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Quarterly Report

Project: Thermoplastic Elastomers as LOVA Binders

Contract No.: N00014-85-K-0880

Period of Report: Jan. 1987 to April 1987

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Publications

"Simulation of Welding Flows, Part 2 - Stress Calculations Compared with Experimental Data", K.H. Wei, M.E. Nordberg, III and H.H. Winter, accepted for publication in Polymer Engineering and Science, 1987.

"A Simple Equation for the Steady Shear Viscosity of Filled Polymer Melts", T.S. Stephens and H.H. Winter, in preparation, 1987.

"Structure-Property Relationships in Thermoplastic Elastomers IV. Dynamic Mechanical Relaxations in Poly(dioxolane), Poly(butyltrioxocant) and Poly(propylene oxide) Polyurethanes", J.C.W. Chien and M.K. Rho, J. Appl. Polym. Sci., submitted 1987.

"Liquid Crystalline Compounds and Polymers from Promesogens", J.C.W. Chien, R. Zhou and C.P. Lillya, Macromolecules, submitted 1987.

"Cationic Polymerizations of 2-Substituted Dioxepanes", C.P. Lillya, Y.G. Chaun and J.C.W. Chien, Macromolecules, submitted 1987.

Technical Reports Issued

Number 19 "Acidolysis of Poly(4-methyl-1,3-dioxolane)".

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I. Synthesis

A. Liquid Crystalline TPE

1. Twin LCTPE from Promesogens

Alkyl-4(4'-alkoxybenzoyloxy)benzoates (with C₁-C₁₀ alkyl and alkoxy groups) are monotropic compounds which melt directly to isotropic liquids. Twin liquid crystalline compounds, TLCC, of alkoxybenzoyloxybenzoic acid have been synthesized. The TLCC with methoxy end groups and trioxyethylene spacer is weakly mesogenic; but replacement of the methoxy with an n-butoxy end group results in a smectic mesophase. With the decamethylene spacer, the TLCC with a methoxy end group shows a nematic mesophase whereas the compound with n-butoxy end groups exhibits both smectic and nematic mesophases. The latter has much higher ordered liquid crystalline states than the former. The polymeric TLCC with n-butoxy end groups and $\bar{M}_n = 650$ poly-THF and $\bar{M}_n = 725$ poly(propylene oxide) spacers display weak liquid crystalline order with only one mesophase transition. Decreasing the \bar{M}_n of the poly(propyleneoxide) spacer to 425 resulted in much stronger liquid crystalline order exhibiting both smectic and nematic phases. It is suggested the microphase separation due to dissimilar solubility parameters can be an important contributing factor toward mesophase formation.

The synthesis of liquid crystalline TPEs have been scaled up to provide samples for rheological studies the results for which are described below.

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B. Segmented LCTPE from Mesogens

A series of polymers have been prepared using azo- and azoxy-benzoyl chlorides with poly(THF) (MW 650 and 1000) and poly(propylene oxide) (MW 42). All six products are rubbery or semi-solid. None of these polymers exhibited any liquid crystalline phases by DSC or microscopy. One possible reason for no liquid crystal behavior could be that the mesogenic unit is too weak in the polyether medium to form the mesophase. One way to overcome this would be to increase the size of the mesogen, thus increasing its stability and hopefully its propensity to phase separate in polymer form.

To test this premise a series of aromatic alkyl benzoate derivatives of azo and azoxy benzoyl chloride were prepared. These derivatives were synthesized by adding dropwise a dioxane solution of the diacid chloride to a solution of p-hydroxy alkyl benzoate. The reaction mixture then precipitated into water, filtered, dried and recrystallized from chloroform ether solution. The derivatives were identified and characterized by spectroscopic methods. See Table I.

