b] Thiophenol.
[c] Methyl acetate.

only fractionally greater than that of the mixture contained in it, and mastication carried out for a period selected on a time-delay switch to the driving motor. Each viscosity measurement represents a separate experiment.

A later and more versatile uni-rotor machine[5] was used for mastications at elevated temperatures. After abstraction of the small portion for initial viscosity determination, the masticator containing the sample was again flushed through with nitrogen and heated before carrying out the selected period of mastication. A further sample of ca. 0.2 g. was taken out, and the cycle repeated. A plough-shaped rotor[5] running at 46 rpm was used except when variation of shear was examined, when the speed was altered or the rotor was replaced by a spiral-grooved fitting.[5]

Samples containing solvent were broken up and solvent removed by heating to 40–60°C. for 18 hr. on a vacuum hot-plate. Viscosity numbers

were determined at 25°C. in Ostwald B.S.S. No. 1 specification[6] viscometers and the linear curves of viscosity number-concentration extrapolated to zero concentration. Benzene was the solvent for polystyrene and polymethyl methacrylate, toluene for polyvinylacetate, methyl acetate for cellulose acetate, and tetrahydrofuran for polyvinyl chloride.

Bulk viscosity measurements on polystyrene swollen with liquids were measured with a Wallace Rapid Plastimeter.[7] Sample PS2 was disintegrated to a powder passing through a 120-mesh sieve. Plasticities in the range measured by the Plastimeter at room temperature were obtained by dripping 1.8 g. liquid on 5 g. polymer in a shallow weighing bottle and permitting this to stand overnight at 40°C. to give a swollen disk a few millimeters thick. Samples from different parts of the disk gave plasticity figures within 2 units of the mean.
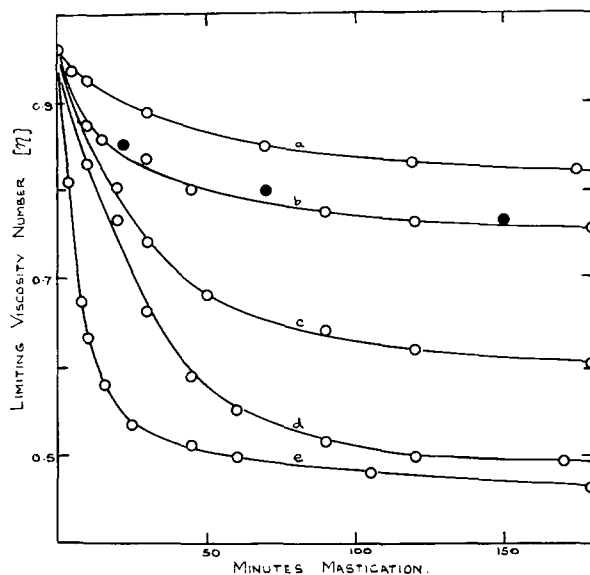
Fig. 2. The degradation by mastication of plasticized polystyrene PS1.

Curve	% benzene	Temp., °C.	Scroll design	Rotor speed, rpm	% thio-β-naphthol
a	23	30	Plough	76	0.1
b(O)	"	"	"	120	"
b(●)	"	"	"	"	1.0
c	"	12	Spiral	"	0.1
d	"	"	Plough	"	"
e	16	"	"	"	"

Fig. 3. The degradation by mastication of plasticized polyvinyl chloride.

Curve	% tetra-hydro-furan	Temp., °C.	Scroll design	Rotor speed, rpm	% thio-β-naphthol
a	10	40	Spiral	120	0.1
b	"	12	"	"	"
c	"	"	Plough	"	"
d(O)	13	"	"	"	"
d(●)	"	"	"	"	1.0

EXPERIMENTAL RESULTS AND DISCUSSION

Survey

The polymers were all degraded on mastication in an inert atmosphere when brought into a rubbery state by temperature change alone or by incorporation of a solvent, as exemplified by the results of Figure 1. Maintenance of the polymers at the temperatures of mastication gave no detectable degradation, and so a wholly thermal mechanism can be discounted.

