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Research paper

Synthesis and Characterization of New Energetic Plasticizers: Benzoyl-terminated Poly(epichlorohydrin) Modified by Phenylhydrazine and its Derivatives

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Abstract: Nitrobenzoyl-terminated poly(epichlorohydrin) (NB-PECH) was synthesized through the reaction of poly(epichlorohydrin) (PECH) with 3-nitrobenzoyl chloride. The NB-PECH was then modified by reaction with phenylhydrazine, 4-nitrophenylhydrazine and 2,4-dinitrophenylhydrazine, and these derivatives were evaluated as plasticizers. Poly(epichlorohydrin), poly(epichlorohydrin) with terminal 3-nitrobenzoyl groups (NB-PECH), terminal nitrobenzoyl poly(epichlorohydrin-phenylhydrazine) (NB-PECH-PH), terminal nitrobenzoyl poly(epichlorohydrin-4-nitrophenylhydrazine) (NB-PECH-4-NPH) and terminal nitrobenzoyl poly(epichlorohydrin-2,4-dinitrophenylhydrazine) (NB-PECH-2,4-DNPH) were examined by Ultraviolet-Visible spectroscopy (UV-VIS), Fourier Transform Infrared spectroscopy (FT-IR), Proton Nuclear Magnetic Resonance (^{1}H NMR) spectrometry, elemental analysis of carbon, hydrogen and nitrogen (CHN) an Thermal Analysis methods: Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). In the TGA examination, the highest thermal stability was exhibited by NB-PECH. The glass transition temperature for the potential plasticizers

was determined from their DSC curves. The DSC tests indicated that the highest energy of the plasticizers was exhibited by NB-PECH-2,4-DNPH containing two nitro groups. In addition, by comparing the thermograms of the samples heated with poly(tetrahydrofuran) the energy content of the NB-PECH-PH, NB-PECH-4-NPH and NB-PECH-2,4-DNPH plasticizers was clearly demonstrated.

Keywords: poly(epichlorohydrin), PECH, terminal nitrobenzoyl poly(epichlorohydrin-phenylhydrazine), terminal nitrobenzoyl poly(epichlorohydrin-4-nitrophenylhydrazine), terminal nitrobenzoyl poly(epichlorohydrin-2,4-dinitrophenylhydrazine), synthesis, properties

1 Introduction

The demand for powerful propellants and explosives has prompted considerable developments in their energetic and mechanical properties. The results have indicated that improvements in propellants and explosives can be achieved by using energetic ingredients, such as binders, plasticizers, *etc.* [1-4]. The main objective for developing energetic plasticizers and binders is to improve the properties of a propellant or explosive, such as thermal stability, glass transition temperature, oxygen balance of a formulation, energy content, burning behaviour and mechanical properties [5-9]. Plasticizers are important additives in the polymer industry [10, 11]. Plasticizers are usually liquid organic compounds, which improve the mechanical properties of the polymer [5, 12].When added to binders, they impart optimum viscosity and therefore aid in improving a propellant. Furthermore, the molecular structure of the plasticizer considerably affects the mechanical properties of a propellant [1]. The molecular weight of a plasticizer can range from 200 to 2000. Plasticizers with a low molecular weight tend to be volatile, while high molecular weight plasticizers are viscous. Consequently, the optimal molecular weight of plasticizers is from 400 to 1000 [12, 13]. The small plasticizer molecules will migrate faster from the matrix, so there is an inverse correlation between molecular weight and plasticizer mobility [14].

Plasticizers are placed between the polymer chains and thus reduce chain-chain interactions. This reduction leads to a softening of the polymeric composition. Hence, this process decreases the glass transition temperature (T_g) of the propellant [5]. Plasticizers used in propellants can be inert (non-energetic) or energetic [12]. Inert plasticizers are high molecular weight esters that improve the mechanical properties and reduce the sensitivity

of the propellant, but these plasticizers reduce the energy level and burn rate of the propellant [12, 15]. Triacetin (glycerol triacetate), dioctyl phthalate (DOP), dioctyl adipate (DOA), diethyl phthalate (DEP) and dibutyl phthalate (DBP) are used as inert plasticizers [12, 16]. Energetic plasticizers are defined as organic molecules having energetic groups such as azido, nitro, nitrate, fluoronitro and fluoroamino, with positive heats of explosion [5, 12, 17-19]. These groups contain the bonds N–N, N–O and N–F. Using an energetic plasticizer instead of an inert plasticizer is one of the ways to improve the energy level of a propellant [12, 20, 21]. An energetic plasticizer has a low glass transition temperature (T_g), high oxygen balance, low viscosity, lower ability to migrate, positive heat of combustion (H_{comb}), negative heat of formation (ΔH_f), low impact sensitivity and should be thermally stable [12, 22, 23].

In the present study, we report the synthesis and characterization of some new energetic plasticizers, which may be useful for propellants and explosives. Energetic plasticizers were synthesized through the reaction between 3-nitrobenzoyl chloride (NB) and poly(epichlorohydrin) (PECH), then the nitrobenzoyl-terminated PECH was modified by reaction with phenylhydrazine or its derivatives, such as 4-nitrophenylhydrazine and 2,4-dinitrophenylhydrazine.

