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Effects of Mixing Variables and Talc Fillers on Tensile and Impact Fatigue Properties of Some Thermoplastic Blends of Poly(vinyl Chloride) with Acrylonitrile–Butadiene Copolymer Rubber

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Synopsis

An apparatus is described which measures simultaneously a relative change in vibrational damping and in transient electrical charging of a wafer specimen of plastic during the interval immediately following an impact blow. When impacting cycles are repeated regularly (at an energy less than the destructive level for nonfatigued specimen), the curves relating either electrical or mechanical responses to the number of impact blows show significant changes of slope at coincident intervals of the impact fatigue history, and either of these correlated effects can be used to indicate successive changes in microstructure which lead to the ultimate fracture endpoint of the fatigue test. These fatigue tests were used to study the effect of compositional and mixing variables on the properties of some heterophase thermoplastics. This study demonstrated that impact fatigue resistance can be poor in some plastic compositions which are rated to have superior impact resistance by tensile testing. Also, some special fillers in the correct quantity may improve fatigue resistance even though such filler loading will degrade other desirable tensile properties.

In the plastics industry, it was found very early that homopolymers offered limited possibilities for adjustment of their fixed set of physical properties. Demands for controllable adjustability of properties like flexibility, strength, toughness, and impact resistance, or even easier workability lead the compounder into the field of the heterogeneous polymer systems, or polyblends. Many of these mixed polymer systems were developed in the last decade. Among them are many polyblends of rigid poly(vinyl chloride) (PVC) and acrylonitrile–butadiene copolymer rubber (NBR).

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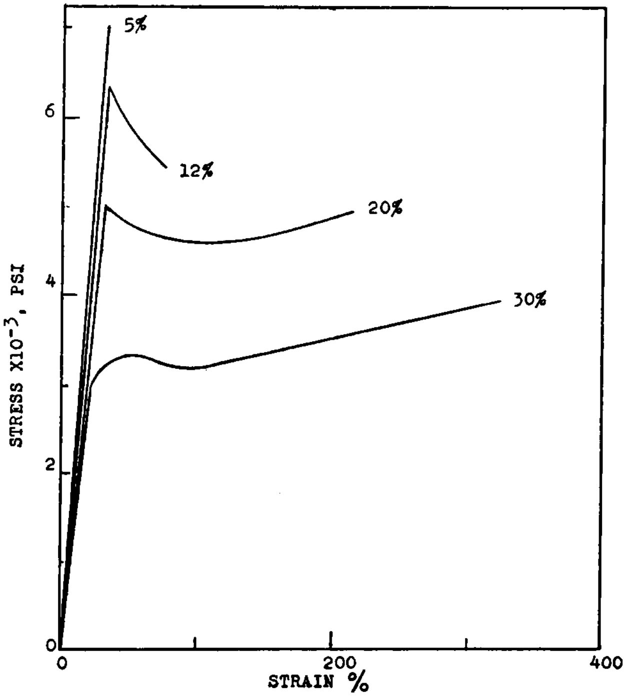

Fig. 1. Effect of rubber content on tensile properties. Mixing temperature 300°F., mixing time 5 min.

The present study is concerned with the modification of the basic tensile properties of PVC by means of nitrile rubber (NBR). Mainly, yield value, ultimate elongation, elastic modulus, rupture energy, and fatigue resistance have been considered. Mechanical properties are influenced as a general rule not only by the resin type and NBR concentration but also by the type of NBR used.

The PVC–NBR system for this investigation has been based on a medium-high viscosity straight PVC resin (inherent viscosity, ASTM D 1243-60 Method A, equal to 0.95) and on carboxylic nitrile rubber with high acrylonitrile content (about 40%) and low Mooney viscosity (about 45–50).

In the present investigation, first of all, the PVC/NBR ratio, mixing temperature, and mixing time were considered. The base formulation was the following: resin, 100 parts; stabilizer, 5 parts; lubricant, 1.5 parts; rubber, variable.

The rubber content was varied in the range of 5–30% by weight of resin. Compounding was carried out on a laboratory $5^1/_2$ in. × 12 in. roll mill. Four mixing temperatures, namely, 275, 300, 315, and 330°F., and four mixing times 1, 5, 10, and 15 min., were tried. Clearance between the rolls was kept constant at about 20 mils.

From polyblend sheets stripped off of the mill, specimens were punched by ASTM-D 378-51 T cutting die, type C. The orientation of cutting was the same. Only the best punched specimens were chosen, and after annealing for 30 min. at 70°C. they were aged at least 48 hr. at constant temperature.

For each specimen, three samples were pulled on the Instron tensile testing instrument, Type TT-C at 20 in./min. In this way, according to Evans, Nara, and Bobalek,[1] a linear correlation between rupture energy calculated from stress–strain curves, and impact resistance determined by falling weight tests, is obtained for this type of polyblend. They also found that thermoplastic materials of high impact resistance have typical

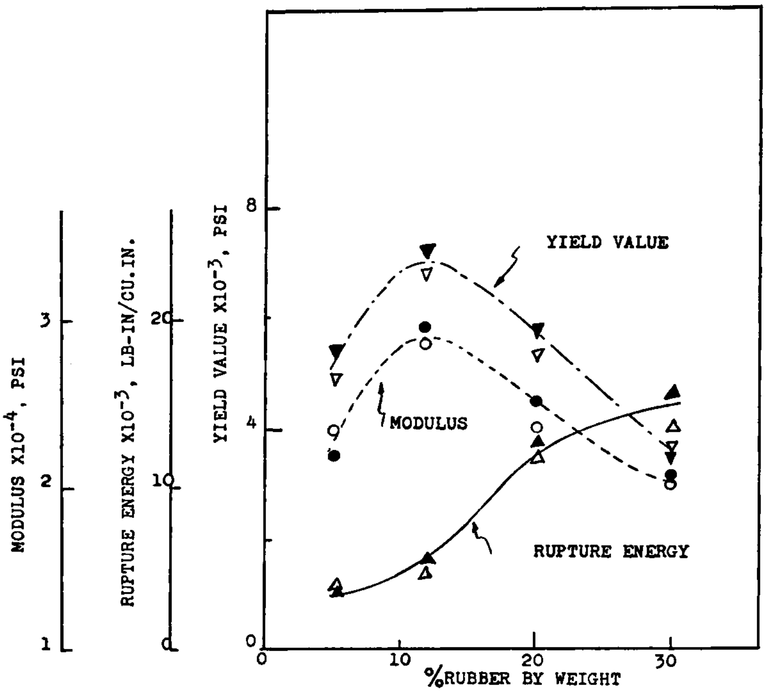

Fig. 2. Effect of rubber content on tensile properties: (∇,O,Δ) mixing time 5 min.; (▼,●,▲) mixing time 10 min. Mixing temperature 300°F.

stress–strain curves at 0.333 in./sec., so that the examination of the general character provides immediate qualitative information regarding whether one has advanced or retrogressed from the objective of upgrading impact resistance, assuming that impact resistance can be related consistently to rupture energy calculated as the area under the stress-strain curve for tensile specimens of consistent geometry. Figure 1 shows typical patterns of such tensile curves.

Tensile data for polyblends of several compositions prepared under different conditions of mixing are summarized in Figures 2, 3, and 4. A microscopic investigation of the structure of these polymers has been reported.[6]

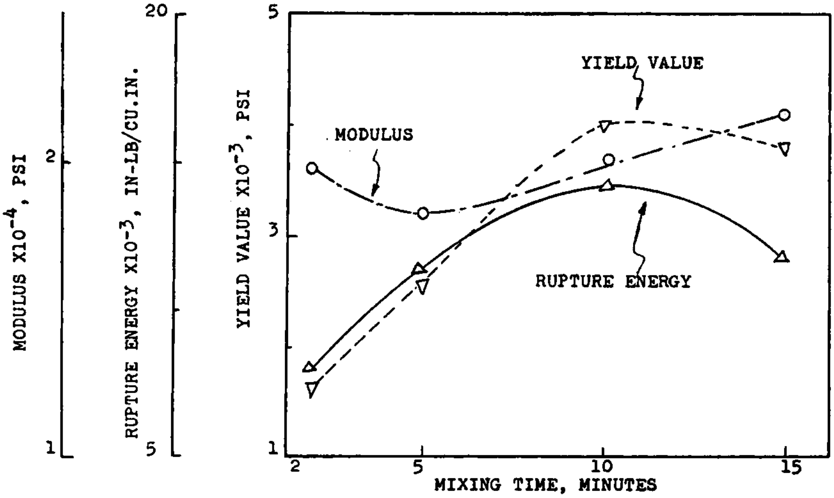

Fig. 3. Effects of mixing time on tensile properties of 70/30 PVC/NBR blend. Mixing temperature 300°F.