Degradation proceeded relatively rapidly at the beginning of mastication, and thereafter its rate slowed down until it virtually ceased while the polymer still had a molecular weight well within the accepted high-polymer range and the work being done by the machine had not greatly diminished. Criticisms have been made of certain claims of results tending to a finite limiting molecular weight,[7] but it seems clear that a limiting molecular weight is attained in the present case on prolonged mastication. Extrapolation of limiting viscosity numbers against 1/(time) and 1/(time)^2 give curves which tend with opposite curvature to the same viscosity at infinite time. An almost linear plot is 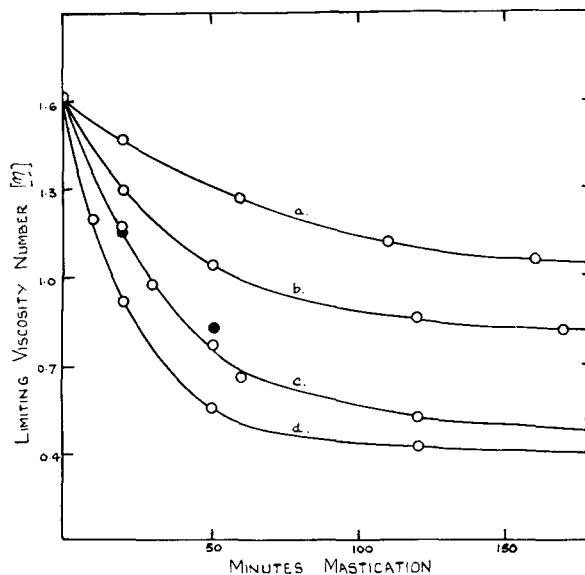obtained for viscosity against 1/(time)$^{2/3}$ to the same extrapolated value; a partial explanation of this linear correspondence is provided by a recent analysis.[7]

This degradation behavior parallels that of rubbers on mastication and can be attributed to the same cause.[8] The molecules are considered as not being ruptured below a certain value of molecular weight, depending on the applied shear, and on being ruptured only in the central sections above this molecular weight. An untested prediction of this explanation is that mastication should result in quite a narrow molecular weight distribution of masticated polymers.

A more detailed account follows of the variation of temperature, shear rate, solvent, molecular weight and radical-acceptor concentration with plasticized polystyrene and polyvinylchloride and unplasticized polystyrene and polymethyl methacrylate. Data obtained with the other plasticized and unplasticized polymers are not given, since they parallel the results reported.

Plasticized Polymers

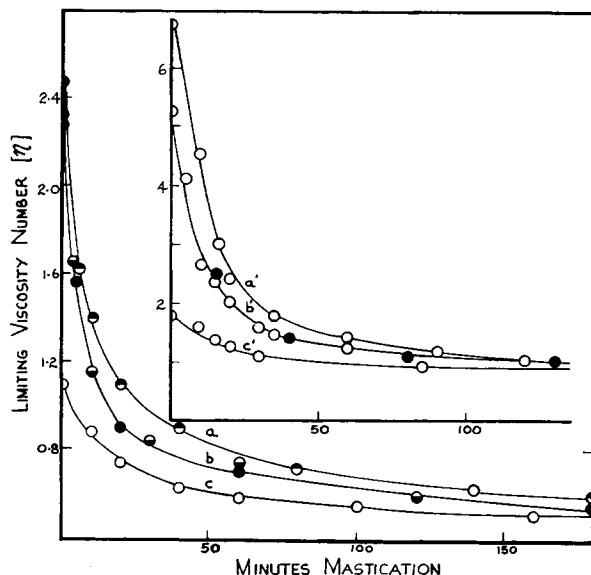**Effect of Temperature.** The mastication of polymer samples containing equal amounts of sol-