2 Materials and Methods

N,*N*-Dimethylformamide (DMF) and *N*,*N*-dimethylacetamide (DMAc) were purchased from Sigma-Aldrich. 3-Nitrobenzoylchloride, phenylhydrazine, 4-nitrophenylhydrazine, 2,4-dinitrophenylhydrazine, toluene di-isocyanate (TDI), tetrahydrofuran (THF) and dichloromethane were obtained from Merck Company. All solvents and other chemicals were used as received without any purification. The poly(epichlorohydrin) ($\bar{M}_n$ = 664 with polydispersity index 1.260) used for this study was synthesized and characterized in the laboratory using a reported method [24].

2.1 Instruments and measurement

Elemental analysis was carried out with an elemental analyzer (Leco CHNS-932). The FT-IR spectra of the synthesized compounds were scanned as KBr pellets on a Jasco-680 FT-IR spectrophotometer. NMR spectra were recorded by using a ^{1}H NMR spectrometer (Bruker Avance 500 spectrometer) in DMSO-d_6 as solvent. The number average molecular weight (M_n) and polydispersity index were determined by gel permeation chromatography (KNAUER smartline).

Thermogravimetric analysis (TGA) of the polymers was performed under an argon atmosphere using a Perkin Elmer thermogravimetric analyzer, heated from room temperature to 600 °C at 10 °C·min^{-1}. Differential scanning calorimetry (DSC) thermograms were recorded in two temperature ranges: –80 to 20 and 200 to 500 °C at 10 °C·min^{-1} (Perkin Elmer). The ultraviolet-visible (UV-vis) spectra of the polymers were measured on a JASCO V-750 UV/Vis/NIR spectrometer in the wavelength range 200-800 nm.

3 Experimental

3.1 Synthesis of 3-nitrobenzoyl-terminated poly(epichlorohydrin) (NB-PECH)

Poly(epichlorohydrin) (18.90 g, 0.0284 mol) was dissolved in THF (100 mL), and DMF (5 mL) was added to the polymer solution. 3-Nitrobenzoyl chloride (13.32 g, 0.0670 mol) was added slowly to the solution and then refluxed for 24 h. The reaction mixture was transferred to a separating funnel and dichloromethane (200 mL) was added. In order to remove all of the unreacted 3-nitrobenzoyl chloride and THF, the organic layer was washed several times with distilled water. Finally, the dichloromethane was removed by vacuum distillation.

3.2 Synthesis of 3-nitrobenzoyl-terminated poly(epichlorohydrin) containing phenyl hydrazine derivatives

3-Nitrobenzoyl-terminated poly(epichlorohydrin) was dissolved in DMAc with magnetic stirring for 10 min at room temperature. A solution of phenylhydrazine or its nitro-derivative, 4-nitrophenylhydrazine or 2,4-dinitrophenylhydrazine, in DMAc was then added slowly to the stirred solution of NB-PECH in DMAc. The reaction mixture was stirred for 24 h at 95 °C. After completion of the reaction, the solution was diluted with dichloromethane (twice the volume of DMAc) and the solution was then washed with distilled water. Finally, the polymer was extracted by dichloromethane, and the dichloromethane was removed by vacuum distillation. The reaction conditions are listed in Table 1.

Table 1. Reaction conditions

Polymeric product	Amount of NB-PECH [g]	Amount of phenylhydrazine or its derivative		Reaction temperature [°C]	Reaction time [h]
		[g]	[mol]		
NB-PECH-PH	20*	30	0.277	95	24
NB-PECH-4-NPH		33	0.215		
NB-PECH-2,4-DNPH		43	0.217		

* 20 g of NB-PECH = 0.02 mol

4 Results and Discussion

4.1 Synthesis and characterization of the plasticizers

The molecular weight of the PECH used was determined by gel permeation chromatography (GPC) [24]; the GPC curve is shown in Figure 1. The number average molecular weight (M_n) was found to be 664 with a polydispersity index of 1.260.

