Elastic Effects in a Linear-Gel Polymer System

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Synopsis

The addition of gelled or crosslinked material to an essentially linear elastomer often decreases "nerve," mill shrinkage, or die swell. In the present work, poly(ethyl acrylate) systems previously characterized in steady flow, were studied in transient flow. Die swell in capillary flow and shear creep recovery in a biconical rheometer were examined and correlated with the amount, crosslink density, and particle size of the gel phase. In general, the addition of gel reduces deformation of extrudates by reducing the amount of elastic strain energy which can be imparted to the material in a stress field. Concurrently, by increasing the viscosity more at low than at high stresses, gel addition also provides an increased resistance to deformation in the low-stress regions outside of the equipment without exacting a comparable toll in increased power requirements.

INTRODUCTION

Mechanical energy imparted to a viscoelastic material in a stress field (e.g., in an extrusion die or calendar nip) is partially degraded to heat (viscous energy dissipation) in the process of viscous flow, but the remainder is elastically stored in the material and is recovered outside the stress field, profoundly influencing the processing behavior.

It has been observed that the addition of gelled or crosslinked material to an essentially linear elastomer decreases "nerve," mill shrinkage, die swell, melt fracture, etc. To understand these processing improvements more completely, the elastic properties of the poly(ethyl acrylate) systems previously characterized in viscous flow¹ have been investigated.

EXPERIMENTAL

Shear-creep recovery data were obtained with the biconical rheometer previously described.¹ The angular recovery was too small to follow with the rotational potentiometer, however, so an optical lever was used to get reasonable deflections. A collar was fastened to the end of the rotor shaft with set screws. A small mirror was glued to the collar and served to reflect a narrow light beam from a slide projector to a scale across the room, approximately 18 ft. away.

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A sufficient period of time was allowed after the application of the weights to insure steady-state viscous flow, and when the beam reached the zero point of the scale, the weights were quickly removed. The recovery as a function of time was followed by photographing the beam on the scale with a 35-mm. camera with a slotted disk rotating in front of the open shutter. By varying the rotational speed of the disk and the number of uncovered slots in it, a fairly wide range of the recovery could be recorded with several runs. When the beam had slowed to the point where a continuous streak would be recorded on the film, the shutter was closed. When essentially complete recovery had been reached, the shutter was again opened for a few seconds and the recovery distance on the scale measured and recorded.

The actual recovery-time data were obtained by projecting the negatives full size and measuring the distance from each discrete spot to that obtained at total recovery. These data were corrected for the deflection of the rotor shaft and the bracket supporting the rheometer. The shear strain was calculated from the angular recovery of the light beam.

Swelling measurements were obtained for the filaments extruded through the stock Instron die (L = 2 in., D = 0.05 in., and entrance angle = 90°) by weighting a measured length of the extrudate. The die swell β is then given by

$$\beta = (w/w_0)^{0.5}$$

where w is the measured weight per unit length and w_0 is the weight of a unit length of extrudate with a diameter of 0.05 in., calculated from the material density.

EXPERIMENTAL RESULTS

The total recoverable shear strain as a function of applied shear stress is shown in Figures 1 and 2 for a series of "tight" (30% triethyleneglycol dimethacrylate) gels and for 20 and 40% "loose" (3% triethyleneglycol dimethacrylate) gel. The first conclusion to be drawn is that these materials are definitely nonlinear, i.e., they do not follow Hooke's law in shear over the range covered, although they do appear to approach linearity at high stresses.

Whereas the biconical rheometer is admirably suited to the direct measurement of recoverable shear strain as a function of shear stress, Bagley achieved essentially the same results indirectly for polyethylene from endcorrection data in capillary flow.^{2,3} This end correction, e, is obtained by extrapolation to a capillary L/R of zero at constant shear rate, and represents the total nonviscous energy losses incurred in flow through the capillary. Bagley found that plots of e versus stress follow a linear relation down to the lowest measured shear stresses, about 2×10^5 dynes/cm.² It will be noted that the highest stress investigated here was only 9×10^4 dynes/cm.² Thus, if Bagley's materials did exhibit a nonlinearity at low stresses, but reached linearity at higher stresses, as observed in this investigation, it could go unnoticed and be absorbed in the Couette intercept.



