Preparation of third components on the conductivity behavior of polymer Epoxy / Ag conductive composites

تحضير سبائك بوليمرية موصلة ثلاثية التركيب من بوليمر الايبوكسي / فضة

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Abstract :-

Conductive polymer , based on highly filled silver partials in a liquid epoxy resin with a diethyltriamine(DETA) as a curing agent . A third component was added to the epoxy \Ag system to obtain composite of better conductivity, or similar conductivity but at lower silver content to modify the conductive properties, epoxy \Ag \ carbon black (CB) , epoxy \Ag\graphite(G), epoxy \Ag\SiO2 when the (CB) , (G) ,and SiO2 as a fillers when this system electrical conductivity properties was studied . The gel time of the epoxy resin with hardener by temperature was studied . Infrared spectra were recorded for preparation polymers.

الخلاصة

تعتمد توصيلية البوليمرات على امتلائها بحبيبات الفضة في رزنات الايبوكسي السائلة مع ثنائي اثيل رباعي امين كعامل مصلب . تم اضافة مركب ثالث لزيادة التوصيلية الكهربائية لتكوين نظام ايبوكسي/ فضة لزيادة التوصيلية وكان المركب الثالث الكاربون الاسود او الكرافيت او ثاني اوكسيد السليكون حيث تم الحصول على الانظمة التالية (ايبوكسي/فضة/ الكاربون الاسود) , (ايبوكسي/فضة/ الكرافيت) , (ايبوكسي/فضة/ ثاني اوكسيد السليكون) . وتمت دراسة الخواص الكهربائية لهذه الانظمة . وكذلك تمت دراسة وقت التصلب للايبوكسي مع عامل التصلب مع درجة الحرارة . كما سجلت امتصاصات الاشعة تحت الحمراء للبوليمرات المحضرة .

Introduction

polymers are generally good electrical insulators because they contain very low concentration and low mobility of free charge carriers . Many efforts were carried out to prepare conductive polymers and using them in various application due to their excellent physical and chemical properties.

The art of making agood conducting composite is to use the minimum quantity of conductive fillers to achieve the required degree of electrical conductivity (σ) . So , the Composites based on metal powders usually correspond to high filler concentration , for example (80% w/w) for nickel powder to a chieve $\sigma = 1.2 \times 10^{-1}$ (S/cm) and (85% w/w) for silver powder to achieve $\sigma = 10^{4}$ (S/cm) [1] . This high concentration tends to destroy the desirable mechanical properties of the plastic , that left the composite to be stiff , brittle and cannot be tailored .

Carbon black and graphite are widely used to produce conducting plastics because they are compatible materials , mixing in , adhering well to the polymer matrix , do not change the overall density very much and they are cheap . Recently Carbon nanotubes [2-4] were used to achieve good conducting composites with only (1% w/w) filler Content [5] **.**

An isotropically conductive adhesive consists of metallic filler particles dispersed in a polymer resin. The matrix polymer provides a physical bond between two surfaces being glued together, whereas the metallic particles provide an isotropic electrical conductivity [6].

The matrix materials typically used in the electronics industry are epoxies. The metallic particles are usually flakes or powdered silver [7,8]. Silver offers
a high specific bulk conductivity and conductivity stability in combination with low chemical reactivity levels. The volume resistivity of the best silver-filled epoxy adhesives is 1×10^{-4} ohm-cm . However, silver obviously has the disadvantage of being expensive. In efforts to minimize the silver loading or even to avoid the use of pure silver, a number of lower cost conductive adhesives have appeared on the market

during the past two decades [9-11].

Epoxy/CB and epoxy/G electrically conductive compounds have been studied extensively with reported. For CB (carbon black) fillers [12 ,13] and for G (graphite) fillers [14,15], respectively. Conductive epoxy composites filled with CB or metallic particles have also been studied as positive temperature coefficient (PTC)materials[16]. In the present investigation, carbon blacks and carbon fibrils were considered as additives in epoxy/Ag adhesives, to obtain composites of higher or similar conductivity, but at lower silver contents. Also, an insulating SiO2 filler was used to modify the viscosity of the epoxy/Ag composites and three kinds of dispersants were used to promote the dispersion of the silver particles. The electrical conductivity behavior and microstructure of the epoxy/Ag composites cured at 100°C were compared with those of composites cured at room temperature. These composites are considered to have practical use in the conductive adhesives field [17].