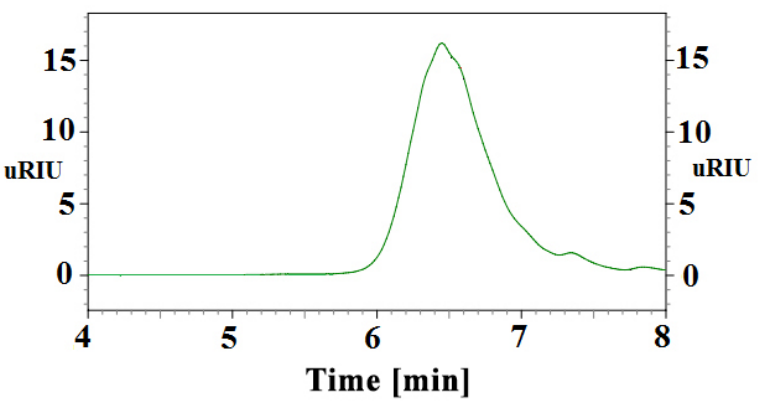
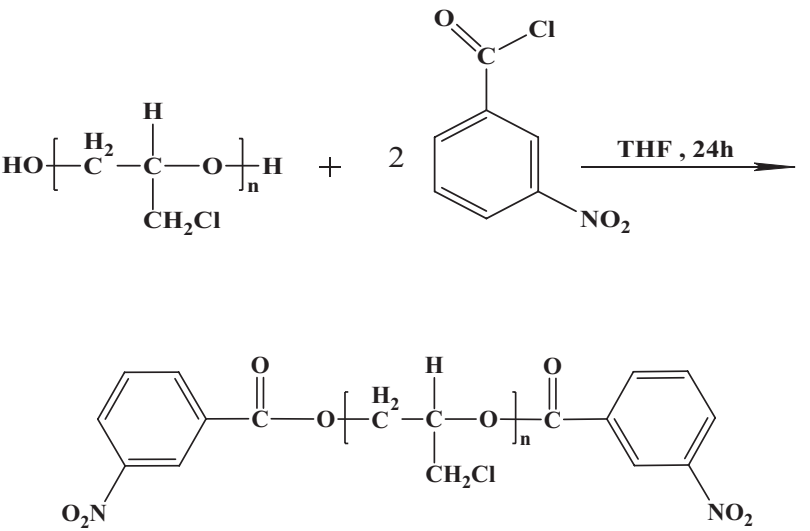
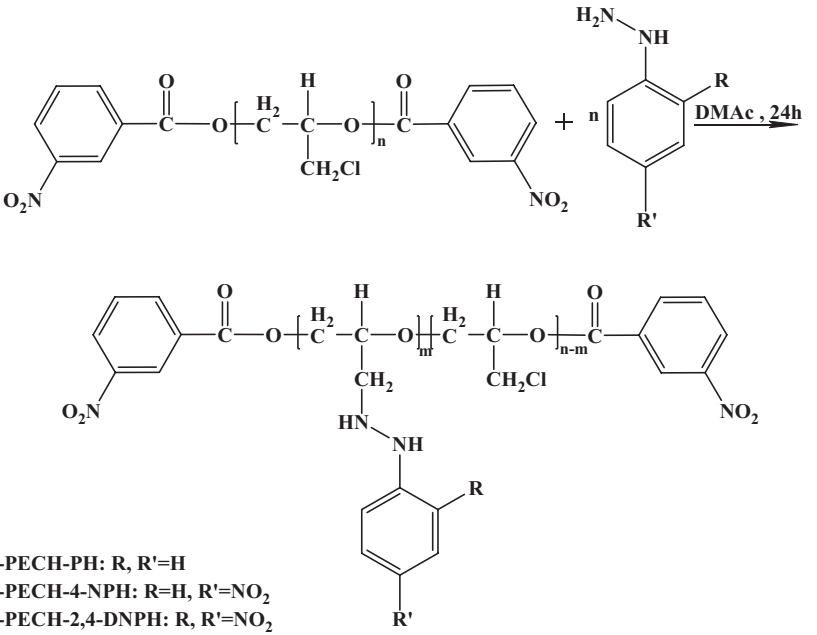


Figure 1. GPC analysis of PECH

NB-PECH was synthesized through the reaction of PECH with 3-nitrobenzoyl chloride in THF (shown in Scheme 1). Scheme 2 shows the chemical modification of 3-nitrobenzoyl-terminated poly(epichlorohydrin) with phenylhydrazine, 4-nitrophenylhydrazine and 2,4-dinitrophenylhydrazine, in order to study the effects of $–NO_2$ groups on energetic plasticizer performance.



Scheme 1. Synthesis of NB-PECH



Scheme 2. NB-PECH modified by reaction with phenylhydrazine and its derivatives

In order to gain an insight into the structures of the polymers, the FT-IR spectra of PECH and the synthesized polymers were measured and are shown in Figure 2. The FT-IR spectrum of PECH showed peaks at about 3434 and 2876 cm^{-1}, which can be assigned to the O–H stretching band and C–H stretching band, respectively. Characteristic peaks at about 1430, 1121 and 746 cm^{-1} showed the deformation of C–H, C–O stretching band and C–Cl stretching band, respectively [25]. The FT-IR spectrum of NB-PECH exhibited peaks at about 3432, 2872, 1730, 1137 and 720 cm^{-1}, which are due to the O–H stretching band, C–H stretching band, carbonyl (C=O), C–O stretching band and C–Cl stretching band. The peaks at 1536 and 1352 cm^{-1} represent the asymmetric and symmetric stretching vibrations of the $–NO_2$ group. In the FT-IR spectrum of NB-PECH-PH, the peaks at about 2930, 1730, 1608 and 1122 cm^{-1} represent the C–H stretching band, carbonyl (C=O), C=C stretching band and C–O stretching band, respectively. Furthermore, the peaks at 1532 and 1350 cm^{-1} are characteristic of the asymmetric and symmetric stretching vibrations of the $–NO_2$ group [26]. The FT-IR spectrum of NB-PECH-4-NPH is shown in Figure 2. As illustrated, the peaks at 2932, 1700, 1600 and 1110 cm^{-1} represent absorptions of the C–H stretching band, carbonyl (C=O), C=C stretching band and C–O stretching band, respectively. The absorption peaks at 1522 and 1345 cm^{-1} correspond to the $–NO_2$ asymmetric and symmetric stretching vibrations [27]. The spectrum of NB-PECH-2,4-DNPH exhibited peaks at about 2936, 1731, 1609 and 1070 cm^{-1}, which can be assigned to the C–H stretching band, carbonyl (C=O), C=C stretching band and C–O stretching band, respectively. In addition, peaks at 1538 and 1348 cm^{-1} appeared which contribute to the asymmetric and symmetric stretching vibrations of the $–NO_2$ groups. It may be stated that the absence of a C–Cl stretching band and the presence of a $–NO_2$ stretching band clearly confirm the substitution of chlorine atoms with phenylhydrazine and its derivatives [27].