Table I
Model Mesogenic Four Ring Compounds

Diacid Chloride	p-Hydroxy Alkyl Benzoate	$T_K \rightarrow T_M \rightarrow T_i$
Azobenzoyl chloride	p-Hydroxy Hexyl Benzoate	160→305
Azoxybenzoyl chloride	p-Hydroxy Hexyl Benzoate	140→285d
Azobenzoyl chloride	p-Hydroxy Octy Benzoate	155→275
Azoxybenzoyl chloride	p-Hydroxy Octy Benzoate	133→290

Due to the promising results obtained with the model compounds a strategy was designed to synthesize thermal plastic elastomers with these four ring mesogenic units. The strategy required three steps; first the preparation of an end capped polyether diol with a protected phenolic benzoate, second deblocking the protecting group, and finally polymerizing with azo or azoxy benzoyl chloride.

Two protecting groups were explored for their utility in endcapping the polyether glycol, anizoyl chloride (methyl ether) and p-benzyl-oxy benzoyl chlorided p-benzyl ether). Removal of the protecting group is being studied.

C. Copolymerizations of Tetrahydrofuran and 2-butyl-1,3-dioxepane

Copolymerization of 2-butyl-1,3-dioxepane (A) with tetrahydrofuran (B) was studied with boron trifluoride etherate as initiators. The GC determination of unreacted monomers during

the reaction indicated that preferential polymerization of bu-DOP occurred. The values of the reactivity ratios, calculated by the Fineman-Ross, were $r_A = 5.1$, $r_B = 0.08$ and $r_A = 3.3$, $r_B = 0.15$ at -10°C and 0°C respectively. The product $r_A r_B$ was approximately equal to unity, which indicated a random copolymerization. The copolymers have been characterized by $^1\text{H-NMR}$ spectroscopy and DSC for the glass transition temperature.

D. LOVA TPE

The objective of this study was to synthesize the acid sensitive hard blocks comprised of trioxane/dioxolane copolymers with predicted T_m , and then couple this hard block with soft segment, i.e., poly-4-methyl-1,3-dioxolane by using diisocyanate.

1. The copolymers of trioxane and dioxolane (PDT) with different T_m ($40 - 140^\circ\text{C}$) were obtained by using $\text{BF}_3 \cdot \text{OEt}_2$ as the initiator. It was found that the PDT with low T_m (below 70°C) was soluble in CHCl_3 , CH_2Cl_2 , and dioxane.
2. The composition of the soluble PDT was determined by proton NMR spectrum and its average molecular weight (ca. 3000) was obtained via Karl-Fisher method (LiAlH_4 as the proton catcher).
3. The coupling reactions of PDT with poly-4-MeDOL have been performed by using MDI or IPDI. The copolymers obtained were solid with T_m range from $68 - 81^\circ\text{C}$. Its composition (from

proton NMR) showed that PDT was the major component of this copolymer.

II. Rheology

A. Twin LCTPE

The twin LCTPE of section IA1 above has been investigated by rheological techniques.

1. There are sharp drops of melt viscosity at temperatures of mesophase transition. Therefore rheological measurement is a more sensitive method for the detection of crystalline to mesophase and mesophase to isotropic transitions than DSC.
2. Surprisingly the twin LCTPE retained liquid crystalline rheological behaviors above the clearing temperature.
3. Flow induced structural changes are slow to relax. Apparently the promesogenic end groups can act as physical crosslinks above T_{MI} .

The last phenomenon is of general interest because it may be important for the processing of other semicrystalline thermoplastics.

B. Flow-Induced Structure in a Block Copolymer

The flow properties of heterogeneous, three-block copolymers have been studied for many years, but these studies have left out

consideration of the flow-induced structuring which also occurs when these materials are processed. These structures are interesting on their own as has been established by Folkes et al.,¹ and Hadziioannou et al.² who established the existence of 'single crystals' of these materials. The goal of the present work is to investigate the production of these highly-ordered materials and to also further understand the flow mechanism of thermoplastic elastomers.