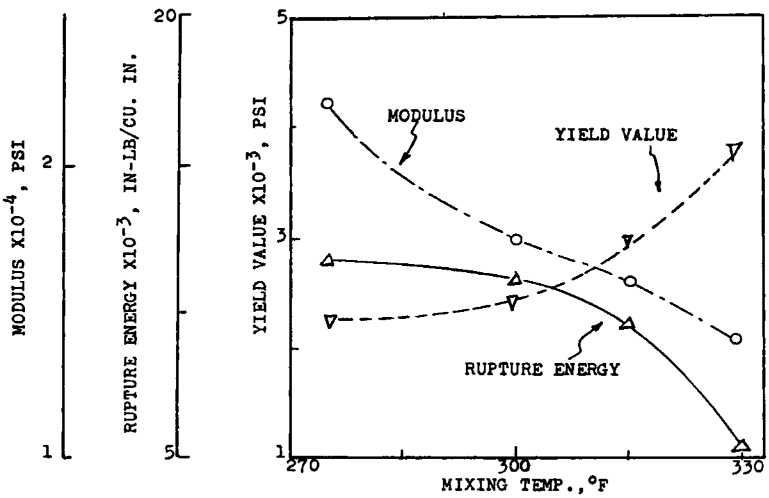

Fig. 4. Effects of mixing temperature on tensile properties of 70/30 PVC/NBR blend. Mixing time 10 min.

In general, as the mixing temperature is increased, the stress–strain curves change from a soft or plasticized material behavior to types expected to show impact resistance. It also appears that for higher rubber content formulation, higher mixing temperature is required to obtain tensile properties consistent with impact resistance.

The efficiency of mixing judged by the attainment of optimum properties depends not only on temperature but also on mixing time. There is a close interdependence between these two parameters. Figures 3 and 4 suggest that for systems of this type simple correlations relate degree of mixing to the time and temperature variables. Undermixed and overmixed polyblends exhibit very low impact resistance, judged by the index of rupture energy determined from tensile data.

As far as PVC/NBR ratio is concerned, Figure 2 indicates three different types of tensile behaviors.

(*a*) *Rubber Content Less than 10%:* These combinations have stress–strain curves typical of brittle polymers. This type of curve shows very little variation in shape by changing mixing condition; only the slope and height change.

(*b*) *Rubber Content Ranging around 20%:* Compositions ranging between 15 and 25% of rubber show a fairly high yield value and fracture energy. Processing conditions are extremely important as far as properties are concerned.

(*c*) *Rubber Content Higher than 30%:* The composition becomes more and more plasticized and the final stress–strain behavior is far less dependent on time–temperature conditions of mixing.

A good compromise between maintaining high modulus together with high rupture energy occurs in compositions with a rubber content of about 10–20%, milled at 300–315°F. for 8–12 min. Where the stiffening effect of fillers is to be superposed on the blend, the 70/30 mixture described in

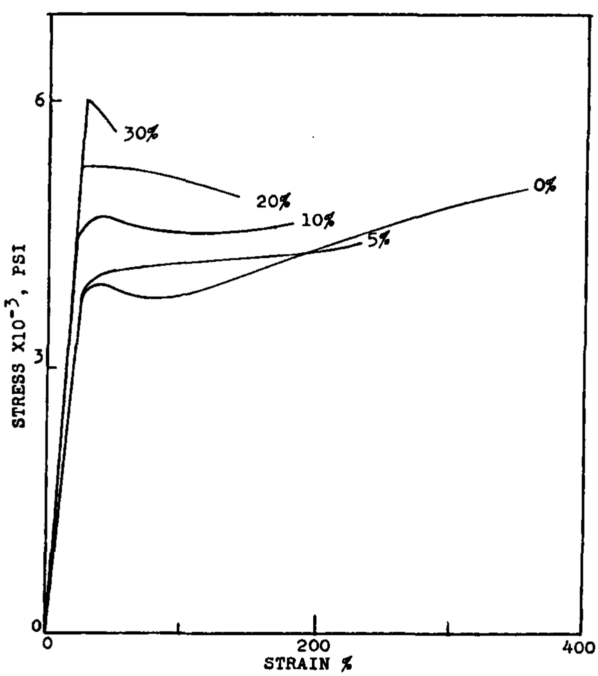

Fig. 5. Effect of filler loading on tensile properties of 70/30 PVC/NBR blend. Mixing temperature 300°F., mixing time 10 min.

Figures 2, 3, and 4 is a preferred polymer base for the more complex compositions to be discussed below.

Some Consideration on the Effect of Fillers

The effect of filler loading upon the properties of many polymers has been studied extensively. However, the effect of filler loading on the properties of polyblends has not been investigated extensively because these alloy polymers are generally estimated as quality products and used without fillers. As a matter of fact, most fillers degrade the toughness of such polymer systems.

Because fillers of the micaceous talc group are claimed to have some reinforcement effect,[2] their effect was studied. Under particular consideration was the possibility that these might improve the fatigue resistance without excessive destruction of other properties expected of polyblends.

Since it is well known that filler effect on polymer depends mainly on the structure and size of the particles, different surface areas (10–25 m.²/g.) and different structure types (platy and acicular) were tried.

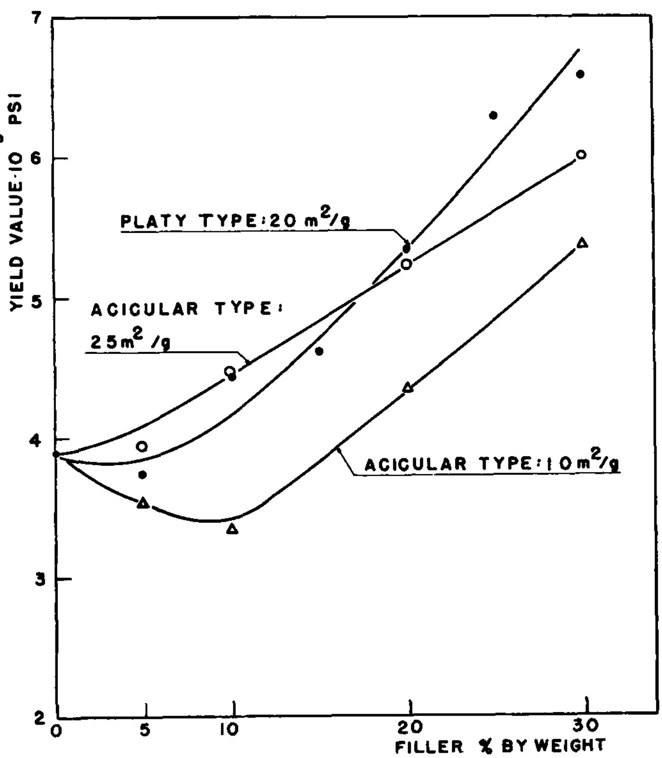

Fig. 6. Effect of filler on yield point of 70/30 PVC/NBR blend. Mixing temperature 300°F., mixing time 10 min.