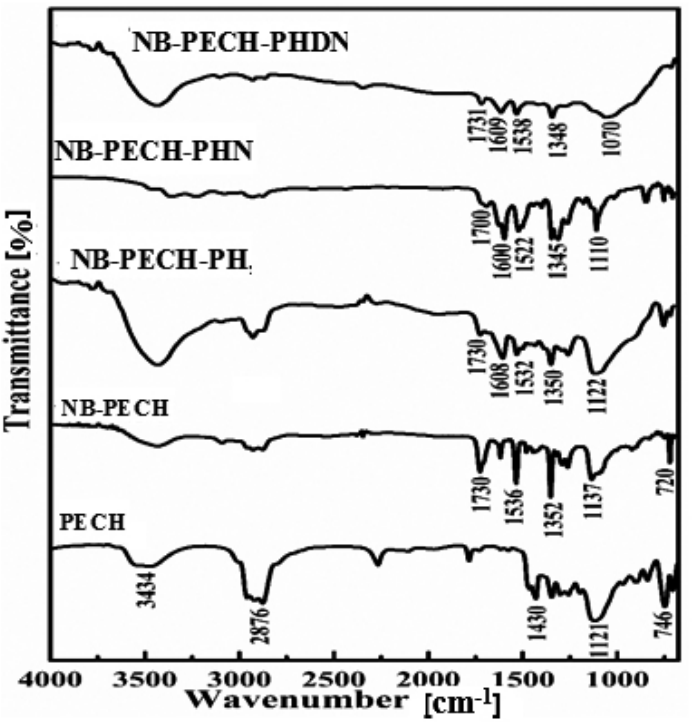


Figure 2. FT-IR spectra of PECH, NB-PECH, NB-PECH-PH, NB-PECH-4-NPH and NB-PECH-2,4-DNPH

The amounts of carbon (C%), hydrogen (H%) and nitrogen (N%) in PECH, NB-PECH, NB-PECH-PH, NB-PECH-4-NPH and NB-PECH-2,4-DNPH are listed in Table 2. The results indicate that the substitutions were successfully carried out.

Table 2. Carbon (C), hydrogen (H) and nitrogen (N) content when reaction time was 24 h

Polymer	C [wt.%]		H [wt.%]		N [wt.%]		m*	n-m**
	Calc.	Found	Calc.	Found	Calc.	Found	[%]	[%]
NB-PECH	43.56	44.01	4.46	4.99	2.90	2.80	96.55	3.45
NB-PECH-PH	63.98	53.43	6.09	5.99	15.51	9.22	59.44	40.56
NB-PECH-4-NPH	52.35	52.65	4.92	5.36	18.24	11.94	65.46	34.54
NB-PECH-2,4-DNPH	44.29	45.18	4.13	4.87	20.13	14.81	73.57	26.43

* Complete substitution by phenylhydrazine or its derivatives.
** Incomplete substitution.

Data for the ultraviolet-visible (UV-VIS) absorption spectra of NB-PECH, NB-PECH-PH, NB-PECH-4-NPH and NB-PECH-2,4-DNPH in the 200-600 nm range are presented in Table 3. The NB-PECH spectrum exhibited a peak at about 255 nm. The NB-PECH-PH UV-VIS spectrum exhibited absorption peaks at 245 and 278 nm, whereas NB-PECH did not show an absorption peak at 278 nm. The UV spectrum of NB-PECH-4-NPH exhibited absorption peaks at around 252 and 348 nm, while NB-PECH-2,4-DNPH exhibited absorption peaks at 246 and 329 nm. The absorption peaks at 348 and 329 nm could be due to 4-nitrophenylhydrazine; they were not observed in the UV-VIS spectrum of NB-PECH. Thus, phenylhydrazine and its derivatives successfully replaced the NB-PECH-chlorine functionality.

Table 3. The maximum absorption peaks of the polymers

Polymer	Maximum absorption peaks [nm]
NB-PECH	225
NB-PECH-PH	245, 278
NB-PECH-4-NPH	252, 348
NB-PECH-2,4-DNPH	246, 329

The ^{1}H-NMR spectrum of PECH (Figure 3) exhibited signals at [28]:

– 4.3 ppm for $–OCH_2$ protons,
– 3.6 ppm for $–ClCH_2$ protons,
– 3.4 ppm for –OCH protons, and
– 2.5 ppm for –OH protons.

The ^{1}H NMR spectrum of NB-PECH is shown in Figure 4. In this case, signals at 7.5 to 8.5 ppm are due to protons of the aromatic segment of the molecule, whereas the pre-polymer (PECH) does not have any aromatic protons. Furthermore, the ^{1}H NMR spectrum of NB-PECH (Figure 4) shows signals at:

– 3.2-3.6 ppm for $–OCH_2$ protons,
– 3-4.5 ppm for CH_2Cl protons, and
– 1.7 ppm for CH_2 protons.

The ^{1}H NMR data for NB-PECH confirmed the complete reaction of PECH and 3-nitrobenzoyl chloride.