Experimental Part

Chemicals and Instruments

Chemicals

-Epoxy polymer based on bisphenol- A resin (GY-257, Almor Fiberglass) and an aliphatic polyamine hardener, diethyltriamine (DETA) .The ratio of epoxy to hardener was kept constant at 90/10. Supplied by Aldrich Co.

-Silver powder Average prime particle size 0.05–0.10 **µ**m Supplied by Degussa Co.

-Carbon Black / Graphite Supplied by Degussa Co.

-The SiO2 powder average particle size of 3.5 µm Supplied by Degussa Co.

Instruments

-Conductivity measurements instrument:-

The conductivity measurements were carried at using conductivity bridge ; wyne kerr ; Auto balance precision bridge, type (B331 MKII); shown in Fig.(1) . An (AC) electrical used for conductivity measurement of frequency, (1597.55±0.5 HZ). Detectors, one of them for capacitor specific and the another for conductivity as well as variable capacitor for capacity balance in cell. At the start, the instrument was equilibrated using box resistance.The equilibrium instrument using the above mentioned resistance box. Instrument precision is(±0.01 %), for range (100-1000 ohm) [18].

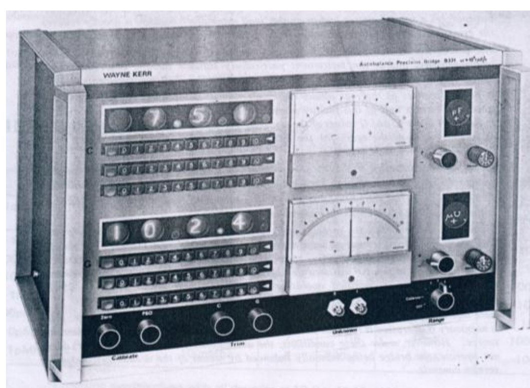

Fig.(1)Auto balance precision bridge, type (B331 MKII) instrument

-Stainless steel molds with different size were manufactured locally suitable for molding sheets with suitable thickness and dimensions.

Infrared spectra were recorded on Shimadzu FTIR-8300 spectrometer as potassium bromide disc.

Composite Preparation

1- Epoxy/Ag Composites

To prepare a concentrate, (0 , 5 ,10 ,15 ,20 , 25)% wt silver powder was dispersed in the epoxy resin first by hand mixing and then on a three-roll paint mill. The concentrate of this composition was blended with some additional amounts of epoxy resin to attain desired different silver concentrations, followed by the addition of the hardener, mixing and casting into molds. Type of molds were used: a disc mold (2 x 2 cm in diameter, 2 mm in thickness). Samples were cured at room temperature for 18–24 hours, followed by a high temperature curing procedure was performed at 100°C for 2h without post curing [19, 20].

2- Epoxy/(CB , G , SiO2) Composites

To prepare a concentrate, (0 – 10)% wt filler (CB , G , SiO2) powder was dispersed in the epoxy resin first by hand mixing and then on a three-roll paint mill. The concentrate of this composition was blended with some additional amounts of epoxy resin to attain desired different filler concentrations, followed by the addition of the hardener, mixing and casting into molds. Type of molds were used: a disc mold (2 x 2 cm in diameter, 2 mm in thickness). Samples were cured at room temperature for 18–24 hours, followed by a high temperature curing procedure was performed at 100°C for 2h without post curing [19, 20].

3-Three-Component Composites

For epoxy/Ag/CB composites, the epoxy resin was separately mixed with the (25% wt) silver powder and desired amounts of carbon black, then both mixtures were combined by hand mixing. For epoxy/Ag/G composites, G was added to the epoxy/Ag composite and mixed by hand. Epoxy/Ag/SiO2 composites were prepared by dispersing Ag powder and SiO2 powder in the epoxy resin and altogether mixed on the paint mill. The content of the third component (CB, G , or SiO2) is related to the epoxy resin. The curing procedure for the ternary component composites was the same as for the two-component ones. When dispersants were used, they were initially added to the (Epoxy/ Ag 25% wt) in an amount within the range of (0 – 10) wt%, based on the fillers. followed by the addition of the hardener, mixing and casting into molds. Type of molds were used: a disc mold (2 x 2 cm in diameter, 2 mm in thickness). Samples were cured at room temperature for 18–24 hours, followed by a high temperature curing procedure was performed at 100°C for 2h without post curing [19, 20].