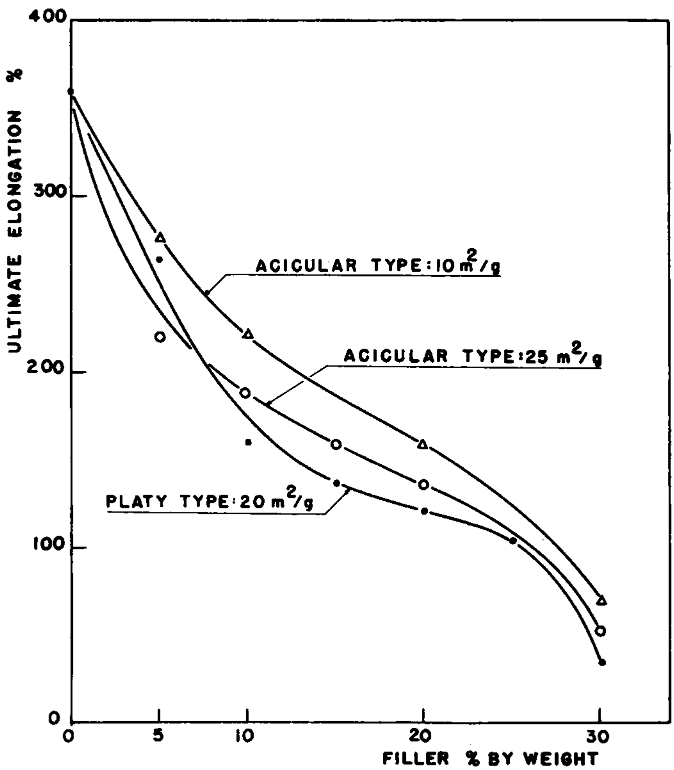

Fig. 7. Effect of filler on ultimate elongation of 70/30 PVC/NBR blend. Mixing temperature 300°F., mixing time 10 min.

The fillers were blended with rubber in a master batch and these mixtures milled with the polymer. The procedures were the same for preparing and testing specimens as that for the unfilled PVC/NBR blends. Figure 5 shows the typical effect of filler loading on tensile properties. Figure 6 shows that the acicular type becomes more effective in raising yield value as the surface area is increased from 10 to 25 m.^{2}/g. There is also some evidence of the effect of the particle structure since the platy type appears

TABLE I
Effect of Filler on Fatigue Resistance of a 70/30 PVC/NBR Composition

Composition	Yield value, psi	Elastic modulus, psi	Rupture energy, in.-lb./in.^{3}	Fatigue resistance, no. of strikes
Without filler	3,900	17,800	15,250	400
With 5% of filler (acicular type, 25 m.^{2}/g. of surface area)	3,950	17,900	8,900	700
With 5% of filler (platy type, 20 m.^{2}/g. of surface area)	3,740	17,600	10,700	900

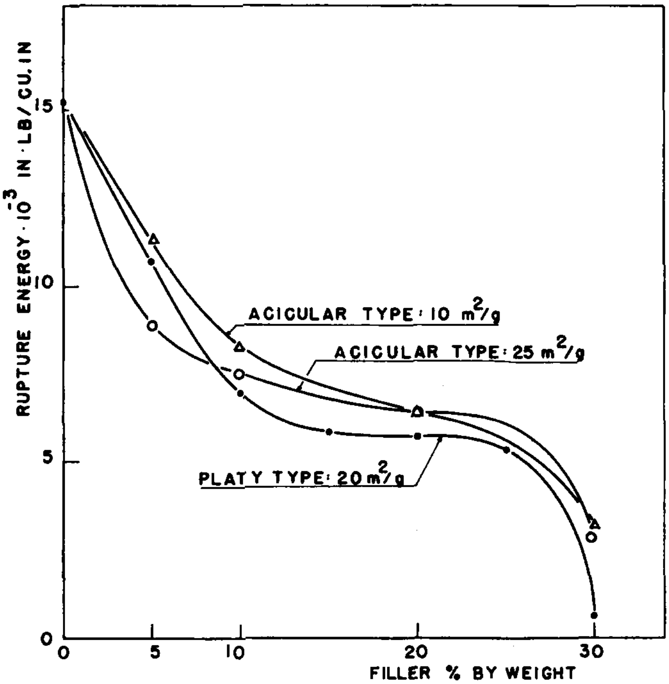

Fig. 8. Effect of filler on rupture energy of 70/30 PVC/NBR blend. Mixing temperature 300°F., mixing time 10 min.

to be the more effective one despite its lower surface area of 20 m.²/g. compared to 25 m.²/g. for the acicular type.

Figures 7 to 10 show the effect of the platy type on polyblends with PVC/NBR ratios of 70/30 and 88/12. Using a highly plasticized composition (30% of rubber), filler loading decreases the elongation at break very sharply. For a low plasticized composition (12% of rubber) ultimate elongation peaks at about 5% filler loading.

If the yield value of the unfilled plastic is low, the filler addition increases the yield value, but ultimate elongation and rupture energy are reduced.

TABLE II
Mechanical Properties and Fatigue Resistance of Different Compositions

Composition	Yield value, psi	Elastic modulus, psi	Rupture energy, in.-lb./in.³	Fatigue resistance, no. of strikes
PVC + NBR (ratio 80/20)	5,800	24,000	10,020	280
PVC + NBR (ratio 70/30) + 15% of filler (acicular, 25 m.²/g.)	5,820	22,400	5,850	360
PVC + NBR (ratio 70/30) + 5% of filler (acicular, 10 m.²/g.)	3,540	23,600	11,300	460

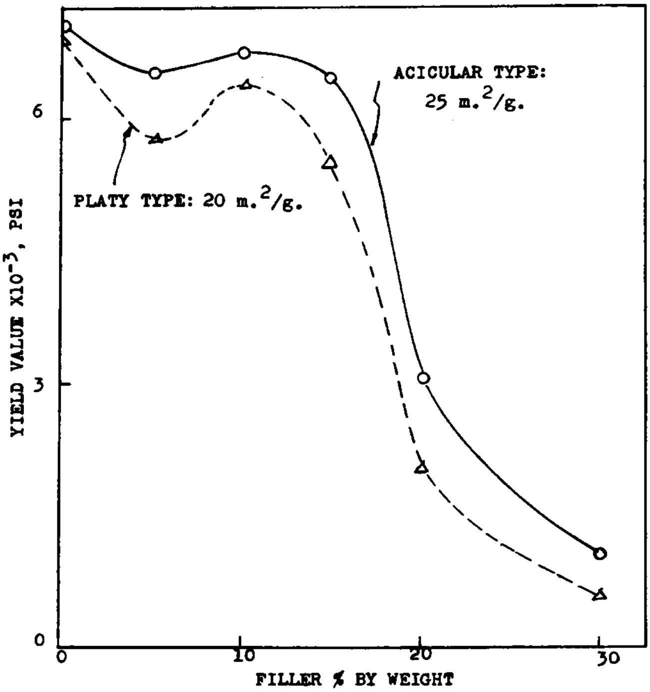

Fig. 9. Effect of filler loadings on yield value of 88/12 PVC/NBR blend. Mixing temperature 300°F., mixing time 10 min.

Where the yield value is high, as in the 88/12 blend, the filler seems to improve the ultimate elongation and rupture energy at optimum loading without significant change in yield value. As was anticipated, the most important effect is related to changes in fatigue resistance. These data are shown in Figures 11 and 12 for the same compositions shown in Figures 6–10. Tables I and II show also that different compositions with approximately the same tensile properties can have very different fatigue resistance, and that fatigue resistance can be increased significantly by addition of optimum quantities of micaceous fillers. The manner of determining the data of Tables I and II and Figures 11 and 12 is described here in detail. The method demonstrates some unusual relationships between electrical and mechanical properties.