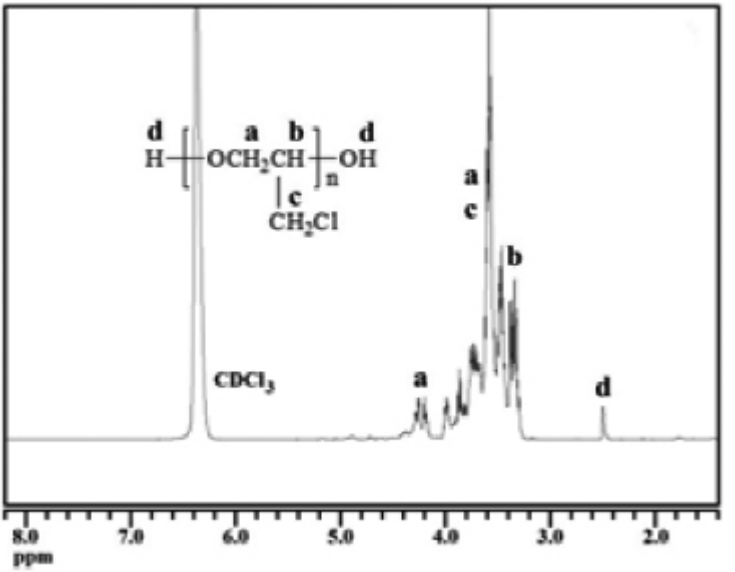


Figure 3. ^{1}H NMR spectrum of PECH

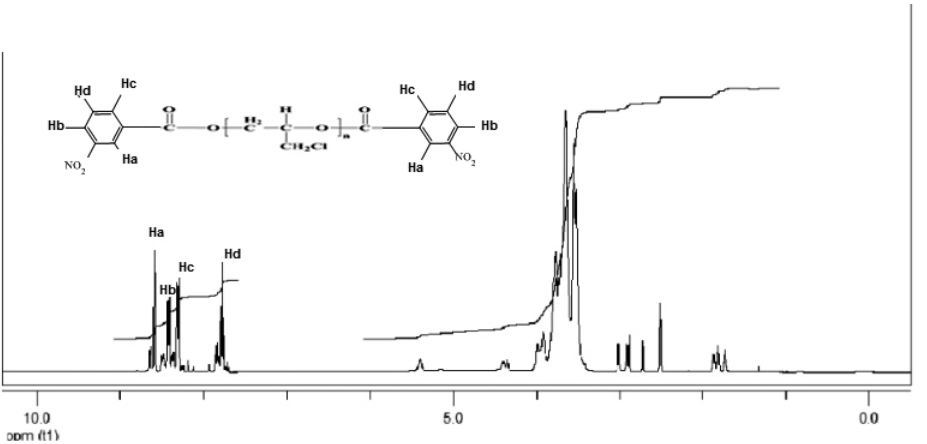


Figure 4. ^{1}H NMR spectrum of NB-PECH

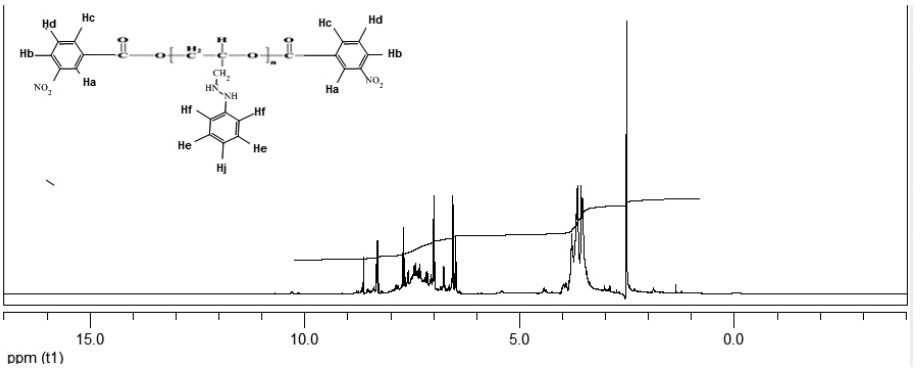


Figure 5. ^{1}H NMR spectrum of NB-PECH-PH

4.2 Thermal properties of the plasticizers

Thermogravimetric analysis is one of the commonly used techniques for investigating the thermal behaviour of polymers. The TGA curves of PECH, NB-PECH, NB-PECH-PH, NB-PECH-4-NPH and NB-PECH-2,4-DNPH are shown in Figure 6. The TGA curve of PECH shows a reduction in weight at 280-380 °C, where the maximum degradation was at about 335 °C. This degradation peak corresponds to the cleavage of the ether bond in the polymer. The TGA thermogram of NB-PECH shows weight loss in the range 175-355 °C. The maximum decomposition temperatures were observed at 276 and 327 °C, which correspond to the destruction of the nitro groups and the polymer skeleton, respectively. The TGA thermogram of NB-PECH-PH shows distinct regions of weight loss. The first region was between 105 and 195 °C, due to phenylhydrazine degradation and production of N_2 gas. The second region was between 200 and 325 °C, with maximum degradation at 290 °C, which corresponds to destruction of the nitro group. The third region was between 325 and 430 °C and was due to the cleavage of the ether bond in the polymer backbone. The TGA scan of NB-PECH-4-NPH shows weight loss in three stages. The first decomposition occurred between 100 and 205 °C, the second in the range 210-320 °C, and the third decomposition occurred between 320 and 420 °C. These stages are due to nitrophenylhydrazine degradation and production of N_2 gas, destruction of the nitro groups and polymer skeleton, respectively. The TGA curve of NB-PECH-2,4-DNPH, exhibited weight loss at 100-345 °C, with maximum degradations at 155, 249 and 303 °C. These weight losses are due to the dinitrophenylhydrazine degradation, destruction of the nitro groups and polymer backbone, respectively. Also, the residues from the 3-nitrobenzoyl-terminated PECH when modified

by phenylhydrazine and its derivations were higher than that from PECH. It was demonstrated that the presence of phenylhydrazine and its derivations were effective and NB-PECH-PH, NB-PECH-4-NPH and NB-PECH-2,4-DNPH had better thermal stability than PECH. These results are listed in Table 4.