Fig. 1. Addition of highly crosslinked particles to a linear matrix reduces the recoverable shear at a given shear stress: (O) 0% tight gel; (Δ) 10% tight gel; (\Box) 20% tight gel; (∇) 30% tight gel; (\Diamond) 40% tight gel.



Fig. 2. Loosely crosslinked particles do not reduce the recoverable shear as efficiently as highly crosslinked particles: (O) 0% loose gel: (\Box) 20% loose gel; (\Diamond) 40% loose gel.



Fig. 3. At high stresses, the fractional decrease in recoverable shear γ_R by crosslinked particles becomes relatively independent of stress level.

It is seen that the addition of gel decreases the recoverable shear strain by an amount which increases with the applied stress and that the tight gel is far more efficient in this process than the loose gel. This clearly shows that at a given applied stress, the presence of gel reduces the amount of energy which can be elastically stored by the material.

The greater efficiency of the tight gels in reducing elastic energy storage can be explained qualitatively. The tighter a gel is, i.e., the less deformable, the smaller the amount of elastic energy it can absorb by itself, thereby reducing the total capacity of the system. Quantitatively, this would mean that the ratio of the recoverable shear of a gel-containing compound to that of the master batch (both at the same stress) is a constant, independent of stress. Furthermore, this ratio should be a linear function of the gel content, with a slope determined by the recoverable shear strains of the master batch and the pure gel.

It is found that in the fairly linear regions of the curves, the ratio of recoverable shear strain to that of the master batch is very nearly constant for a given compound. When the average values of these constants are plotted, they define fairly straight lines (Fig. 3).

Dewey has obtained a relation for the shear modulus of a material consisting of spherical particles of one elastic phase dispersed in another continuous elastic phase, in terms of the volume fraction of filler and the moduli of the individual phases.⁴ Her derivation is analogous to that of Einstein⁵ for the viscosity of a suspension of spherical particles and is subject to the same limitations, namely, the interactions of the dispersed particles are not considered, and so it can be expected to hold only for extremely dilute dispersions.

Neither Dewey nor Einstein considers particle size. As shown in Figure 4. the observed decrease in recoverable shear strain with particle size



Fig. 5. Creep recovery is retarded by increasing gel contents of 10 to 40% by weight.

amounts to only about 10% over a tenfold range of particle size, and so is of little practical significance, because larger and far more easily controlled changes can be obtained by varying gel content or crosslink density.

In addition to the total amount of elastic energy which can be stored in a viscoelastic material, the rate at which this energy can be imparted to or given up by the material should be of some interest, since in any processing operation, the material is subjected to stresses for various finite lengths of



Fig. 6. Loosely crosslinked particles retard creep recovery much less than an equal weight of the highly crosslinked particles in Figure 5.



Fig. 7. Four-parameter viscoelastic model.

time, which will influence the amount of elastic energy actually imparted to it.

To obtain such information, experiments following the rate of recovery from steady-state viscous flow at a stress of 9×10^4 dynes/cm.² were performed.

It is important to realize that the data so obtained cannot be simply converted quantitatively to other stresses, nor can the actual creep behavior be obtained from creep recovery and viscous flow data because the materials are not linearly viscoelastic. Nevertheless, the information obtained here should be qualitatively applicable to other stresses and to the rate of elastic energy absorption as well as its recovery.

Creep recovery curves for the master batch, four concentrations of $0.08 \ \mu$ tight gel, and two of $0.056 \ \mu$ loose gel are shown in Figures 5 and 6, respectively. Each curve is a composite of data taken from several individual photographs, and as expected, the scatter increases as the measured strains decrease. In all cases, there is observed an instantaneous (or at least very rapid) recovery, followed by a more gradual recovery with time.

At first glance, the observed behavior does not seem to make too much sense. It can be shown, however, with the aid of a four-parameter viscoelastic model, to be at least qualitatively consistent and predictable from previous observations. The model shown in Figure 7 is intended only as a conceptual aid, its behavior in tension being roughly and qualitatively only similar to the shear behavior of the materials under consideration.