Apparatus

An apparatus was built to follow impact fatigue through simultaneous measurements of some mechanical and electrical properties on the same specimen. The impact tester was designed to impart a controlled amount of energy on the specimen at each strike and to repeat the schedule of striking at regular frequency. The damping vibrations of each strike were registered on an oscilloscope through a linear variable differential transformer and a signal generator and demodulator and were recorded by an

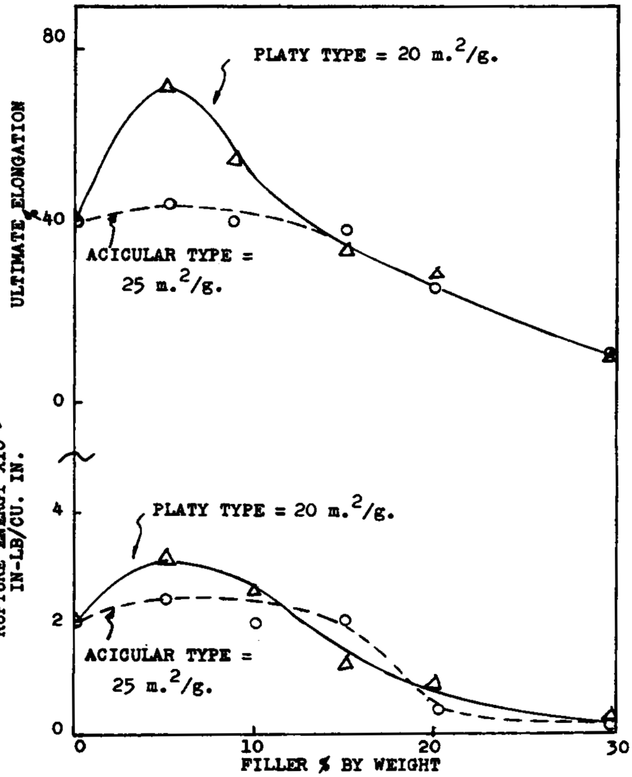

Fig. 10. Effect of filler loading on ultimate elongation and rupture energy of 88/12 PVC/NBR blend. Mixing temperature 300°F., mixing time 10 min.

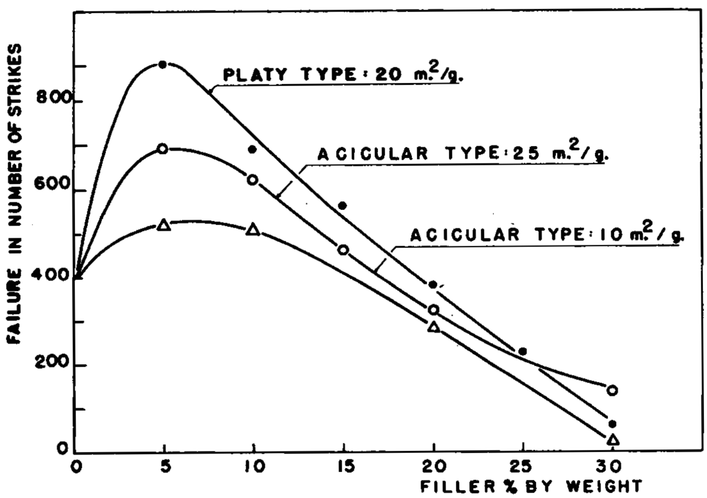

Fig. 11. Fatigue resistance vs. filler content in a 70/30 PVC/NBR blend.

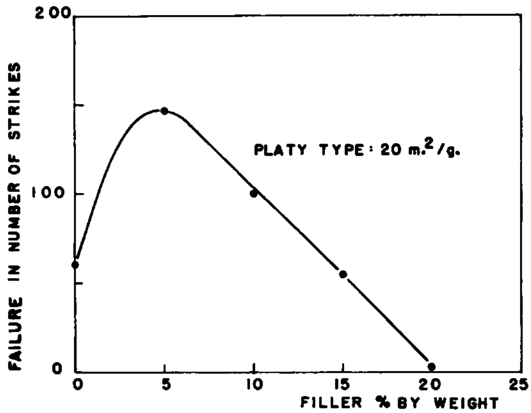

Fig. 12. Fatigue resistance vs. filler content in a 88/12 PVC/NBR blend.

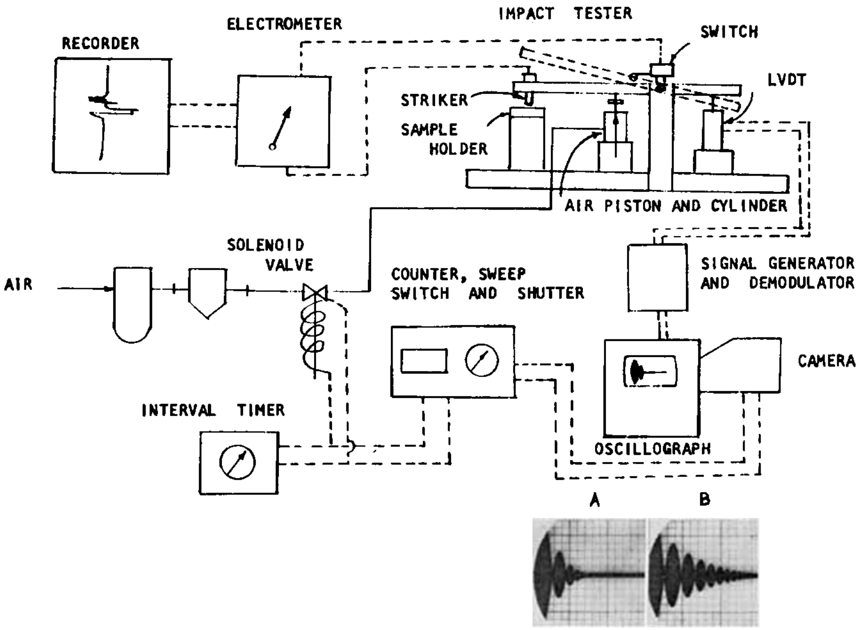

Fig. 13. Setup of impact fatigue test apparatus.

oscillograph camera. For the electrical measurement, the strike head was used as a probe by connecting the striker to the input of an electrometer. Variation of voltage with time was registered on the electrometer and traced by a recorder. The complete setup of the apparatus is shown in Figure 13.

The impact tester was manufactured by Nuclear Ohio Inc., of Bay Village, Ohio. It consists of a balance arm about 26 × 2 × 1.5 in. in dimension and weighing 7.5 lb. on a suitable framework. The arm is pivoted near the center of gravity when unloaded and mounted on ball bearings to reduce friction. The plastic sample, usually a 1-in. diameter disk, is struck by a nickel striker, which is a 0.5-in. diameter rod attached vertically to the

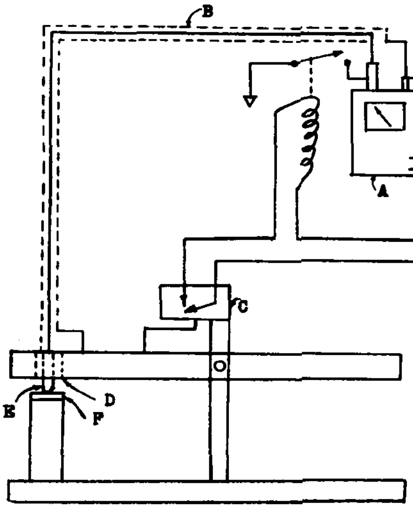

Fig. 14. Circuit of electrical measurement in impact fatigue: (*A*) electrometer; (*B*) shield wire; (*C*) microswitch (normally open); (*D*) insulation; (*E*) probe striker; (*F*) sample.