Electrically measurements for the solid samples:

The conductivity measurements for the Three-Component Composites ,(2x2) cm and 2 mm thickness. The conductivity (G)(ohm) and capacity (C)(F/m) measured for the samples, for different temperature (27-100) ^{o}C .

RESULTS AND DISCUSSION

The electrical conductivity of polymer defined as the charge quantity throughout passing time unit in unit area , for conductor electrical field unit. The electrical conductivity of polymer(x) depends on found free ions which do not chemically connected with large molecular and this molecule do not involve in electrical charges transport process , therefore the polymers conductivity depends on interference founding in large degree for that low molecular weight for ions reference. When the chemical structure of polymer is the limited effect for ions movement , makes the conductivity of polymer in the glass state in the range $(10^{-13} - 10^{-19})$ $ohm^{-1}. cm^{-1}$, the conductivity value increase with temperature increase , equation (1 – 1) become :

$$X = A e^{-\triangle u/RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3\text{-}1)$$

A : is constant ($A \alpha 1/T$)

R : gas constant .

$\triangle U$: activation energy .

When the temperature is higher than glass transition temperature (Tg) , the ions movement will increased , resulted to higher proportion movement of polymer change length ends which lead to higher conductivity [21] . The electrical resistivity of the epoxy/Ag composites(disc samples) versus Ag content is shown in Fig. 2. It displays, for the epoxy/Ag composites, a usual percolation behavior. The epoxy/Ag composite containing 25%wt Ag is the conductivity ≈ 10^{-5} $ohm^{-1}.cm^{-1}$, for disc samples,. The difference seems to be due to the different thickness of the samples. In the former case, partial sedimentation of silver particles could occur
during the relatively long room-temperature curing time.

The amount of silver powder while maintaining a high conductivity level of the composite by combining silver powder with other conductive fillers. Carbon black, which is commonly used as a conductive filler in polymer matrices, was the first candidate. It was assumed that the addition of CB particles to Ag-containing composite may lead to the formation of a two-hierarchy morphology, where continuous CB chains bridge Ag particles, thus amount of the Ag concentration (25%wt)needed for conductivity is shown in Fig. 3.When the conductivity for the system (Epoxy/CB (10% wt)≈ 10^{-5} $ohm^{-1}.cm^{-1}$, Epoxy/G (10% wt)≈ 10^{-4} $ohm^{-1}.cm^{-1}$ and Epoxy/SiO2 (10% wt)≈ 10^{-2} $ohm^{-1}.cm^{-1}$) , all system compounds without Ag .
Shows that the electrical resistivity of the composites containing (10%wt) CB does
not practically change with the increase of the Ag content (25%wt). The resistivity's of the CB-containing composites are significantly higher than that of the composite without CB at around (25%wt) Ag [22] . However, the distribution of the Ag and CB particles in the composites containing both conductive fillers is quite Fig. 3. The resistivity of epoxy/CB composite (disc shape) versus CB content role of a third Component on Conductivity Behavior Polymer composites, while CB networks are no longer clearly seen, implying a possible mechanism of mutual disturbance of the two conductive networks. It seems that the CB presence hinders the good distribution of the Ag particles in the resin. The presence of Ag particles also disturbs the connectivity of the CB network. A reason for such undesired mutual effects is not well understood; however, it can be partially related to the build up of static electrical charges accumulating on the filler particles' surfaces during mixing, as reported for epoxy/Ag/CB composites [12, 13] the resistivity ≈ 10^{-2} ohm .cm is shown in Fig .4. , when the conductivity for CB = 10^{2} S/cm [23] .
Graphite (G) were also considered an interesting candidate for the epoxy/Ag system. The electrical resistivity of epoxy/G composites versus G content is shown in Fig. 3. The resistivity of the epoxy/G composite at 10 wt% G content is ≈ 10^{-4} ohm-cm.
The variation of the electrical resistivity of the epoxy/ Ag/G three-component composites . Fig. 3. The curve of the epoxy/Ag composite without G is also shown as a reference. The resistivity's of the epoxy/Ag composites at 25% Ag content are beyond the measurement limit; however, upon addition of 10% G, the resistivity's are higher, one order of magnitude lower than the epoxy/G composite at the same G content. Hence, the 10% wt G addition has significantly contributed to the conductivity of the composites within the 25%wt Ag .
Fig. 4. The resistivity's of epoxy/Ag /10% G composites versus G content.
Role of a third Component on Conductivity Behavior Polymer composites. At a higher Ag content, 25% wt Ag, the resistivity of the epoxy/Ag/10%wt G composite is ≈ 10^{-1} ohm .cm, four orders of magnitude lower than the corresponding composite without G, thus achieving a better bulk conductivity of the composites. A similar morphology was actually expected for the epoxy/ Ag/ CB system , when the conductivity for G = 10^{4} S/cm [23] .