After the instantaneous elastic recovery (spring 1), the recovery-time behavior is governed only by the Voigt element (G_2, η_2) whose recovery is given by eq. (1) (assuming a Hookian spring and Newtonian dashpot):

$$\gamma_{\mathbf{R}}(t) = \tau/G_2 \exp\left\{-G_2 t/\eta_2\right\} \tag{1}$$

where t is the time in seconds and τ the stress during creep. It is obvious that this is a crude approximation of the experimental facts, because the equation gives a linear relation on semilogarithmic coordinates, compared to the slightly curved experimental relations.

The experimental curves could be much more accurately described by the usual procedure of using a series of linear Voigt elements with different constants and determining the distribution of the constants (distribution of retardation times). In this case, however, this procedure would be strictly curve fitting, valid only for the particular applied stress, because the materials are not linearly viscoelastic.

The values of the Voigt-element parameters of the four-parameter model may be easily evaluated from these linear portions of the curves and are given in Table I. From this table, it is seen that the curves are described by regular increases in the modulus and viscosity of the Voigt-element parameters with increasing gel content. This agrees with the increase in modulus observed in the total recoverable shear strain measurements and

Material	$\gamma_R(t=0)$	G_2 , dynes/cm. ² $ imes 10^{-5}$	η_2 , poise \times 10 ⁻⁶	
Master batch	0.42	2.1	2.1	
10% Tight gel				
$(d_{\rm p}=0.08\ \mu)$	0.40	2.3	5.2	
20% Tight gel	0.30	3.0	5.5	
30% Tight gel	0.26	3.5	6.8	
40% Tight gel	0.19	4.7	8.3	
20% Loose gel				
$(\dot{d}_{\rm p} = 0.056 \ \mu)$	0.29	3.1	3.6	
40% Loose gel	0.29	3.1	4.9	
20% Tight gel				
$(d_{\rm p} = 0.80 \ \mu)$	0.35	2.6	6.4	
20% Tight gel				
$(d_{\rm p}=0.16\ \mu)$	0.30	3.0	5.0	
20% Tight gel				
$(d_{\rm p} = 0.063 \ \mu)$	0.27	3.4	3.7	

TABLE I Voigt-Element Parameter

Fig. 8. Although particle size does not affect total recoverable shear greatly, larger particles retard recovery rate more than the smaller ones do.

the increase in pseudo zero-shear viscosities previously reported with increasing gel content. As before, the tight gel is more efficient in producing these increases than the loose gel. It should be pointed out that the two viscosities represent basically different processes. The flow viscosity (η_1) describes the resistance of the molecules to slipping past their neighbors, whereas η_2 is a measure of the resistance of the molecules to reaching their equilibrium elongations from a more randomly coiled state. Thus, the two would not necessarily be expected to be the same, or to be affected by gel particles in the same manner, but intuitively, the presence of gel particles in the melt might be expected to increase both by hindering chain motion.

The recovery curves for three particle sizes of tight gel at 20% loading are shown in Figure 8, and their Voigt-model parameters are included in Table I. Again, as could have been predicted from the steady-state viscosity and total recoverable shear strain measurements, η_2 decreases and G_2 increases with decreasing particle size. These curves cannot be directly compared with the 20% gel curve in Figure 5. The materials used for the measurements in Figure 5 were made up about six months after the other materials discussed here, and the master batch had undergone a viscosityincreasing change in the interim. It is seen, then, that the major effect of increasing the particle size is to further hinder the mobility of the linear molecules.

INTERPRETATION OF PROCESSING PROPERTIES IN TERMS OF EXPERIMENTAL RESULTS

Melt Fracture

The problem of melt fracture—gross distortion of the extrudate emerging from a die—is of prime importance in extrusion, because it establishes the upper limit of production. Early work on the phenomenon has been comprehensively reviewed by Metzner⁶ without reaching any positive conclusions as to its causes. A more recent study by Bagley and Schreiber, using high-speed motion pictures and transparent quartz dies, has demonstrated its causes fairly conclusively.⁷ The latter investigation definitely shows melt fracture to be an elastic effect.

In the present work, the progressive addition of gel definitely decreased the severity of distortion. At a given loading, the distortion also decreased as the tightness of the gel increased. Gel particle size at any given weight fraction of gel had no noticeable effect on the extrudate distortion. These observations are in accord with the facts that the distortion is due to the recovery of elastic strain, and that the addition of gel cuts down the amount of elastic strain of a material in a stress field, tight gels more so than loose gels. It will be remembered that particle size influenced the recoverable strain only slightly.