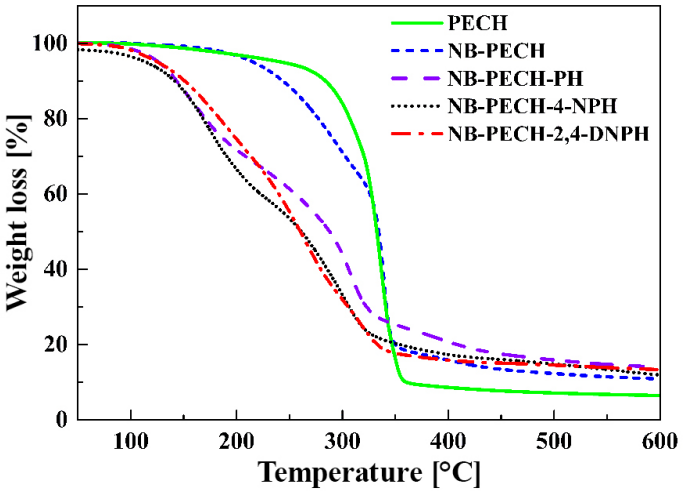


Figure 6. TGA thermograms of PECH, NB-PECH, NB-PECH-PH, NB-PECH-4-NPH and NB-PECH-2,4-DNPH

Table 4. Thermal analysis data for the polymers

Polymer	TGA analysis				DSC analysis		
	Weight loss at temperature [°C]			Ash yield [%]	Peak decomposition temperature T_d [°C]	ΔH [J/g]	T_g [°C]
	First	Second	Third				
PECH	280-380	–	–	6	340	33	–50
NB-PECH	175-355	–	–	10	340	180	–51
NB-PECH-PH	105-195	200-325	325-430	14	297, 315	223	–54
NB-PECH-4-NPH	100-205	210-320	320-420		316	408	–64
NB-PECH-2,4-DNPH	100-345	–	–		290, 330	473	–64

The glass transition temperature (T_g) and thermal decomposition enthalpies of the polymers were measured by DSC analysis in two different temperature ranges, –80 to 20 °C and 150 to 500 °C. Glass transition is one of the important properties of a polymer, and directly affects the mechanical and application properties of the polymer [29]. Figures 7 and 8

show the DSC analysis curves of PECH, NB-PECH, NB-PECH-PH, NB-PECH-4-NPH and NB-PECH-2,4DNPH polymers. According to Figure 7, the T_g values of PECH, NB-PECH, NB-PECH-PH, NB-PECH-4-NPH and NB-PECH-2,4-DNPH were about –50, –51, –54, –64 and –64 °C, respectively.