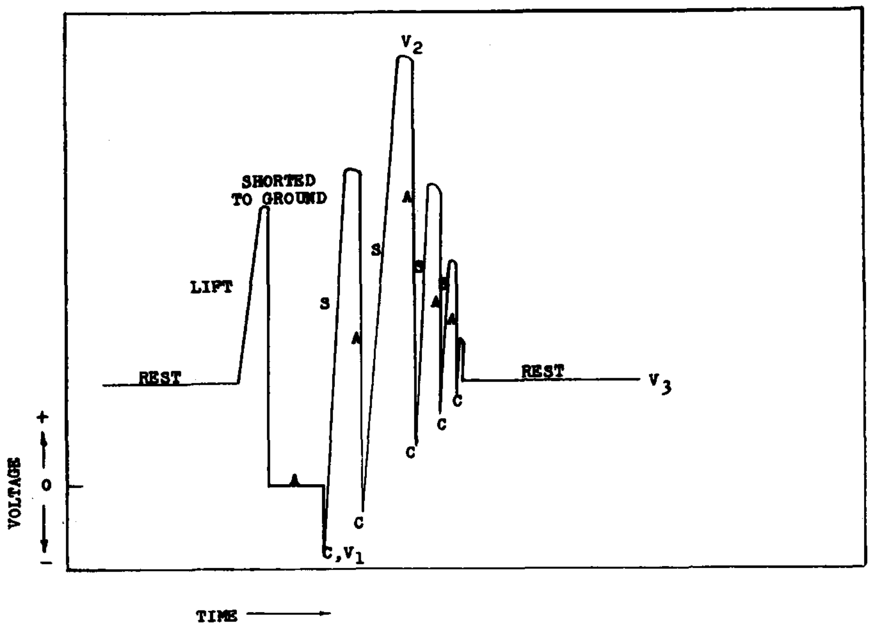

Fig. 15. Voltage curves of one impact cycle: (V_1, V_2, V_3) reference voltage index; (*A*) approach; (*C*) contact; (*S*) separation.

main axis of the arm near one end. This striker has a 0.25-in. radius machined on the striking face. The striker is threaded into a Teflon sleeve. This serves as insulation between the nickel striker and the brass arm in electrical studies. Height adjustment to give a minimum signal amplitude can be obtained by threading the striker to different depths in the Teflon sleeve.

Changing the material of the insulating sleeve could change the response of the probe because here also we have a dielectric–metal contact which interacts to modify the electrical response measured. The excellent reproducibility on each sample type exhibited by this apparatus when sample types were randomly fed to the apparatus over extended periods of time suggests that this insulator gives a very stable system exhibiting a constant effect toward each sample measured once it has been conditioned by exposure to several hundred cycles of impact loading. In further theoretical and experimental development of this principle, attention will need to be given to the role of the insulating sleeve.

Voltage transients generated by the striking process are measured on the striker against the striking arm which is at ground potential (see Fig. 14). The lead from striker to electrometer is attached on the striker over the Teflon sleeve. A switch is provided over the arm to short the striker to ground potential at the peak separation of vertical displacement before the first strike in each cycle of rebounds. The voltage transients observed on the nickel hammer in an impact-rebound cycle are shown in Figure 15.

A copper screen cage encloses the impact tester to minimize space charge effects. The plastic sample is clamped to the anvil with a ring and four bolts. The ring overlaps about $^1/_4$ in. over the edge of the specimen disk. The anvil was bored with a cylindrical depression that matches the bore of the damping ring. This allows for considerable vibration of the plastic sample in response to a blow. Anvils and rings can be adjusted for different sample sizes and different vibration characteristics of polymers. Both anvil and clamping ring bores have corner radii to minimize cutting in flexure. A threaded rod fixed horizontally on top of the striker arm allows for attachment of variable weights, which conditioned the severity of the test by reducing or increasing the number of blows required to induce fracture. As the height to which the hammer is elevated is nearly constant, the magnitude of the weight attached determines the energy imparted to the sample in the first blow.

The arm is raised by an air-actuated piston manufactured by Clippard, Cincinnati, Ohio. The height of rise can be adjusted for each run by setting the piston position. The cylinder is so valved that the piston retracts automatically at the peak of the strike, thereby ensuring free fall of the arm. The air flow and piston actuation are controlled by a solenoid valve operated by an interval timer which is so adjusted as to give adequate "air-time-on" to raise the striker arm and enough "air-time-off" to allow the bounces to damp out to complete rest before lifting the hammer for the next blow.

The movement of the arm is translated into an electrical impulse by means of a linear variable differential transformer manufactured by Schaevitz Engineering, Camden, N. J. This is mounted on the base perpendicular to the arm. The transformer is mounted on a pivot on the arm, and the core movement and the signal generated by it is linearly proportional to the movement of the striker.

The specimens were cut from plastic sheets into disks of 1 in. diameter and stored for several days at 23 ± 1.1°C. and 50 ± 2% R.H.[4] All tests were performed in this same atmosphere. The plastic disk was mounted in a sample holder with a damping ring, which had the same free area as the anvil, and four bolts. Air was turned on, and the air pressure was adjusted to give proper "air-time-on" to raise the striker to the peak from which the striker was released and enough "air-time-off" to allow the sequenced bounces to damp out. The initial amount of energy imparted depends on the height of fall of a fixed mass. The oscilloscope was set to a linear voltage and the amplitude was adjusted to a minimum by means of the height adjustment provided in the striking threads. Proper sweep rate and amplitude scale of the oscillograph were selected to fit convenience for each sample type. For example, glass-filled thermosets had different requirements than tough thermoplastics.

The counter was rest to zero. Film was fed into the camera, and rate of film transport was adjusted, depending upon how often a picture was to be recorded. The interval timer was turned on to start an experiment.

The 10,000 cycle sine wave signal was fed into the linear variable differential transformer from the signal generator where it was modulated by the movement of the striking arm which changed the reluctance to the transformer by changing the relative position of the core to the windings. The modulated signal was returned to the demodulator, the carrier wave was rectified, and the signal was amplified and advanced to the oscillograph.

Meanwhile, at the beginning of the operation, the horizontal sweep with the vertical signal applied appeared on the face of the cathode ray tube as a series of decreasing waves. Zero amplitude was set at the center of the tube so that these waves registered plus and minus full side or twice the proportional amplitude as the actual bounce. The traces of damping waves on the cathode ray tube were recorded at a predetermined interval set on the shutter operator counter. The shutter opening time was set to record a complete trace without overlapping or clipping. The pictures of damping bounces were projected in a microreader after developing and drying and measurements were made of relative amplitudes in the damping wave pattern.

For the electrical measurement, zero point and proper voltage scale were set before the experiment. Zero point was so set that the initial charge on the specimen was always zero. The switch that shorts the striker to zero was set to turn on only at the peak rise of the arm which initiated each strike sequence. That is, the striker started at ground zero for each strike.

The experiment was terminated when cracks, or crazing, were observed by visual inspection of the specimen. The mechanical and electrical responses to repeated impact were recorded automatically.

Damping Decrement

By considering sequential pairs of waves in photographs of the damping curve, the natural logarithm of amplitude ratios was calculated. This is regarded as a measure of the capacity of the material to dissipate mechanical energy imparted during the striking process (see appendix). Loss of capacity to dissipate energy is used here as an index of impact fatigue. Inserts *A* and *B* in Figure 13 illustrate the damping curve types for plastics which have high and low capacities to dissipate energy. The damping decrement, ln (A_n/A_{n+1}), was plotted as a function of the number of strike repetitions. The damping decrement calculated from different selections of successive peaks in the damping curve is not constant for conditions of this apparatus. However, if a consistent selection is made as to which pair of peaks to select of the rebound sequence in each repetitive cycle, the values of damping decrement so obtained correlate well with the number of strikes, and produce curves which allow for clear discrimination between samples.

On using the plot of ln (A_n/A_{n+1}) versus number of strikes as an index of different behaviors, several patterns were observed for different plastic types. Some of the more significant patterns are worth showing before use of the apparatus is discussed with reference to this compounding experiment.