The purpose of adding a filler, SiO2 fine powder, was to increase the viscosity of the epoxy/ Ag composite and thus to decrease the extent of sedimentation of silver particles during the curing process. In another approach the curing temperature is raised to reduce gel time and thus sedimentation. The success of this approach depends on whether the gel time reduction effect is more dominant than the viscosity reduction effect. As previously mentioned, sedimentation affects the bulk conductivity of the sample, when the system Epoxy/Ag/ SiO2 has the resistivity ≈ 10 ohm .cm . Shown in Fig . 4. we notice the system Epoxy/Ag/ SiO2 higher conductive from system

Epoxy/Ag/ G and last system higher conductive from system Epoxy/Ag/ CB, are show in Fig .4. [24]
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The gel time of the epoxy/hardener system is markedly reduced with temperature (Fig .5), 2 minutes for curing at 100°C and 3 hours at room temperature.

Gel Time of Epoxy/Hardener (3.6 gm Epoxy + 0.4 gm Hardener (DETA)) [25].

I.R Spectra shows (C-O) at (1150)cm^{-1} , (N-H) at (3200)cm^{-1} , (C=C) aromatic (1465) $cm^{-1}$and (720) cm^{-1} (C-H bending aromatic) and (C-H) at (2980)cm^{-1} for preparing polymers.