The material used is a commercially available block copolymer, Kraton 1102 (Shell) which is a three-block copolymer of polystyrene-polybutadiene-polystyrene ($M_n = 81,300$, $x_{ps} = 0.26$).³ The samples are cast from toluene at room temperature and annealed at 150°C for 24 h. The samples are characterized in small-amplitude oscillatory shear (G' , G'' ; Rheometrics Dynamic Spectrometer, RDS). Large shear strains at constant stress are imposed in the Rheometrics Stress Rheometer (RSR), after which the samples are transferred back to the RDS for oscillatory measurements.

The effect of large shear strains ($\gamma < 5$; $T = 160^\circ\text{C}$) is to decrease the moduli, G' , G'' at all frequencies. At higher strains, the moduli increase at high ω , eventually recovering to the unstrained value. It is proposed that the initial lowering of the moduli is due to the disruption of the network which is formed when the material phase separates. The initial flow disrupts the segments from their preferential domains, and this weakens the network. As flow continues, the molecules become aligned in the flow field. Then, when the flow is turned off to

allow for the RDS measurement, the fast relaxation mechanisms are allowed, and the network can recover somewhat. This recovery is evidenced in the change in the high- ω end of the moduli curve. This portion of the curve is the result of the contributions of the short relaxation times.

This mechanism implies that if the sample is annealed long enough at 150°C, even the low- ω end of the graph will relax. We cannot check this easily since the samples cannot be annealed for long periods without degradation, but we can try the same experiment at a higher temperature. At 180°C the same trends are observed as were seen at 160°C, but at high strains the curve does indeed recover back to the initial, unstrained curve, at all ω 's. The material itself is different from the starting material, however, as is evidenced by small-angle x-ray scattering and whole-field birefringence results.

References

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2. Hadziioannou, G., A. Mathis and A. Skoulios, *Colloid Polym. Sci.*, 257, 136 (1979).
3. Morrison, F.A., G. LeBourvellec, H.H. Winter, *J. Appl. Polym. Sci.*, 33, 1585 (1987).

C. Rheology of Highly-filled Polymer Melts

Filled polymer melts exhibit very complicated rheological behavior. Various rheological material functions have been measured for many different filled polymers. In steady shear flow, filled polymers often exhibit an apparent yield stress

which dominates the viscosity at low shear rates, and shear thinning at high shear rates. The viscosity of filled polymer melts is accurately described by a new equation, the dual structure equation. The proposed equation is based upon a linear superposition of the effects of particle-particle interaction and shear thinning of the polymer melt. The equation fits data for TiO_2 -filled polyethylene.

The object of rheological characterization is to obtain material properties which are independent of the properties of the rheometer used to make the measurement. However in some cases the apparent viscosity of highly-filled polymer melts depends on the dimensions of the rheometer. At low apparent shear rates, the flow curve is independent of capillary radius, but at high rates the radius dependence is large. For a given wall shear stress, the apparent shear rate differs by a factor of ten.

Radius dependence of the flow curve can result from the existence of a boundary layer at the capillary wall. If it is assumed that the material within a distance of δ of the wall is unfilled polymer and the rest of the material is filled polymer, and that the viscosity of the filled and unfilled polymer is described by a power-law relation, then the flow curve can be calculated for the two values of radius used in the experiments.

The CaCO_3 particles are very irregular and have a broad size distribution. To eliminate the effect of particle shape and size distribution, a suspension of glass beads with a narrower particle size distribution has been prepared. The glass beads

were suspended in a PDMS of lower molecular weight than used with the CaCO_3 suspension. This lower molecular weight polymer is less elastic and less shear thinning. The steady shear viscosity of the glass bead-filled PDMS has been measured at high shear rates in the capillary rheometer. This simpler system does not exhibit a yield stress or thixotropy. However the flow curve of this suspension does show radius dependence in capillary rheometer measurements.

