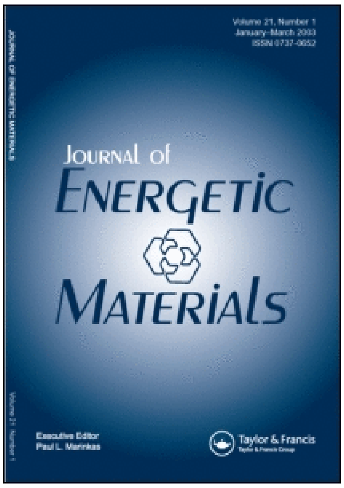

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Energetic Plasticizer Migration Studies

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Exudation of plasticizers through a polymeric matrix still remains a persistent problem in the life cycle of polymer-bonded explosives. This article is concerned with the migration of two energetic plasticizers, K10 and GLYN oligomer, which are commonly employed in combination with energetic polymers such as polyGLYN. Isothermal thermogravimetric analysis was used to determine migration rates, where it was found that the oligomer migrates slower than the K10 plasticized binder systems with a polyGLYN binder. Migration rates follow an inverse correlation with molecular weight, as is the case for the oligomer over the K10 plasticizer.

Keywords: energetic plasticizers, polymer bonded explosives, isothermal TGA, exudation

Introduction

Plasticizers are used in energetic binder systems for PBXs (polymer bonded explosives) to fulfill a number of requirements including lowering viscosity to improve processing, lowering the T_g (glass transition temperature point) to improve mechanical properties, altering the explosive performance of the PBX, and finally improving PBX safety [1]. Most plasticizers that find use in PBXs commonly display exudation from the binder matrix even under moderate storage conditions. This is highly undesirable since a degradation of mechanical and hazardous properties typically results. To counter exudation, it is well known that if the plasticizer closely resembles the PBX polymer,

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exudation can be lowered or reduced markedly. Use of the energetic polymer polyGLYN in our PBX formulations has necessitated the use of GLYN oligomer, a plasticized version of the parent polymer.[1] Furthermore, there is an inverse correlation between molecular weight and plasticizer mobility: the smaller the molecule, the quicker it will exude through a polymeric matrix. GLYN oligomer has a higher molecular weight than most energetic plasticizers including K10 and should reduce the migration of plasticizer through the polymer matrix. K10 is an energetic plasticizer comprising a 65/35 mixture of dinitroethylbenzene and trinitroethylbenzene (Figure 1).

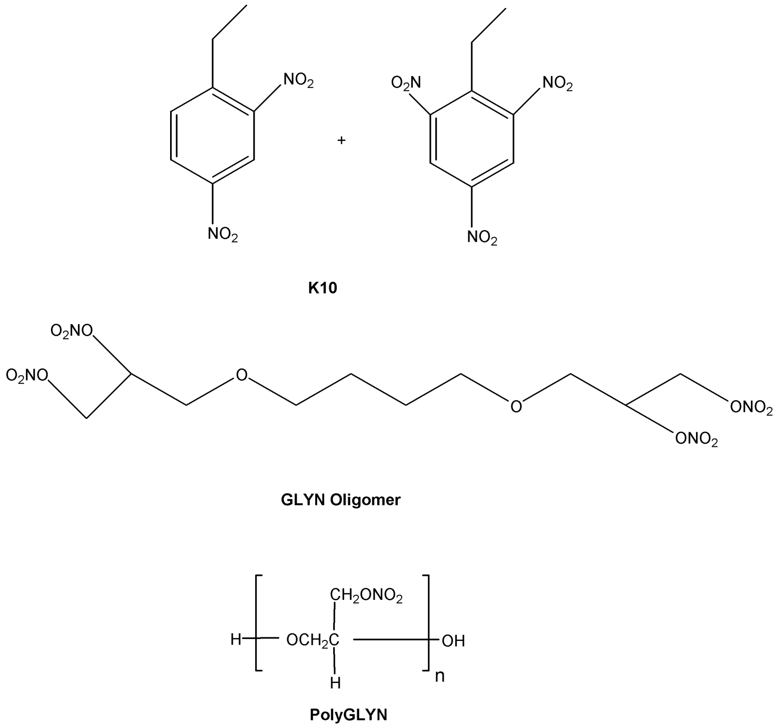

Figure 1. K10 and GLYN oligomer energetic plasticizers. Also shown is the energetic binder, PolyGLYN.