The average volumetric holdup times of material in the die are given in the Table II as a function of the Instron plunger speed S. On comparing these values with the rate of recovery curves (recalling that the rate of elastic extension is not equal to that of recovery for non-linear materials, but assuming they are of the same order), it is seen that most of the strain responsible for the violent distortion at high throughputs must be imparted to the material before it actually enters the die. Similarly, at lower throughputs, material entering the die in a relatively unstrained state has sufficient time in the die to "catch up" with the material entering in a more highly strained state. Thus, a homogenization of strain occurs, minimizing the tendency toward nonuniform distortion of the extrudate.

Crosshead	Volumetric	Average	Average
speed	flow	velocity	holdup time
S, in./min.	Q, cm. ³ /sec.	V, cm./sec.	l_{H} , sec.
0.02	0.000604	0.0477	106
0.05	0.00151	0.119	42.7
0.1	0.00302	0.238	21.3
0.2	0.00604	0.477	10.6
0.5	0.0151	1.19	4.27
1	0.0302	2.38	2.13
2	0.0604	4.77	1.06
5	0.151	11.9	0.427
10	0.302	23.8	0.213
20	0.604	47.7	0.106

TABLE II

In addition to reducing the elastic driving force for distortion, the higher viscosities of the gel-containing materials, particularly in the low-stress regions outside the die, provide an increased resistance to distortion of the filament. In summary, gel definitely reduces the severity of extrudate distortion at a given throughput. Since it is probable that distortion is a progressive phenomenon with flow rate, the addition of gel should allow the use of higher extrusion rates while maintaining the product within specified limits of uniformity.

Die Swell

The swelling of an extrudate emerging from a die is also of great commercial importance. In the case of extrudates of circular cross-section, the swelling can often be easily overcome by using a takeoff speed high enough to draw the extrudate down to the required dimensions. For extrudates whose cross sections are not cylindrically symmetrical, however, the nonuniform swelling usually necessitates a laborious trial-and-error die design to obtain the desired cross section in the extrudate. Of course this problem can be overcome by using very low extrusion rates, which minimize swelling, but this solution has obvious economic drawbacks.

Two general experimental conclusions may be drawn about die swell: (a) die swell increases with the rate of extrusion, confirming previous observations on polymer melts,⁸⁻¹⁰ and (b) it is decreased by the addition of gel, the tight gels being more effective than the loose gels at a given loading.

Several reasons have been proposed for the swelling of streams emerging from a die. Velocity-profile relaxation^{11,12} can account for only a portion of the observed die swells, and in most cases only a minor portion, due to the highly pseudoplastic nature of the gel-containing materials, which results in relatively "flat" velocity profiles.

A second, and in this case major, cause of die swell is the storage of elastic energy in the steady-state flow of a viscoelastic material in a tube, which gives rise to the so-called normal stresses. Experimentally, Gavis and Gill have presented direct evidence for an axial tension in a viscoelastic jet,^{13,14} and Goren, Middleman, and Gavis have developed an expression relating die swell to the decay of this tension.¹⁵ Braun and Reiner have theoretically predicted the presence of both radial and axial stresses by a purely continuum-mechanical approach,¹⁶ and Lodge has presented a molecular argument for such stresses.¹⁷

The question now comes up as to how the strains resulting from these stresses are connected with die swell, the ultimate aim being to predict the swelling quantitatively from a minimum of experimental data on a given material. In principle, if the exact mechanisms by which these strains are recovered were known, the swell could be determined from data relating stress and strain for a given material.

As a first approximation, it is assumed that die swell is a function only of the recoverable strain stored in the flowing material. It is assumed further that the tensile and shear properties of the material bear a constant relation.

To evaluate these assumptions rigorously, data are required for recoverable shear strain and die swell at the same stress levels. These were not obtained here. Recoverable shear measurements were made with the large biconical rotor and die swell with the Instron, and the stress ranges covered in each did not overlap. In the absence of such data, linearity of the γ_R versus τ curves at high stresses will be assumed, and the linear portions of the experimental curves used to obtain the equations shown in Table III for the master batch and the 0.08 μ "tight" gel series.