Low shear rate measurements were made in a parallel plate rheometer. The plate separation distance was v to determine the dependence of the apparent viscosity on this distance. It was expected that formation of a boundary layer near the plates or some arrangement of the particles between the plate may cause the apparent viscosity to depend on the distance between the plates. For plate separation distances of 0.3 mm to 2.0 mm, no such dependence was observed.

The viscosity of the glass bead-filled PDMS was measured at 30, 40 and 60°C. The viscosity curves could be shifted by time-temperature superposition. The viscosity was found to obey the Arrhenius equation. The complex viscosity of the glass bead-filled PDMS was measured in oscillatory shear and is compared with the steady shear measurements made in parallel plates and in capillaries for the temperatures 30°C, 40°C, and 60°C. The glass bead-filled PDMS is simpler and better characterizable than the CaCO_3 -filled PDMS. Both suspensions exhibit radius dependence in the capillary rheometer. This dependence is apparently due to a boundary layer at the capillary wall.

III. Mechanics

A. Introduction

The prediction of the mechanical behavior of particulate composites under thermal or mechanical stresses is of great importance in the effective design of solid propellants. The presence of voids due to the debonding of oxidizer particles results in significant changes in burn rate which cannot be tolerated. Prediction of the stress-strain and volumetric behavior of particulate composites over the range of strain where debonding occurs would allow design of proper processing techniques to avoid this problem. The method presented appears to have the potential to accurately predict the stress-strain and dilatation-strain curves for systems filled with spherical particles subjected to uniaxial tension and superimposed pressure.

B. Theory

An energy balance, similar to that used in crack-propagation problems, may be written for the debonding of a single particle. The balance is derived from the first law of thermodynamics, written over the small strain increment where debonding occurs. The change in internal energy of the sample may be regarded as the change in strain energy. The work expended in the process may be taken as the sum of the observable work and the internal work. The observable work is simply that done to change the sample dimensions, and is easily measured experimentally. The internal work is that necessary to debond the particle, creating

new surfaces in the sample. If the heat generated in this process is neglected, a simple surface energy coefficient can be used to compute the internal work. Using the laws of linear elasticity, the following equation can be derived:

$$2 G_c \delta A = 3 V_0 P_0 \delta e - \epsilon^2 V_0 \delta E \quad (1)$$

where dE = change in modulus after debonding

de = relative change in volume of sample

dA = free surface generated by debonding

Thus if a relationship between dE , de , and dA exists, the balance can be used to solve for the strain at which debonding occurs. Evaluation of the composite properties after debonding and repeated calculation of critical strains will produce the stress-strain curve over the entire range of debonding.

Several idealized models of the debonding process can be used to find the desired relation between dE , de , and dA . The simplest model, equating the surface area to twice the particle's surface area, and attributing the change in modulus to a decrease in the filler concentration, reduces the above equation to the following, when no superimposed pressure is considered:

$$\epsilon_c = \sqrt{\frac{12\gamma}{R \left(\frac{dE}{dc} \right)}} \quad (2)$$

The reciprocal square-root dependence has been previously noted in the literature.¹ The change in modulus with concentration must be evaluated using an effective modulus equation. The method of Farber and Farris,² which gives material constants for an elastic matrix filled with spherical particles over the entire concentration range, is used here. The stress-strain behavior predicted from this model is shown in Figure 1. The sharp bend in this curve contrasts with the rounded curves observed experimentally, given in Figure 2 for polyurethane filled with forty volume percent glass beads of 25 micron radius.³

An alternative simple model attributes the change in properties entirely to the formation of voids. The filler concentration is assumed constant. A relation between $d\epsilon$, dA , and dE is then straightforward if the entire volume change is assumed to be due to the voids. The equation which results from this model is a cubic equation for the critical strain. The stress-strain curve which results is shown in Figure 3. This model gives a much better approximation of dilatation observed, but overestimates the highest stress level reached. Other more complicated models, taking into account both the void formation and the loss in reinforcement due to the debonded particles, result in more complicated expressions for the critical strain. The simple models give good first approximations for this process and indicate that the approach is valid. Future work will concentrate on developing more realistic three-phase models which include both void formation and decreased reinforcement.