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[1] The GLYN oligomer was obtained through a UK collaborative arrangement with Defence Science Technology Laboratories (dstl).

To determine the diffusion coefficient, isothermal thermogravimetric analysis (TGA) is employed. This technique has been used to determine the migration rates of energetic materials like nitrocellulose propellants [2], employing TGA to measure discs of a known geometry and that were held at specific elevated temperatures for extended periods of time (typically 4000 mins). The method works by diffusion rates, whereby a loss in sample weight over an extended period equates to migration of plasticizer. The diffusion constant D is determined from weight loss and rate decay constants over a temperature range for both plasticizers.

Experimental

PolyGLYN was obtained from ICI Nobel Enterprises (Ardeer, Scotland) and degassed prior to use. The GLYN oligomer was shipped as a 5% solution of plasticizer in dichloromethane and solvent stripped off under vacuum to leave a clear, yellow fluid of GLYN oligomer. K10 was purchased from Royal Ordnance, UK, and used as received. Desmodur N100 was purchased from Bayer and used as received.

For diffusion studies, isothermal TGA analysis was carried out on a TA Instrument 2950 TGA at the Ian Wark Research Institute, University of South Australia. Weight ranges were calibrated over two points, one at ambient temperature and one at the Nickel Curie point (357.9 °C). A heating rate of 10 °C/min under a nitrogen atmosphere (50 mL/min) was used to obtain calibration points. Plasticized samples (containing 15% by weight plasticizer in a polyGLYN matrix with dibutyltin dilaurate catalyst and aliphatic polyisocyanate Desomdur N100 as cross-linking agent) were contained in 70 μL aluminium pans and degassed for several hours at 60 °C and then allowed to cure for 7 days. Samples were then held isothermally at 83.0, 99.0, 115.0, and 126.0 °C for 4000 mins at each temperature under a nitrogen atmosphere (50 mL/min). Sample weights were normalized to initial weight = 100.

Diffusion Theory

The evaporative rate of loss of a volatile liquid, according to diffusion theory, for a homogeneously distributed semi-infinite double-sided slab of thickness I, can be best approximated by [2,3]:

$$W_t - W_e = (W_c - W_e)\left(\frac{8}{\pi^2}\right)e^{\left[-Dt\left(\frac{\pi}{I}\right)^2\right]},$$

where

W_t = Volatile content of the solid at time t
W_c = Initial volatile content
W_e = Volatile content in equilibrium with environment
D = Diffusivity.

The above equation is derived directly from Fick's second law of diffusion and assumes that D is independent of time and concentration and that the solid's thickness is small relative to its diameter. Thus it can be shown to have first-order decay dependence with time. Cartwright has shown that this holds true for NG migration from cross-linked double-base propellants [2]. Resulting rate of weight loss for a first-order fit is given by

$$\ln\left[\frac{W_t - W_f}{W_i - W_f}\right] = -kt + c,$$

where

W_t = Sample weight at time t,
W_t = Sample weight at infinite time
W_i = Initial sample weight
k = First-order rate constant
t = Experiment time.

Diffusion values for migration rates of plasticizer through a polymer matrix [2] for a double-sided slab of thickness l can be obtained by

$$D = k\left(\frac{l}{\pi}\right)^2.$$

However, we are using single-sided theory, since the TGA pans allow for migration only from the top, while plasticizer migration from the bottom and sides of the alumina pan is prevented by interfacial bonding between binder and alumina pan. Thus, a single-sided thickness $(2l)$ equation is used:

$$D = k\left(\frac{2l}{\pi}\right)^2.$$

Results and Discussion

Plasticizer migration is a common problem for most PBX formulations and use of the GLYN oligomer plasticizer is expected to lower migration rates over K10 since it has a higher molecular weight (416 for GLYN oligomer; *cf.* 196 and 241 for dinitro- and trinitro-K10). To verify the inverse correlation of plasticizer migration rates with molecular weight, polyGLYN binder systems containing either 15% K10 or 15% GLYN oligomer plasticizer were analyzed by isothermal TGA at 83, 99, 115, and 126 °C under a nitrogen atmosphere. All runs show a decaying weight loss that approaches first-order decay behavior (a typical example is shown in Figure 2). Kinetic investigations into the decay rate constants, k, were determined via the slope of the linear regression plot and used to calculate diffusion coefficients D (Table 1 and Figure 3). In addition, glass transition points for the 15% plasticized systems were determined via DSC, the GLYN oligomer having a glass transition point of −23.3 °C and K10 possessing −19.5 °C (Figure 4).

The activation energy E_a or Arrhenius temperature dependence is obtained by a straight line from the plot of ln D versus 1/T (K)

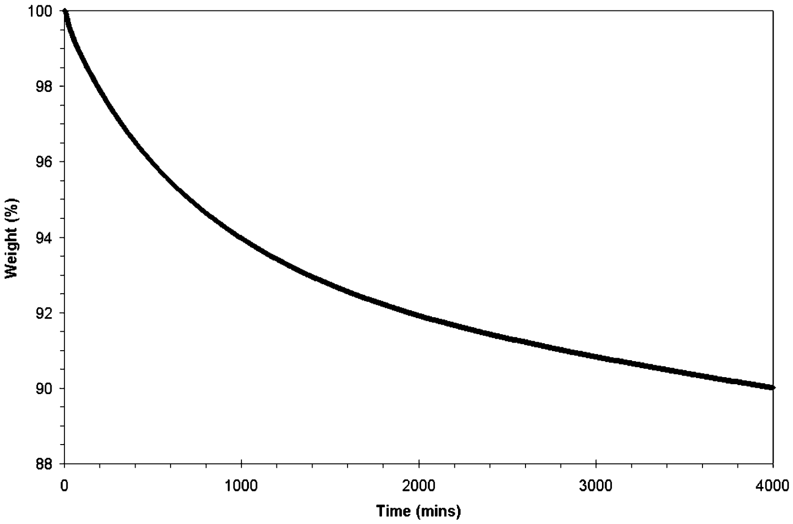

Figure 2. Isothermal TGA of 15% K10 in PolyGLYN binder at 115 °C.

Table 1
K10 and GLYN oligomer plasticized binder diffusion and rate constant values as determined by isothermal TGA

Plasticizer	Temperature (°C)	Time (min)	k (s^{-1})	D(cm^2s^{-1})
K10	83	4000	4.94×10^{-6}	5.60×10^{-8}
	99	4000	1.17×10^{-5}	1.32×10^{-7}
	115	4000	2.83×10^{-5}	3.21×10^{-7}
	126	4000	6.18×10^{-5}	7.01×10^{-7}
GLYN oligomer	83	4000	6.71×10^{-6}	7.62×10^{-8}
	99	4000	1.55×10^{-5}	1.76×10^{-7}
	115	4000	4.37×10^{-5}	4.96×10^{-7}
	126	4000	7.18×10^{-5}	8.15×10^{-7}

(Figure 3). For K10 plasticized binder systems, an activation energy of 68.5 kJ/mol was obtained, while the GLYN oligomer has an activation energy of 66.5 kJ/mol.

Isothermal TGA experiments show that transport properties for both systems obey Fick's diffusion laws and allow for a reliable estimate of plasticizer migration. However, several assumptions must be made, most importantly that plasticizer loss is the only source of

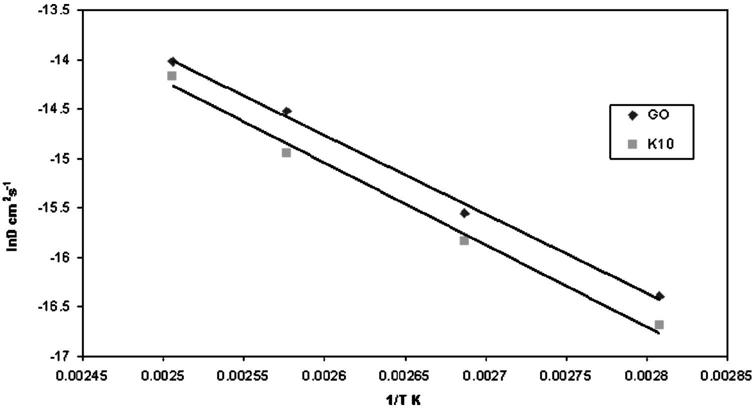

Figure 3. lnD vs. $1/T$ plot of 15% K10 and GLYN oligomer in PolyGLYN matrix. Line is least-squares best fit.