Fig. 4. The effect of molecular weight, fractionation, and extraction on the degradation of plasticized polystyrene and polymethyl methacrylate. All samples contained 23% benzene and 1% thiophenol and were masticated with water cooling at 12°C. by the plough scrolls rotating at 120 rpm. (a) PS4. (a') PMMA4. (b) PS5. (b') (○) PMMA1. (b') (●) PMMA1, methanol-extracted. (c) PS3. (c') PMMA5.
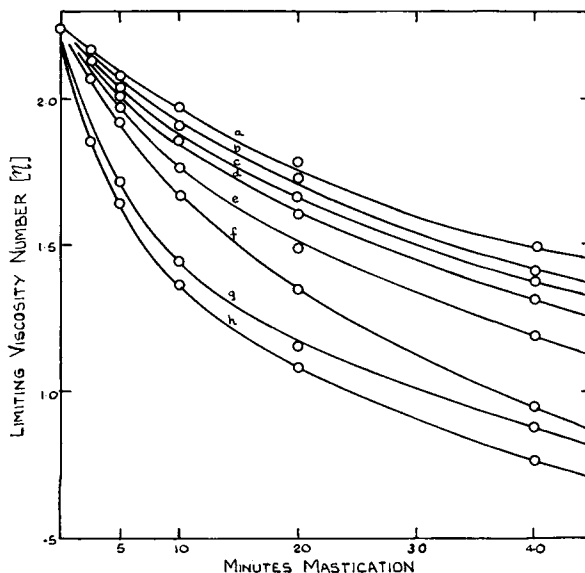

Fig. 5. The effect of changing the plasticizing solvent on the mastication-degradation of polystyrene PS2. Conditions: 30% by volume of plasticizing solvent, plough scrolls at 120 rpm, mastication at 40 ± 1°C. under nitrogen in absence of added radical acceptor. (a) Toluene. (b) Ethylene dichloride. (c) Methyl ethyl ketone (d) Acetone. (e) Benzene. (f) n-Butyl acetate. (g) Carbon tetrachloride. (h) 60°/80° petroleum ether.

vent at different temperatures demonstrated that the rate of degradation *decreased* with increase in temperature. In addition, the limiting value of molecular weight to which the polymer approached on prolonged shearing was higher with the higher temperature (Figs. 2–3).

This unusual temperature dependence is one of the main criteria of a shear-dependent reaction.[1] The effect of temperature is not direct, as it is in normal chemical reactions, in promoting the reaction, but is mainly an indirect effect on the reaction involving a change in the physical state of the system. The softening of the polymer-liquid system, on raising the temperature, results in the imposition of less shear energy, and, consequently, a reduced rate of degradation and a higher critical molecular weight below which rupture does not occur.

Effect of Rate of Shear. A more direct demonstration of dependence of degradation on applied shear was obtained by varying the rotor speed of the masticator. Higher rotor speeds produced greater rates of breakdown to lower limiting molecular weights (Figs. 2 and 3). The rate of shear could also be varied by change in design of rotor and chamber. Previous work showed that the spiral-grooved fitments imposed less shearing on rubbers than the plough-grooved assembly. The spiral-grooved fitments similarly produced mark-

edly less degradation of plasticized polymers (Figs. 2 and 3).

Influence of Initial Molecular Weight. Initially, polystyrene of relatively high molecular weight degraded more rapidly on mastication and eventually reached the same limiting molecular weight as samples of originally lower molecular weight. Polymethyl methacrylate yielded similar results (Fig. 4). The complementary factors involved, according to the mechanicodegradative mechanism, are the higher viscosities of the polymer-liquid mixtures with the polymer of higher molecular weight and the greater proportion initially in those of rupturable molecules.

Effect of Solvent. Mastication of polymer with varying amounts of solvents showed that the rate of degradation decreased rapidly with increase in the proportion of solvent (Figs. 2–3). Clearly, the slow rotor speed would give only a very moderate stirring action with fluid polymer solutions, causing negligible rupture of the polymer; thus, a gradation of rates of degradation to very low values is anticipated on further dilution.