Gel, %	γR			
0	$\gamma_R = 0.65 \times 10^{-5} \tau + 0.37$			
10	$\gamma_R = 0.52 \times 10^{-6} \tau + 0.32$			
20	$\gamma_R = 0.38 \times 10^{-5} \tau + 0.24$			
30	$\gamma_R = 0.33 \times 10^{-5} \tau + 0.19$			
40	$\gamma_{R} = 0.27 \times 10^{-6} \tau + 0.12$			

TABLE III

From the equations in Table III, values for the recoverable shear strain at the tube wall have been calculated, and representative values are listed in Table IV. Of course die swell should not be a function of the maximum recoverable shear strain at the tube wall, but of some average value. Since the mechanism relating to the recoverable shear strain to die swell is unknown, the proper average is also unknown.

Up to this point, comparisons of the strains of gel-containing materials have been made at constant stress. For practical purposes, comparisons of die swell are more meaningful at constant volumetric throughput, and because gel increases the viscosity along with decreasing the recoverable shear strain, it also brings about an unavoidable increase in stress at a

	Master batch with Tight Gel of Diameter = 0.080μ							
		Shear				Ratio of		
Material	Cross- head speed <i>S</i> , in./min.	Holdup time t_H , sec.	stress τ _w , dynes/ cm. ² 10 ⁻⁵	Recover- able shear, γ _{Rw}	Rate of shear, γw	energy dissi- pations, $2\dot{\gamma}_{w}t_{H}/\gamma_{R}$	Die swell, ωβ	
Master batch	0.02 0.2	106 10.6	$\begin{array}{c} 2.76 \\ 5.03 \end{array}$	2.16 3.64	5.08 50.8	498 296	1.25 1.44	
	2 20	1.06 0.106	9.40 15.2	6.48 10.25	550 6610	180 137	$\frac{1.89}{2.58}$	
20% Tight gel	$\begin{array}{c} 0.02 \\ 0.2 \end{array}$	106 10.6	$\begin{array}{c} 3.62 \\ 7.33 \end{array}$	$\begin{array}{c} 1.61 \\ 3.02 \end{array}$	4.46 48.8	588 342	$\begin{array}{c} 1.20 \\ 1.37 \end{array}$	
	$2 \\ 20 \\ 20 $	1.06 0.106	$\frac{13.2}{20.5}$	$\begin{array}{c} 5.25 \\ 8.03 \end{array}$	596 6650	240 176	1.73 2.28	
40% Tight gel	$\begin{array}{c} 0.02 \\ 0.2 \end{array}$	106 10.6	4.76 9.59	1.40 2.71	4.40 51.1	666 400	$1.09 \\ 1.24 \\ 1.50$	
	2 20	1.06 0.106	$\frac{16.2}{24.8}$	4.49 6.90	656 6710	310 206	$\frac{1.50}{1.85}$	

TABLE IV

Recoverable Shear and Ratio of Elastic Energy Dissipation for Extrusion of Linear Master batch with Tight Gel of Diameter = 0.080μ

Fig. 10. Die swell vs. ratio of viscous to elastic energy dissipation.

given volumetric flow rate. Table IV clearly shows, however, that in spite of the increased stress, the addition of gel regularly decreases the recoverable shear stress at constant throughput. When the die swell is plotted as a function of the recoverable shear strain (Fig. 9), it is seen that to a good approximation ($\pm 5\%$ or so), the data can be represented by a single curve. In view of the approximations, extrapolations and experimental errors involved, the scatter is not excessive. This curve applies only to the particular experimental geometry for which the data were obtained, because the details of the straining and strain recovery processes depend on geometry, as indicated by the recent work of Bagley, Storey, and West.⁸ It should be noted that the data in Figure 9 include the region of melt fracture, where β is a root-mean-square average diameter.

Also included in Table IV is an estimate of the ratio of the rate of viscous energy dissipation to the rate of elastic energy dissipation occurring in the extrusion process. As has been shown, the rate of viscous energy dissipation per unit volume is given by the product of the shear rate and the shear stress, $\tau \dot{\gamma}$. For a linearly elastic material, the energy storage per unit volume is half the product of the shear stress and the shear strain, $(1/2)\tau\gamma_{\rm R}$. For the nonlinear materials investigated here, this is a conservative value, since the initial strain is incurred at low stress, and it is far more readily calculated than the true value. To convert this to a rate of dissipation, it is multiplied by the average volumetric holdup time, $l_{\rm H}$. This is again a conservative estimate, because it assumes that the material has had time to reach its equilibrium elastic strain (and energy content) before issuing from the die.