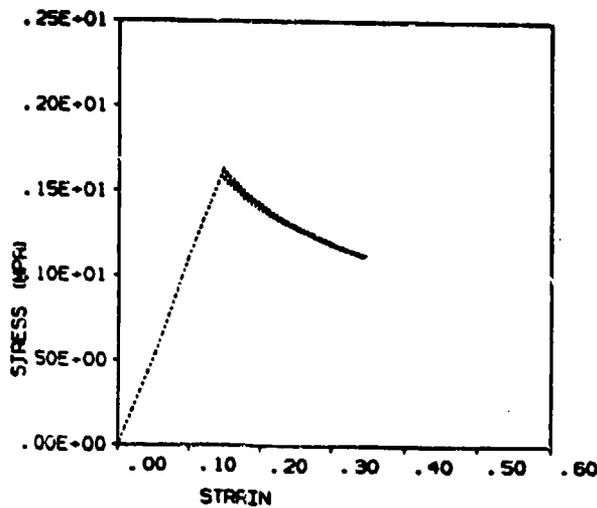


Figure 1 Stress vs. strain for Model 1 predictions: $C_0 = .40$, $R = 25 \mu\text{m}$

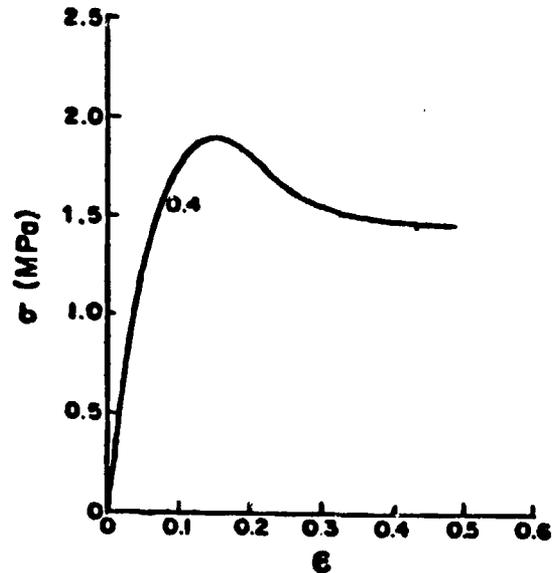


Figure 2 Stress vs strain for Reference 3.

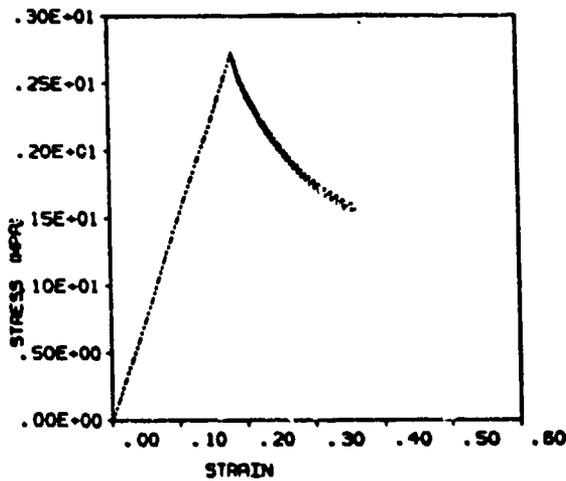


Figure 3 Stress vs. strain for Model 2 predictions: $C_0 = .40$, $R = 25 \mu\text{m}$