The nature of the solvent had a marked effect on the rate of degradation (Fig. 5). Wallace plasticity measurements recorded on powdered polystyrene plasticized with the same solvents, i.e., (a) with toluene, 10; (b) ethylene dichloride, 10; (c) methyl ethyl ketone, 63; (d) acetone, 64;
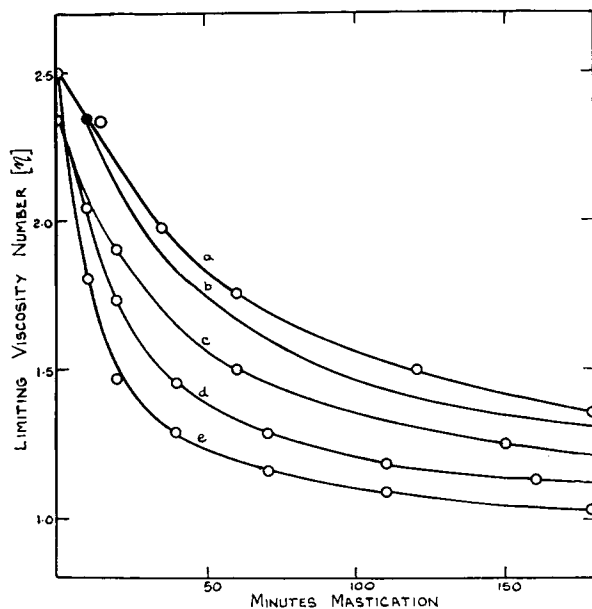
Fig. 6. Effect of radical acceptor on the degradation of un-
plasticized polystyrene.

Curve	PS	Temp., °C.	Scroll design	Rotor speed, rpm	% radical acceptor
a	PS4	130	Plough	47	0
b	PS2	"	"	"	0
c	PS2	"	"	"	4% thio-β-naphthol
d	PS2	"	"	"	1% "
e	PS4	"	"	"	Oxygen

(e) benzene, 62; (f) n-butyl acetate, 74; (g)
carbon tetrachloride, 88; (h) 60/80°C. petroleum
ether, 95, showed that the rate of degradation
varied inversely with the degree of softening of the
polymer by the liquid.

Influence of Radical Acceptors. Extraction of
polymers by swelling liquids and partial precipita-
tion from solution to obtain fractions of different
molecular weights effectively removed low molecu-
lar-weight radical acceptors. These treatments
had no significant influence on the rate of degrada-
tion (Fig. 4). Likewise, the addition of thio-β-
naphthol had no marked effect on rate of degrada-
tion (Figs. 2–3).

Unplasticized Polymers

The rate of degradation on mastication of
polymers made rubbery simply by rise in tempera-
ture also displayed the negative temperature
coefficient characteristic of a shear-dependent
reaction (Figs. 6–7). This was again shown more
directly by alteration of rotor speed or the design
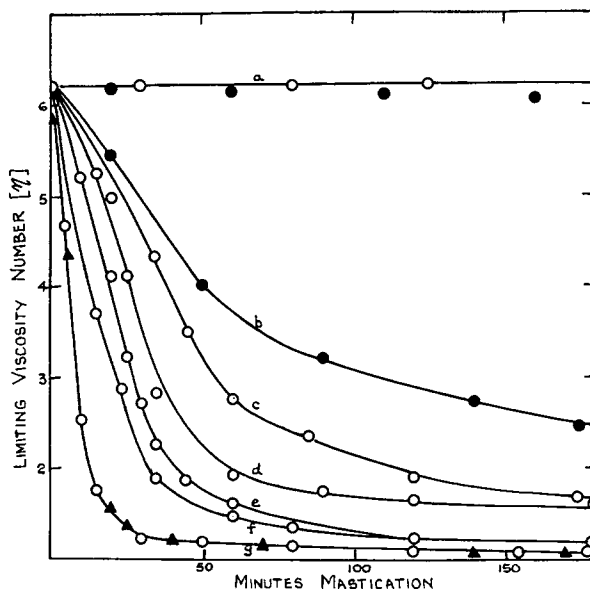of the masticating assembly (Figs. 6–7).