Thus, the ratio becomes

$$\frac{\text{Rate of viscous energy dissipation}}{\text{Rate of elastic energy dissipation}} = \frac{2\gamma_w \bar{t}_H}{\gamma_{Rw}}$$

Again, the values in Table IV are calculated with the use of the stress at the tube wall to provide a convenient representation of the unknown true averages.

When die swell is plotted as a function of the ratio of viscous to elastic energy dissipation (Fig. 10), the data may again be represented by a single curve. The slightly greater scatter than in Figure 9 is not unexpected, in view of the additional experimental quantities involved.

On the basis of the limited experimental data available at present, no definite conclusions can be drawn, but the latter approach appears to be quite promising as a general means of correlating and quantitatively predicting die swell as a function of easily obtained material parameters. Other processing properties which depend on both the elastic and viscous properties of the material, such as mill shrinkage, should be amenable to a similar treatment.

CONCLUSIONS

Much of the difficulty encountered in the processing of polymers results from undesired deformation of the material after it emerges from the processing equipment. It has been shown that this deformation is directly related to the recovery of elastic strain energy imparted to the material while in the stress field of the equipment. The addition of gel reduces the deformation by reducing the amount of elastic strain energy which can be imparted to the material in a stress field. Concurrently, by increasing the viscosity of the material, but by a greater amount at low stresses, it also provides an increased resistance to deformation in the low-stress region outside of the equipment without exacting a comparable toll in increased power requirements. At a given loading, the greatest improvements should be obtained with small particle size, tight gels, which are most effective in producing the desired rheological modifications. A method has been proposed for correlating and quantitatively predicting die swell (and other strain-recovery phenomena) in terms of easily determined material properties. This method looks promising on the basis of a bare minimum of experimental data, but more work must be done to verify completely its practical value.

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Résumé

L'addition de matériaux sous forme de gel, ou de matériaux pontés, à un élastomère essentiellement linéaire, diminue souvent le "nerf" du retrécissement par moulage, ou le gonflement. Dans le présent travail, des systèmes à base de poly(acrylate d'éthyle), antérieurement caractérisés par un écoulement stationnaire, ont été étudiés en écoulement rapide. Le gonflement en cours d'écoulement cappillaire, et le recouvrement de cisaillement dans un rhéomètre à deux cônes ont été examinés et mis en corrélation avec le nombre de ponts, leur densité et les dimensions des particules de la phase gel. En général, l'addition d'un gel diminue la déformation des produits extrudés en diminuant l'énergie de tension élastique, qui peut être donnée au matériau dans un domaine sous tension. Concurément, en augmentant la viscosité plus fortement aux petites qu'aux fortes tensions, l'addition de gel provoque aussi un accroissement de la résistance à la déformation dans le domaine des basses tensions, et cela sans avoir d'exigences comparables en ce qui concerne un accroissement de puissance de l'appareil.

Zusammenfassung

Der Zusatz von geliertem oder vernetztem Material zu einem im wesentlichen linearen Elastomeren setzt oft den "Nerv", die Walzschrumpfung und die Pressquellung herab. In der vorliegenden Arbeit werden schon früher bei stationärem Fliessen charakterisierte Polyäthylacrylatsysteme bei nicht stationärem Fliessen untersucht. Die Pressquellung bei kapillarem Fliessen und die Scherkriecherholung in einem bikonischen Rheometer wurde untersucht und zur Menge, Vernetzungsdichte und Teilchengrösse der Gelphase in Beziehung gesetzt. Im allgemeinen vermindert der Zusatz von Gel die Deformation des extrudierten Materials durch Herabsetzung des Betrages an elastischer Verformungs energie, welche in einem Spannungsfeld auf das Material übertragen werden kann. Gleichzeitig liefert der Gelzusatz durch stärkere Erhöhung der Viskosität bei niederer als bei hoher Spannung eine grössere Deformationsbeständigkeit im Bereichniederer Spannung ausserhalb des Geräts, ohne einen vergleichbaren Betrag an erhöhtem Kraftaufwand zu erfordern.

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