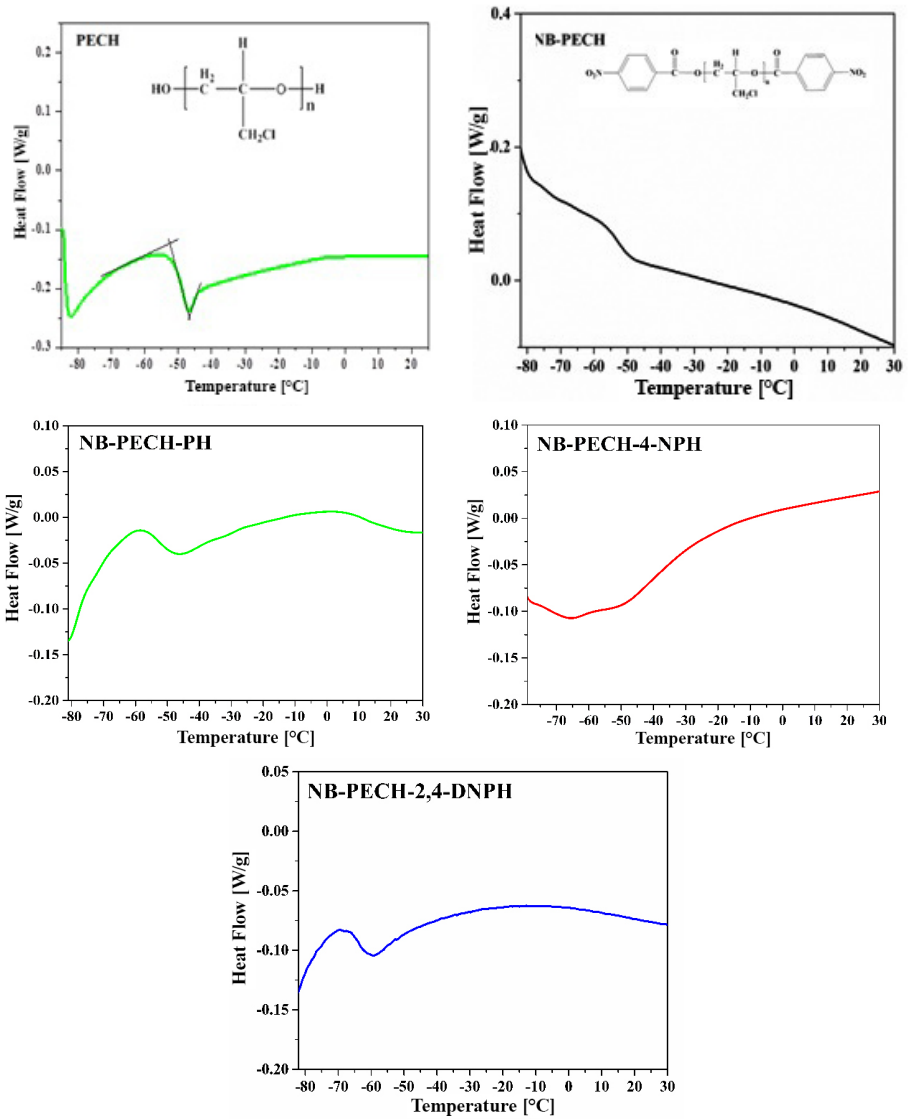


Figure 7. Glass transition temperature (T_g) of PECH, NB-PECH, NB-PECH-PH, NB-PECH-4-NPH and NB-PECH-2,4-DNPH

From Figure 8, it may be observed that in the thermogram of PECH prepolymer, a significant peak appeared at 300-400 °C, which is attributed to the destruction of the PECH structure. The thermogram of NB-PECH shows an exothermic peak in the range 295-375 °C, with a maximum at about 340 °C. This peak is due to degradation of the nitro group. As shown in Figure 8, the curve for NB-PECH-PH has the peak at 250-370 °C, with maxima at about 297 and 315 °C. The first maximum is due to the decomposition of the phenylhydrazine moiety and released of N_2 gas, while the second maximum is due to degradation of the nitro group. Figure 8 also shows the DSC curve of NB-PECH-4-NPH. This curve has an exothermic peak in the range 250-375 °C. This peak is due to the degradations of phenylhydrazine and the nitro groups, as well as the release of N_2 gas, where they overlap each other. The DSC curve of NB-PECH-2,4-DNPH shows two exothermic peaks, at about 290 and 330 °C, which are attributed to the destructions of dinitrophenylhydrazine and the nitro groups, respectively. The results of thermal analysis are listed in Table 4. According to Table 4, 3-nitrobenzoyl-terminated poly(epichlorohydrin) as modified by reaction with phenylhydrazine, 4-nitrophenylhydrazine and 2,4-dinitrophenylhydrazine, favorably improved their energetic characteristics.

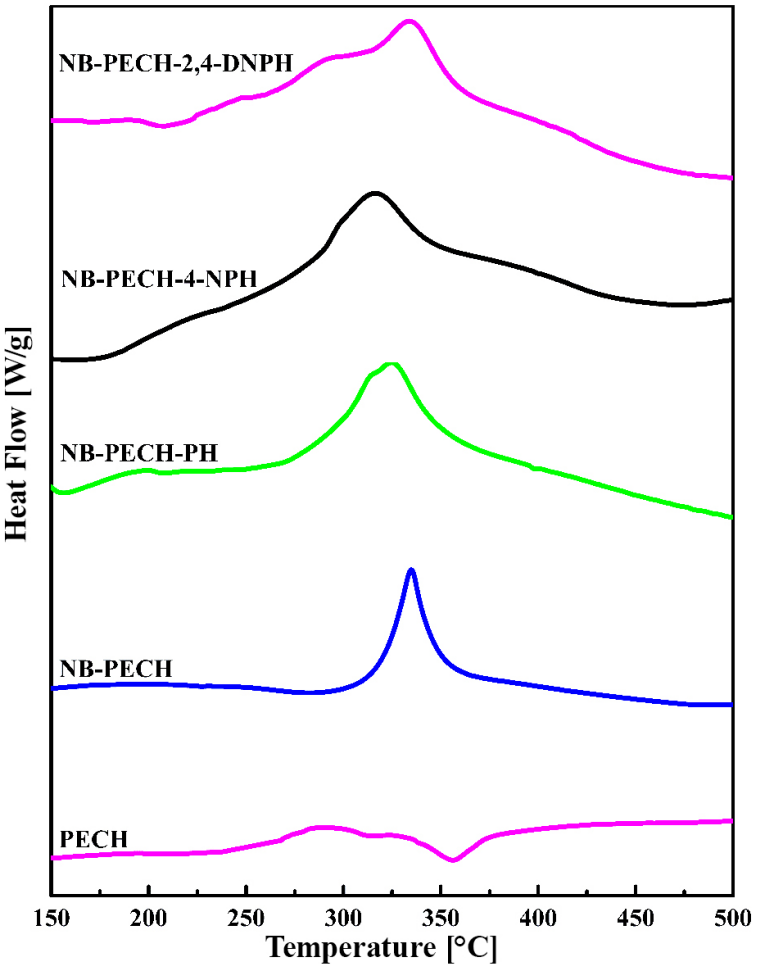


Figure 8. DSC thermograms of PECH, NB-PECH, NB-PECH-PH, NB-PECH-4-NPH and NB-PECH-2,4-DNPH

4.3 Examination and interpretation of the thermal analysis of PTHF/plasticizer blends

To examine the thermal behaviour of PTHF/plasticizers (2:1 w/w) blends, these were cured by mixing with sufficient toluene di-isocyanate (TDI). The mixtures obtained were then transferred into molds and kept in a vacuum oven for 48 h at 70 °C. The codes of the cured samples are listed in Table 5.