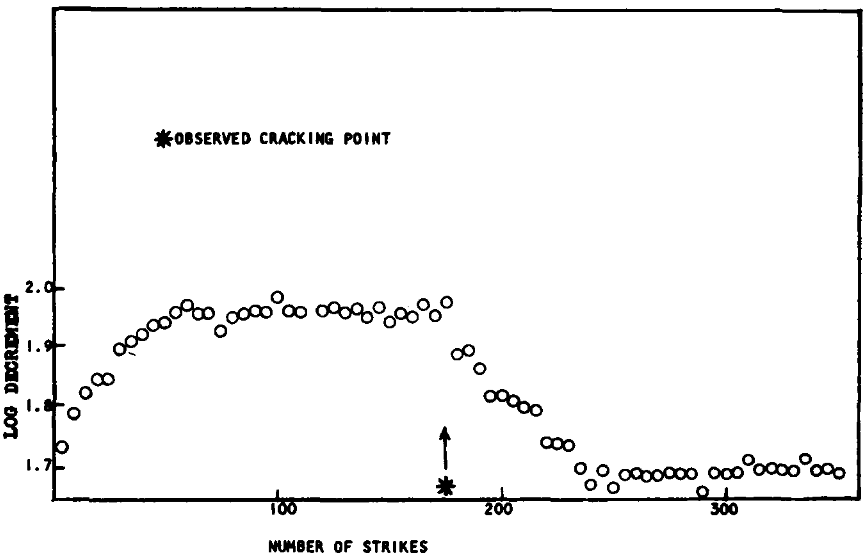

Fig. 16. Impact fatigue pattern I. 88/12 PVC/NBR blend, 1/8 in. thick.

Impact fatigue pattern I is illustrated by a polyblend plastic containing 12 parts of nitrile rubber per 88 parts of poly(vinyl chloride) in Figure 16. Here the log decrement increases with increasing number of strikes in the beginning of the process, stays for a number of blows at a high value, and then declines only after cracking is sufficiently severe to be seen by visual observation. Plastics which conformed to this pattern all showed low resistance to impact fatigue. Many of these same plastics have extraordinary resistance to fracture in terms of energy required to damage the plastic in the first blow.

Impact fatigue pattern II, was of the type obtained from a commercial polyblend of 20 parts of nitrile rubber and 80 parts of poly(vinyl chloride) (Fig. 17).

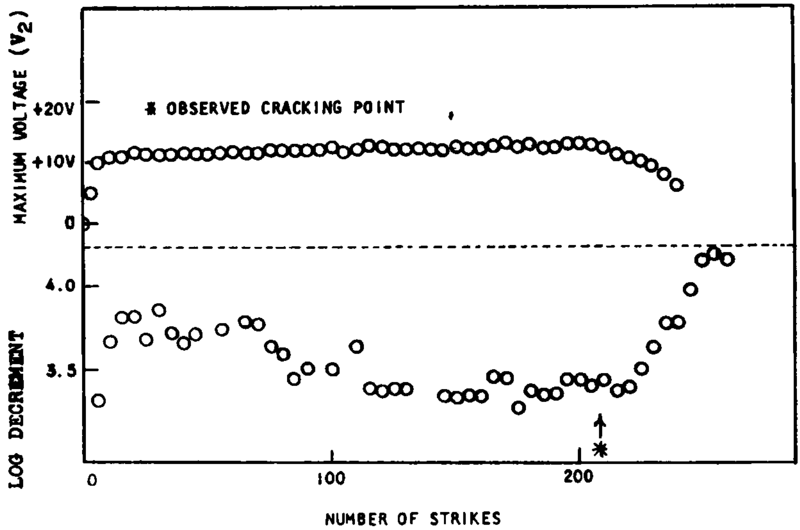

Fig. 17. Impact fatigue pattern II. 80/20 PVC/NBR blend, $^1/_{16}$ in. thick.

For this pattern, as for pattern I, the decrement first increases with the early number of strikes, maintains a high value for a time, then starts declining to a lower value. Finally, at the cracking point, it climbs rapidly. Two possible explanations present themselves. Referring to the appendix the decline in force at cracking in this set of samples may have been compensated by an increase in the displacement possibly during energy absorption so that the integral assumes larger values. This means that even after cracking, the material remains a good impact material because of the greater freedom to displace itself during the contact period, which is achieved upon cracking. The second hypothesis involves the possibility of a drastic change in the structure of the plastic during the repetitive impact process. Whatever may be the explanation, the fact was clear that nearly all plastics which showed this pattern II in our tests showed a high resistance to impact fatigue even if some were less impact-resistant than those showing pattern I, as measured by falling weight tests to fracture unworked samples in one blow.

Impact fatigue pattern III is illustrated by the performance of a glass-reinforced polyester plastic (Fig. 18).

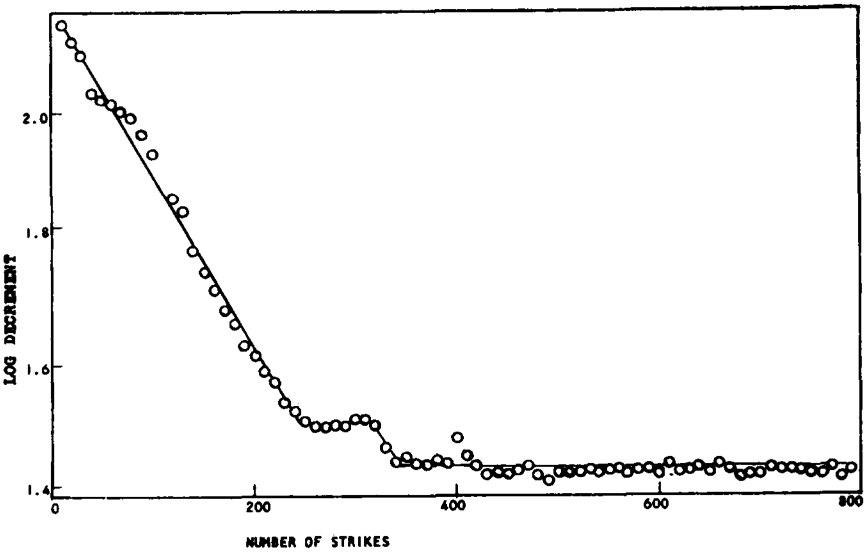

Fig. 18. Impact fatigue pattern III. Glass-reinforced polyester.

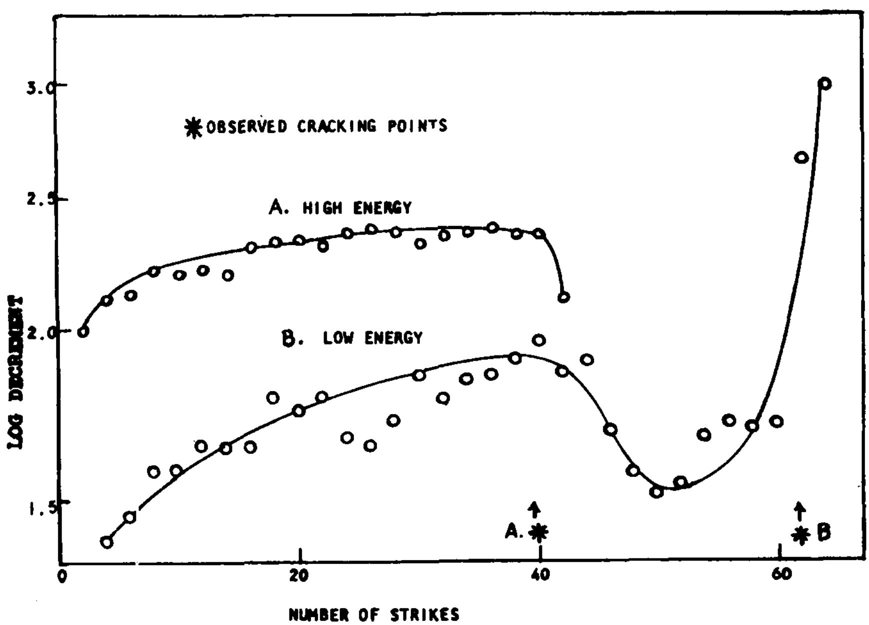

Fig. 19. Effects of energy on impact fatigue. PVC, $^1/_{16}$ in. thick.

For this pattern, the log decrement declines steadily and finally stabilizes at relatively low values. This pattern is generally characteristic of brittle plastics, except that total failure occurs if no fibers are present to stabilize a steady state after some number of blows.