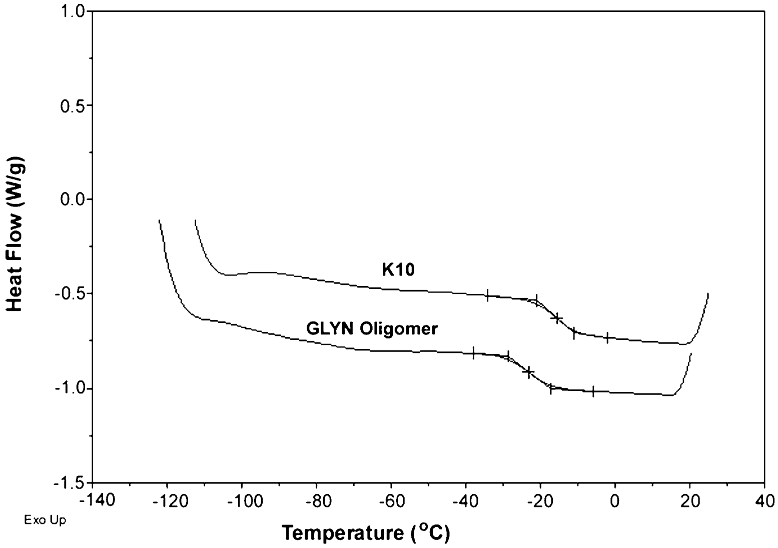

Figure 4. Glass transition temperatures for 15% K10 and GLYN oligomer in PolyGLYN matrix.

weight variation. The binder system however, is a lightly cross-linked, amorphous structure that can undergo several chemical reactions at higher temperatures, primarily degradation via thermolysis or chain cleavage. Thermolysis of similar nitrated polyethers like polyNIMMO have been shown to possess activation energies of 150–160 kJ/mol [4]. Furthermore, the lightly cross-linked network of polyGLYN should readily allow migration of small plasticizer molecules. Based on free-volume theory, elastomeric materials, such as the polyethers like polyGLYN, should have high free volumes over polymers with highly cross-linked densities.

Kinetic investigations into plasticizer mobility gives activation energies comparable to literature reports, including Cartwright's migration of NENA energetic plasticizers (15% methyl, ethyl, or butyl NENA in nitrocellulose binder) [2]. Activation energies for the NENA series ranged from 89 kJ/mol (BuNENA) to 120 kJ/mol (MeNENA), a result that also clearly demonstrates the molecular weight effect of the plasticizers on mobility through lightly cross-linked systems, with molecular weights for the NENA series ranging from 165, 179, and 207 for the methyl, ethyl, and butyl variants, respectively. Activation energy results obtained for the GLYN oligomer (nominal molecular weight of 418) are lower than those of the MeNENA and EtNENA activation energy values.

Further research conducted on the thermal decomposition of polyGLYN at 110 and 125 °C also follow first-order rate decay kinetics with an activation energy of 125 kJ/mol [5]. Results for energetic binders nitrocellulose (NC) and polyvinylnitrate (PVN), obtained using pyrolysis-FT-IR, give activation energies of 138 kJ/mol for NC and 133 kJ/mol for PVN [6].

Conclusions

Isothermal TGA experiments allow for a reliable estimate of plasticizer transport properties to migrate through a cross-linked polymer. Examination of the migration rates of both K10 and GLYN oligomer by isothermal TGA show that the GLYN oligomer has a slower migration rate compared to K10. Migration rates follow an inverse correlation with molecular weight, and this has been shown to be the case for the oligomer over the K10 plasticizer, which also compares well to other energetic plasticizers such as MeNENA and EtNENA.

Acknowledgments

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