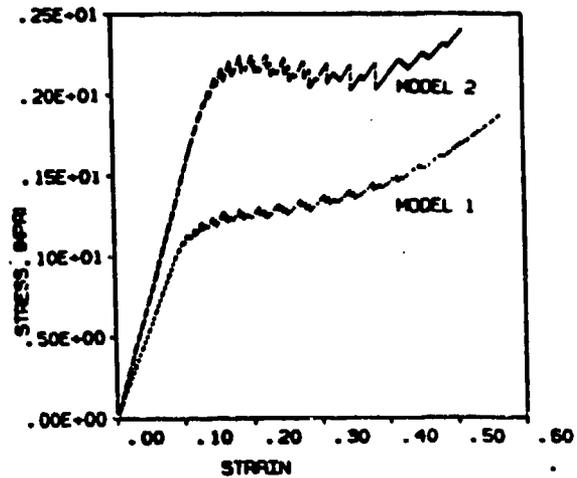


Figure 4 Stress vs. strain for Models 1 and 2 with log normal distribution

As indicated in the Equation 2, the inclusion size has an important effect on the critical strain for debonding. When a single particle size is considered, a sharp bend is observed in the stress-strain curve, as shown in Figures 1 and 3. If a normal or log-normal distribution of particle sizes is allowed, however, the resulting predicted curve is smoother and matches the experimental curve more closely. It appears from product

literature that a log-normal distribution is most likely to represent the ac distribution. The stress-strain curves predicted for each of the simple models described with allowance for a log-normal particle size distribution are shown in Figure 4. It appears that the experimental curve falls between the approximations of Models 1 and 2.

C. Results

The model presented appears to have good qualitative as well as quantitative agreement with the experimental data cited for the two approximations presented. It appears from the model predictions that the model correctly predicts the effect of particle size and size distribution. The effects of superimposed pressure, filler concentration and matrix properties show the correct trends in initial evaluation, and further work should confirm their effects to be correctly predicted by the model.

References

1. J. Leidner and R.R. Woodhams, J. Appl. Polym. Sci., 18, 1639 (1974).
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IV. Collaboration with Naval Surface Weapons Center

A. Synthesis

Liquid crystalline TPE has been synthesized from hexafluoropentanediol polyformal (FPF-1, H.G. Adolph, NSWC) and promesogens of section IA1 above. Larger samples will be

prepared for rheological studies.

B. Characterizations

TGA has been performed on a number of polyformals in the presence of toluene sulfonic acid and also in its absence. The thermal stabilities and acid sensitivities of these materials can be divided into three groups.

1. Poly(fluoroformals)

The TGA showed poly(fluoroformals) with β and γ fluorines having very high thermal stability. In fact they are more stable than polypropylene oxide. Acid has no effect whatsoever on their decompositions because of the inductive effect of making the acetal non-basic.

The TGA curve of FPF-3 showed lower thermal stability because the α fluorines can leave forming a cation of the polymer. This effect is more pronounced in the presence of acid. Nevertheless at elevated temperatures the polymer is slightly more stable in the presence of acid.

2. Polyformals with nitramine groups

Hexanitrodecapentandiol polyformals decompose very sharply at 230°C with and without acid. This is as expected from known thermal properties of RDX.

3. Polynitroformals

DINOL and DNHDF have very similar TGA curves aside from the

greater stability and more residues for the latter.

Apparently some carbonization of DNHDF occurs which can be completely suppressed by acid. Otherwise the effects of acid are small. In the case of the copolymers it can be said there is virtually no acid catalysis. Their decomposition behaviors are consistent with those of the component substances. We believe that the decomposition of the nitro groups limit their thermal stability.

V. Collaboration with Olin

Olin has undertaken the task of large scale preparation of our best LOVA candidate based on crystalline block of trioxane-dioxolane copolymer and soft block of 4-methyl-dioxolane. They have coupled the blocks with hexamethylene diisocyanate. The resulting TPE has melting transition at +85°C and glass transition at -45°C. It will be thoroughly characterized at UMass and Olin for thermal and acid catalyzed depolymerizability, mechanical property, melt rheology, continuous processability with inert and energetic fillers, nitramine sensitivity, etc.