Fig. 7. Effect of temperature and shear rate on the
degradation by mastication of unplasticized polymethyl
methacrylate.

Curve	Temp., °C.	Scroll design	Rotor speed, rpm	% thio-β-naphthol
a(○)	185	—	0	1.0
a(●)	215	—	0	"
b	"	Spiral	47	"
c	185	"	"	2.5
d	"	"	"	1.0
e	"	Plough	"	"
f	"	Spiral	140	"
g(○)	"	Plough	"	"
g(●)	"	"	"	0 (PMMA2)

An attempt was made to collect any monomer
evolved during mastication by briskly flushing
volatiles by nitrogen into a liquid air trap. Less
than 0.5% weight of monomer on weight of polymer
masticated would have been measured. No mono-
mer was detected with polystyrene masticated up
to 130°C.; 3.4% monomer was collected on
masticating polymethyl methacrylate for 2 hr.
at 185°C. with the plough rotor.

Radical Acceptors. The only effect noted on the
addition of radical acceptors was a tendency to slow
down the degradation when present in amounts
which might give a polymer-dilution effect similar
to that of plasticizers (Figs. 6–7).

This is in contrast to their effect on the overall
degradation of natural rubber. In absence of
radical acceptors, the much slower breakdown of
rubber is attributable to a large measure of combi-
nation of the radicals formed by rupture. It is
apparent that no radical recombination is detect-
able on the mastication of the plasticized or

unplasticized polymers. At present only *ad hoc* suggestions can be advanced on the basis of the very viscous medium or the reaction of head-and-tail-type radicals formed by rupture.

References

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Synopsis

The degradation on mastication of polymers brought into a rubbery state by incorporation of liquids or rise in temperature is accounted for by the mechanicochemical mechanism previously advanced to explain the degradation of rubbers. The dependence of the reaction on shear rate has been shown indirectly, as with rubbers, by the negative temperature coefficient of reaction, and also directly by variation of masticator rotor speed and design. A further new feature is the influence of the nature as well as concentration of plasticizer on the rate of degradation and a correlation with the softening of the polymer. A limiting molecular weight is reached on prolonged mastication from whatever initial molecular weight.

Résumé

La dégradation par mastication de polymeres rendus caoutchouteux par incorporation de liquides ou par une élévation de température est, responsable des mécanismes mécano-chimiques antérieurement avancés pour expliquer la dégradation des caoutchoux. La dépendance de la réaction en fonction de la tension de cisaillement a été montrée indirectement, comme dans le cas des caoutchoux, par le coefficient négatif de température de réaction, et directement par la variation de vitesse et de forme du rotor masticateur. Un autre nouveau détail est l'influence de la nature ainsi que de la concentration du plastifiant sur la vitesse de dégradation et la corrélation avec le ramollissement du polymère. Un poids moléculaire limite est atteint par mastication prolongée à partir du poids moléculaire initial.

Zusammenfassung

Der Abbau von Polymeren, die durch Aufnahme von Flüssigkeiten oder eine Temperaturerhöhung in den kautschukartigen Zustand gebracht wurden, bei der Mastizierungm wird durch den schon früher zur Erklärung des Abbaus von Kautschuk vorgeschlagenen mechanochemischen Mechanismus erfasst. Die Abhängigkeit der Reaktion von der Schubgeschwindigkeit wurde, ebenso wie bei Kautschuk einerseits indirekt, nämlich durch den negativen Temperaturkoeffizienten der Reaktion, und andererseits direkt durch Änderung der Geschwindigkeit und des Baus der Mastikatorwalze gezeigt. Ein weiteres neues charakteristisches Merkmal ist der Einfluss sowhol der Natur als auch der Konzentration des Weichmachers auf die Geschwindigkeit des Abbaus und eine Beziehung zur Erweichung des Polymeren. Unabhängig vom Anfangsmolekulargewicht wird bei langdauernder Mastizierung ein Grenzmolekulargewicht erreicht.