Varying striking energies by increasing weights on the arm or varying the striking amplitude can modify the severity of the test so as to change number of strikes to failure or even the shape of the curve. For example, we see in Figure 19 for poly(vinyl chloride) that 40 strikes caused cracking at the high energy level, while 60 strikes were needed to crack the plastic at the lower energy level. It is to be noted that at low energy levels poly(vinyl chloride) exhibits impact fatigue pattern II, while at a higher energy level the pattern I behavior is shown. If the explanation of the difference between impact fatigue patterns I and II based on the appendix is true, this implies that low level impacts on PVC cause only minor damage and create a pattern of cracks which permit extension without fully destroying resistance, but high energy impacts destroy the ability to resist as well as the geometrical integrity of the material. Hence the shape of these curves may reflect less a typical characteristic of the material than it does the relative severity of the test condition for the sample type.

Electrical Measurements

The electrical impulse during the striking process was recorded automatically. A typical pattern for each cycle is illustrated schematically in Figure 15. The nickel electrical probe was shorted to zero at the peak of each strike sequence. Thus the voltage at the instant of contact measures something close to the charge on the plastic (expressed by V_1 in Fig. 15). Recording of V_1 is one way to follow the electrical transients during the impact fatigue testing process. Still, considering one strike, after the first contact of the striker (electrical probe) with the plastic, the striker bounces up and down freely for a number of periods. Charges are transferred and neutralized during the bouncing process due to repetitive contact and separation between the striker and the plastic. Charges on the striker were always positive for the plastic systems studied. A maximum positive voltage on the striker (expressed by V_2) occurred near the peak separation when the striker bounced into the air. V_2 was recorded during the impact fatigue testing process. After a series of bounces, the striker came to rest on the plastic. The charge decayed during this rest period until it approached a steady value. The voltage measured just before the next lift of the striker designated V_3. Recording V_3 provides a third way to follow the electrical transients on the plastic during the testing process. V_1 is essentially a contact potential, V_2 is a voltage across a capacitance, and V_3 is a decayed contact potential. Each one of the three ways of registering the voltage transients of plastics during the repetitive striking process is useful in establishing curves which can be correlated with changes in capacity to damp mechanical energy.

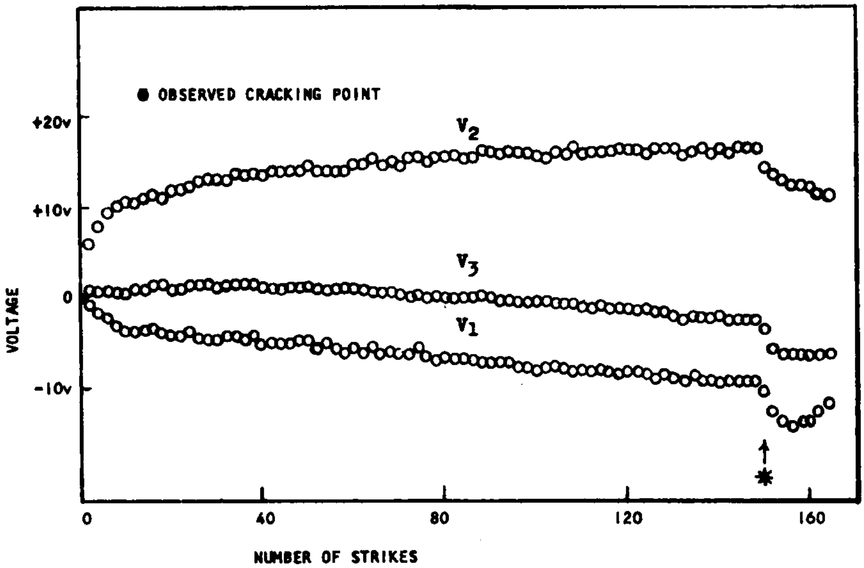

Fig. 20. Three ways to follow impact fatigue by electrical measurements. 70/30 PCV/NBR blend with 30% filler, $^1/_8$ in. thick.

As shown in Figure 20, V_2 increases rapidly in the beginning of the test, levels, and declines abruptly at the cracking point. While the three types of curves based on V_1, V_2, or V_3 have different patterns to some degree, all show abrupt change in slope of the impact cycle range where the dissipation factor for mechanical energy also changes significantly.

Up to now, the origin of this electrical charge has not been commented upon. The reasons for its existence are not yet clearly defined. As an experimental fact the phenomenon has been studied extensively. Data to this point and much speculation as to mechanism of charging can be found in the publications of Kern,[7] Trivisonno,[8] Flynn,[9] and Gaynor.[10] Skinner[11] summarized significant parts of this work.

Impact Fatigue of Polyphase Polymers with and without Fillers

It appears that the loading of filler degrades initial impact resistance of these polyblends according to the index deduced from stress–strain curves.[5] This is also confirmed by engineering experience with uses of these polymers.[2]

In filled plastics, the crazing pattern showing first failure in impact fatigue test cannot be seen as easily by visual inspection as is possible with unfilled plastics. For these plastics the electrical test is most useful. Four series of filled polyblends were tested for impact fatigue resistance by electrical measurements. Some typical results are shown in Figure 21. Data then obtained for a number of plastics are summarized in Figures 11 and 12 and Tables I and II. Polyblends with up to 15% of fillers exhibited comparable or better fatigue resistance than the unfilled polyblends, even

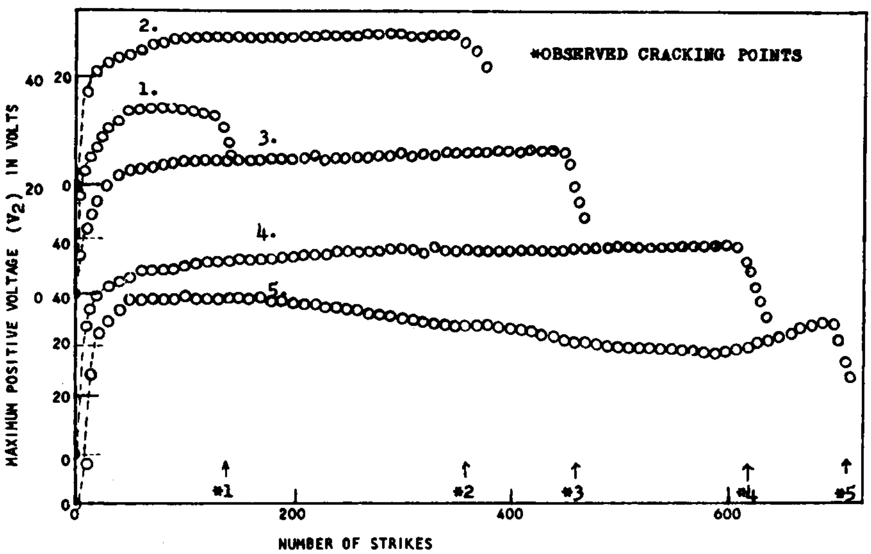

Fig. 21. Impact fatigue of 70/30 PVC/NBR blend with acicular filler (25 m.²/g.): (*1*) 30% filler; (*2*) 20% filler; (*3*) 15% filler; (*4*) 10% filler; (*5*) 5% filler.

though other tensile properties had declined as a result of filler loading. The platy filler with a surface area of 20 m.²/g. shows greater improvements than the acicular filler which has a surface area of 25 m.²/g. The acicular filler, being of smaller particle size, has a greater effect then the coarser filler.

Although micaceous fillers with their organophilic nature and large particle surface might be expected to provide a high wetting capability by polymer and perhaps good interphase adhesion, it seems that such bonds in the plastics are not very strong. A marked decrease rather than improvement occurs in most tensile properties. On the other hand, the weaker adhesive bonds between polymer and filler seem to be able to reform after being broken by relatively low energy level blows. Hence, impact fatigue resistance is better even at impact load levels which will eventually disrupt polymers not containing the wettable filler. At an extreme when too much filler has been loaded into the structure, then too many weak bonds add up to a total weakening effect, resulting in a damage to both fatigue resistance as well as to initial impact resistance.

Another possible explanation of the increases of fatigue resistance by optimum loading with adhesive fillers may lie in the faster dissipation of energy by aggregated powders of dispersed filler due to reshuffling of single particle elements in flocculates.