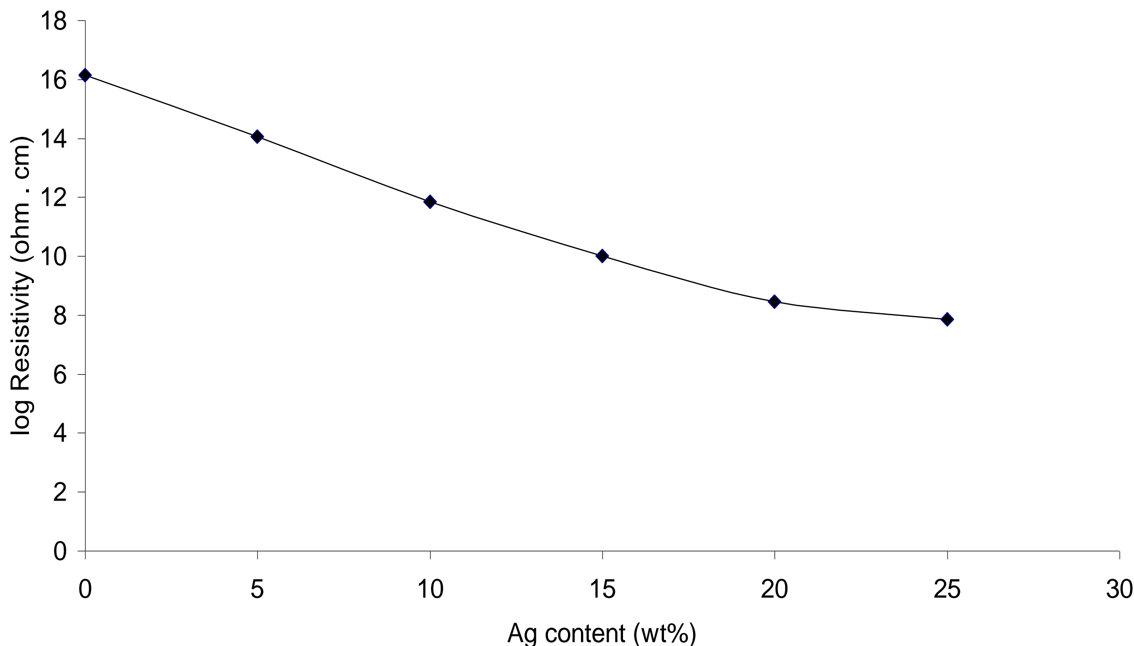

Fig.(1) . The Resistivity of Epoxy/Ag composities veries (Ag) content

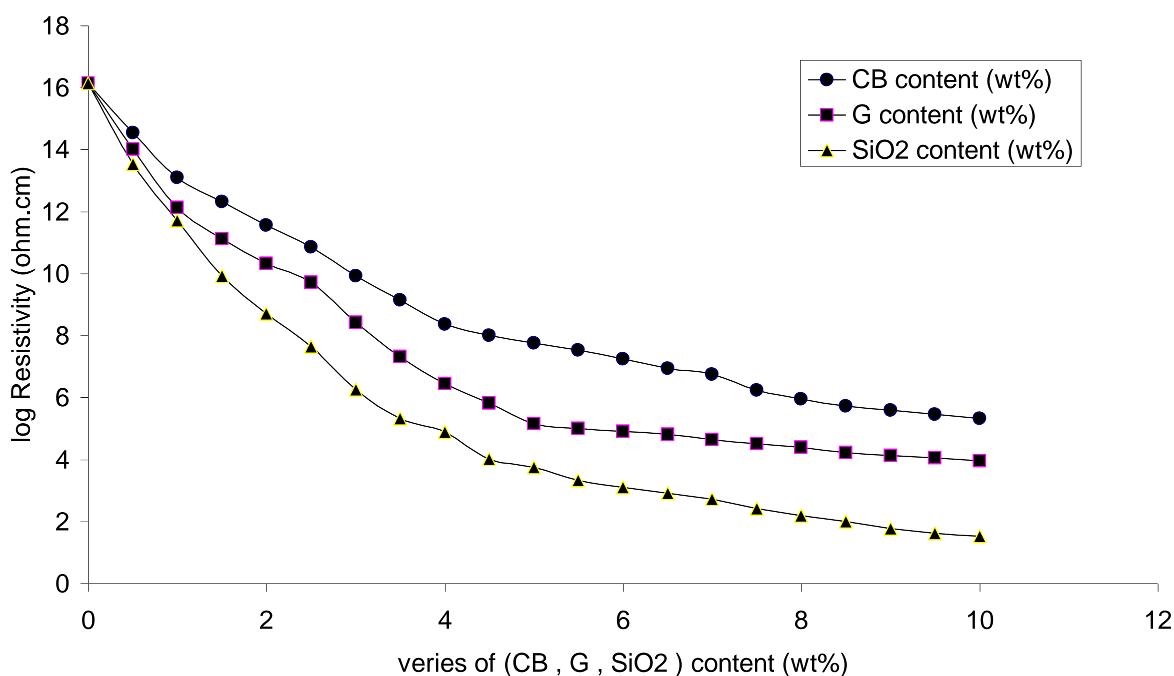

Fig.(2). The Resistivities of Epoxy with veries of (CB , G , SiO2) contents

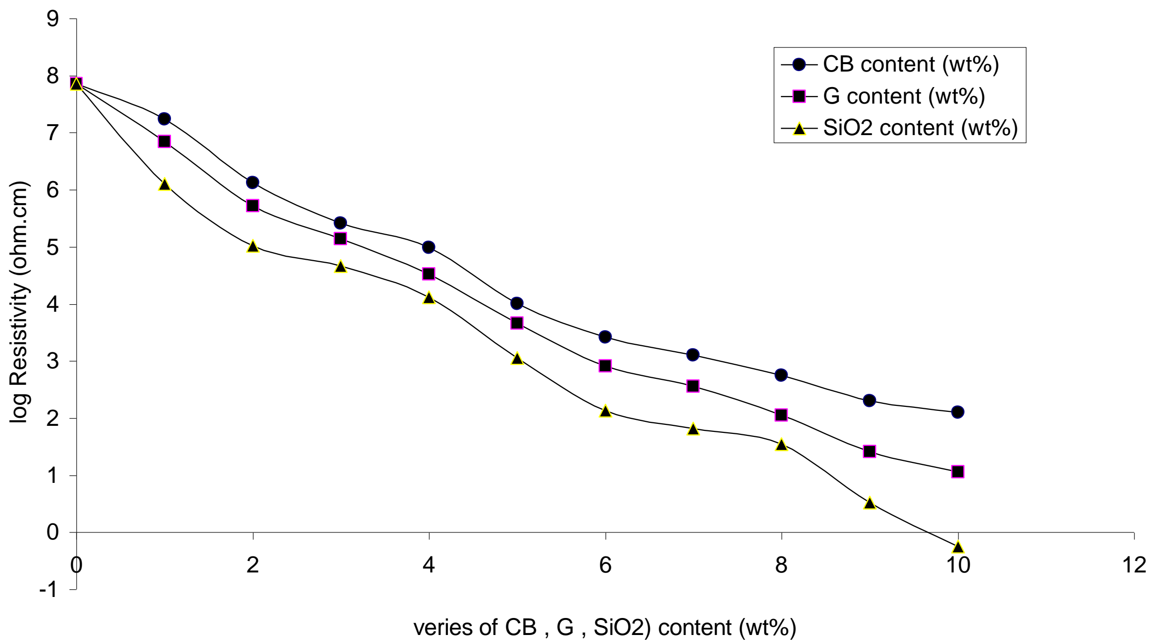