The two viewpoints are not contradictory; both or either may apply in particular structures. Until some way is obtained for microscopic observation of the dynamics of cycle loading, the mechanism involved in the effect of the filler on impact fatigue or the pattern of rheological behavior in composite plastics will remain highly speculative, with a number of plausible explanations competing for our attention.

Some Speculations Regarding the Relationships Between Electrical and Mechanical Behavior

A heterophase plastic may be conceived of having a domain structure in which at least three or more types of domains exist. For example, two phases can be distributed in a variety of ways and the phases are bonded to each other by some sort of adhesive forces. These adhesive forces exist because of formation of a less organized transition region between the two homogeneous phases which we can call the interphasal region. We might say that this interphasal region is equivalent to a third phase existing as a very thin film continuum interlaced between the more bulky volume elements of primary phases. The areas A, B, and C have different mechanical behaviors. For example, A may be brittle and glassy, B may be quite rubbery in its behavior, and C may show some intermediate mechanical behavior. The various elements of the total structure have different capacities for responding to stress applied to the composite structure. An applied stress has different effects upon each of these regions because they also have different rates of stress relaxation and different strain responses to particular levels of stress. In some domains, the stress will be relieved by straining and in others it might be relieved only by microscopic fracture across the domain, or perhaps the straining process might involve a slippage of one domain with respect to the other, and the main retarding force is the magnitude of the adhesive interaction on the very thin interphasal region. Possibly, the flow of one domain versus another might give rise on a microscopic scale to a slip-stick frictional effect of charging and discharge as has been observed in independent studies between materials in bulk.[3] Fracture may also cause some charge separation, which in part is dissipated by flow of electrons to the air interface where charge is drained off to the atmosphere.[7,8,10]

The extent of charging observable on the air interface of the bulk material at a particular time depends on whether charge separation and flow of charge to where it can be drained is faster than escape of charge by ionization of the atmosphere or flow to ground along high resistance paths. A part of the charge caused by fracture of slip-stick frictional flow on a microscopic scale may be neutralized by healing of transient fractures. The opposite polarity of fractured surfaces may contribute to healing of small fractures or restoration of interphasal adhesive bonds when the domains slide against each other. The part of the charge not so neutralized has to be dissipated. The extent of the charge being dissipated by flow away from the fracture (or slip) areas may be a measure of this irreversibility of the fracture or dislocation mechanism associated with stressing composite structures.

We can surmise further that when the destruction of microstructure by microscopic fracture or domain slippage and distortion hits a relatively steady state for a particular level of stress, then application of further cycles of stress will show a steady state response of the piezoelectric effect produced. At this steady-state level, the total structure responds and relaxes to application and withdrawal of strain without further changes in microstructure. At this stress level the structure is stable.

Fatigue to obvious catastrophic failure may involve the endpoint of a process where loading causes defects to accumulate with each cycle of strain faster than they can be healed or restored. For example, with reverse of the straining cycle, some of the microfracture which occurs may heal and some of the damage may be irreversible. With repeated cycles, there is an accumulation of fracture defects to a point where the healing mechanism is seriously interfered with because too many stress concentration points exist of such dimensions as to promote stress propagation at a faster rate than can be interfered with by the available stress relaxation mechanism in one or more domains. Repeating stress cycles beyond this critical point causes reinforcement of stress distributions which leads to catastrophic failure of the structure in bulk.

The plausibility of these sorts of internal changes is suggested by the microscopic studies of Rovatti[6] which were done in collaboration with this study. These microscopic investigations do indicate that straining causes a pronounced change in the fracture pattern of heterophase polymers, particularly at those levels of strain where the polymer seems to lose elastic rigidity and begins to exhibit rubbery behavior. Straining heterogeneous structures causes some irreversible changes in structure, even when the amount of strain is less than the apparent yield value suggested by tensile data.

This suggestion of an interaction between a mechanism of rheological flow and fracture formation and fracture healing is very hypothetical. The existence of a correlation between the piezoelectric response and the capacity of a polymer to damp out impact energy is an experimental fact. If the broad qualitative outlines of a structural model suggested here is not real, then some other models will have to be found to rationalize the fact of the experimental correlations here reported.

APPENDIX

Potential energy of the strikes and associated weight at maximum height (h_1) is equal to $K = mgh_1$ which is equal to the energy at impact (at the first cycle). Potential energy at the second cycle is equal to mgh_2. The difference ($mgh_1 - mgh_2$) represents the energy absorbed by the plastic, $E = \int \delta f dx$, over the period of contact.

$$mg(h_1 - h_2) = E$$

or

$$h_2/h_1 = 1 - (E/mgh_1) = 1 - (E/K)$$

$$\ln (h_2/h_1) = \ln [1 - (E/K)]$$

If h_2 is nearly equal to h_1, then $E/K \ll 1$, since $\ln [1 - (E/K)] \simeq - E/K$ for $E/K \ll 1$.

Thus

$$\ln (h_2/h_1) \simeq - E/K$$

or

$$\ln (h_1/h_2) \simeq (E/K)$$

and

$$\ln (h_1/h_2) = \int \delta f dx/K$$

Therefore, log decrement is a measure of capacity of the plastic to absorb impact energy.

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Résumê

On décrit un appareil qui permet de mesurer simultanément un changement relatif dans l'amortissement de vibration et dans la charge électrique transitoire d'un échantillon de plastique sous forme de pastille pendant l'intervalle de temps qui suit immédiatement une vibration de choc. Lorsque les cycles de choc se répètent régulièrement (à une énergie inférieure au niveau destructif pour les échantillons non fatigués), las courbes reliant soit les réponses électriques, soit les réponses mécaniques au nombre de vibrations de choc presentent des changements significatifs de pentes à des intervalles coïncidants avec l'historique de la fatigue due au choc; chacun de ses effets reliés entre eux peuvent être employés pour indiquer des changements successifs dans la microstructure ce qui conduit à la rupture finale du test de fatigue. Ces tests de fatigue ont été employés pour étudier l'influence des variables de composition et de mélange sur les propriétés de certains thermoplastiques en hétérophase. Cette étude démontre que la résistance à la fatigue d'un choc peut être faible pour certaines compositions de plastiques qui sont estimées avoir une résistance supérieure au choc par les essais de tension. Aussi, certaines charges spéciales ajoutées en quantité correcte peuvent augmenter la résistance à la fatigue même si de telles quantités de charge détruisent d'autres propriétés de tension souhaitables.

Zusammenfassung

Ein Apparat zur gleichzeitigen Messung einer relativen Änderung der Vibrationsdämpfung und der momentanen elektrischen Aufladung einer waffelartigen Kunststoffprobe während des einer Stossbeanspruchung unmittelbar folgenden Intervalls wird beschrieben. Bei regelmässiger Wiederholung der Stosszyklen (bei geringerer Energie als der Zerstörungsenergie ermüdungsfreier Proben entspricht) weisen die Kurven für die Abhängigkeit des elektrischen oder mechanischen Verhaltens von der Anzahl der Stossbeanspruchungen eine charakteristische Änderung der Neigung bei nicht zusammenfallenden Intervallen der Stossermüdungsvorgeschichte auf, und jeder dieser zueinander in Korrelation stehenden Effekte kann als Anzeichen für die aufeinanderfolgenden Änderungen der Mikrostruktur verwendet werden, welche zum schliesslichen Bruchendpunkt des Ermüdungstests führen. Diese Ermüdungstests wurden zur Untersuchung des Einflusses der Zusammensetzungs- und Mischungsvariablen auf die Eigenschaften einiger Heterophasenthermoplaste verwendet. Die Untersuchung zeigte, dass gewisse Kunststoffe, welche nach einem Zugtest eine besonders gute Stossfestigkeit besitzen, eine schlechte Stossermüdungsbeständigkeit aufweisen können. Weiters können gewisse spezielle Füllstoffe in der richtigen Menge die Ermüdungsbeständigkeit verbessern, obgleich die Einbringung solcher Füllstoffe andere erwünschte Zugeigenschaften verschlechtert.

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