Fig .(3) . The Resistivities of Epoxy/Ag(25%wt) with veries of (CB , G , SiO2) content

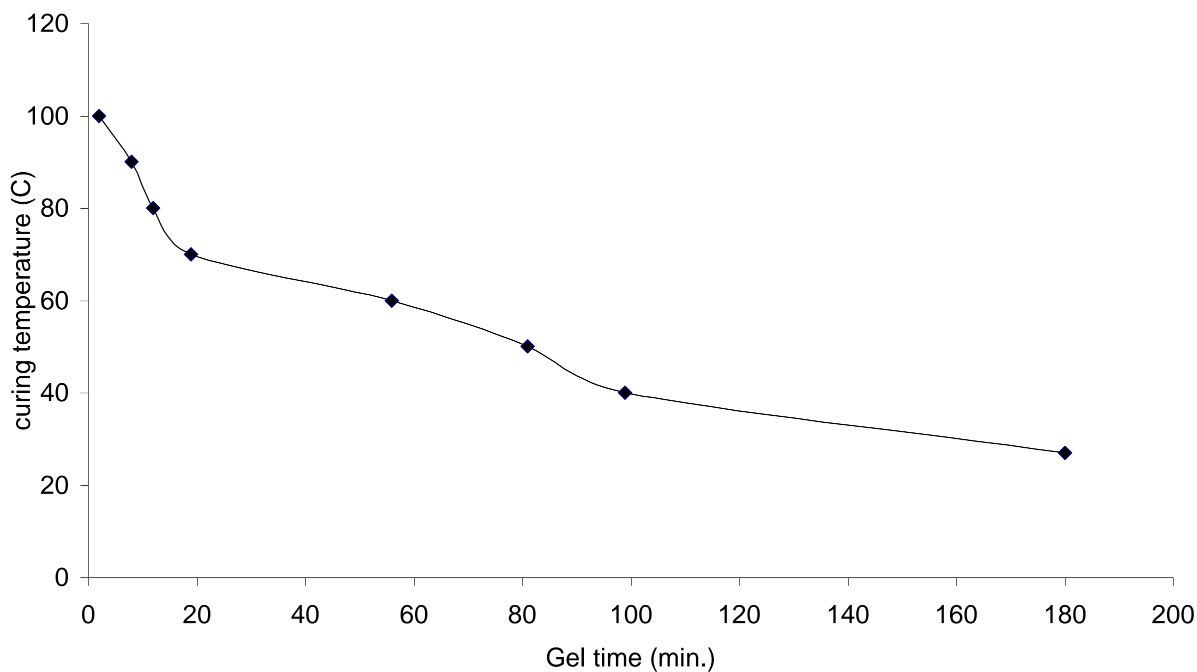

Fig .(4). The Gel time Epoxy/hardener (3.6 gm Epoxy + 0.4 gm hardener)

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