Table 5. Codes of PTHF/plasticizers

PTHF/plasticizer	Code
PTHF/DOA	P/DOA
PTHF/NB-PECH-PH	P/NB-PECH-PH
PTHF/NB-PECH-4-NPH	P/NB-PECH-4-NPH
PTHF/NB-PECH-2,4-DNPH	P/NB-PECH-2,4-DNPH

A chart of the thermal gravimetric analysis of the heated samples is shown in Figure 9. As may be seen, the initial thermal behaviour of all the samples is approximately the same, and all begin to lose weight in the region of about 250 °C. This weight loss is due to the breakdown and destruction of the main chain of PTHF. The heated PTHF polymer has a weight loss in the range of 250-410 °C. However, samples containing the plasticizers DOA, NB-PECH-PH, NB-PECH-4-NPH and NB-PECH-2,4-DNPH exhibited two stages of degradation. The second stage of weight loss for P/DOA was from 370 to 470 °C and for P/NB-PECH-PH, P/NB-PECH-4-NPH and P/NB-PECH-2,4-DNPH was in the range of 365-490, 365-500, and 363-500 °C, respectively. This phase of the weight loss, which is not seen in PTHF without a plasticizer, is due to the degradation and decomposition of the plasticizer. Also, the temperature at which a PTHF polymer lost 50% of its weight was 364 °C. The temperatures at which P/DOA, P/NB-PECH-PH, P/NB-PECH-4-NPH, P/NB-PECH-2,4-DNPH lost 50% of their weight were 389, 389, 414 and 420 °C, respectively. In addition, the residue yields from P/NB-PECH-PH, P/NB-PECH-4-NPH, P/NB-PECH-2,4-DNPH were higher than that from PTHF and P/DOA, as shown in Table 6. This result confirmed that phenylhydrazine and its derivatives improves the thermal stability of the plasticizers. According to the TGA curves of the heated samples, it may be concluded that the use of the plasticizers had increased the thermal stability, while the NB-PECH-2,4-DNPH plasticizer had the greatest effect. The order of the effect of the plasticizers on the thermal stability was as follows:

DOA < NB-PECH-PH < NB-PECH-4-NPH < NB-PECH-2,4-DNPH

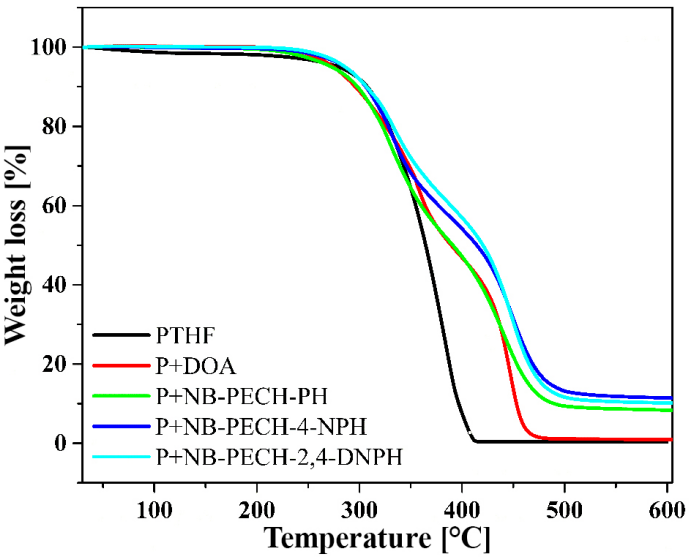


Figure 9. TGA thermograms of PTHF, P/DOA, P/NB-PECH-PH, P/NB-PECH-4-NPH and P/NB-PECH-2,4-DNPH

Figure 10 shows the thermograms of PTHF, P/DOA, P/NB-PECH-PH, P/NB-PECH-4-NPH and P/NB-PECH-2,4-DNPH. As is clear from the figure, the thermogram of the PTHF polymer has a thermosetting peak in the 320-420 °C region. The thermogram of the P/DOA sample also has an exothermic peak in the range of 330-400 °C with a maximum at 356 °C. The thermogram for P/NB-PECH-PH exhibited an exothermic peak at around 330 °C. This peak is related to the NB-PECH-PH plasticizer. The curve for the P/NB-PECH-4-NPH also has an exothermic peak at around 342 °C. This peak results from the NB-PECH-4-NPH plasticizer. The thermogram of P/NB-PECH-2,4-DNPH exhibited two exothermic peaks, both of which are related to the NB-PECH-2,4-DNPH plasticizer and appeared at 290 and 338 °C.

The exothermic peaks in the DSC chart show that the samples of P/NB-PECH-PH, P/NB-PECH-4-NPH and P/NB-PECH-2,4-DNPH are similar to the exothermic peaks observed in the thermograms of their plasticizers. In fact, comparison of these curves shows that the exothermic peaks are due to the presence of the plasticizers in the samples. In addition to comparing the DSC curves, the samples heated with PTHF clearly demonstrate the energy of the NB-PECH-PH, NB-PECH-4-NPH and NB-PECH-2,4-DNPH plasticizers.

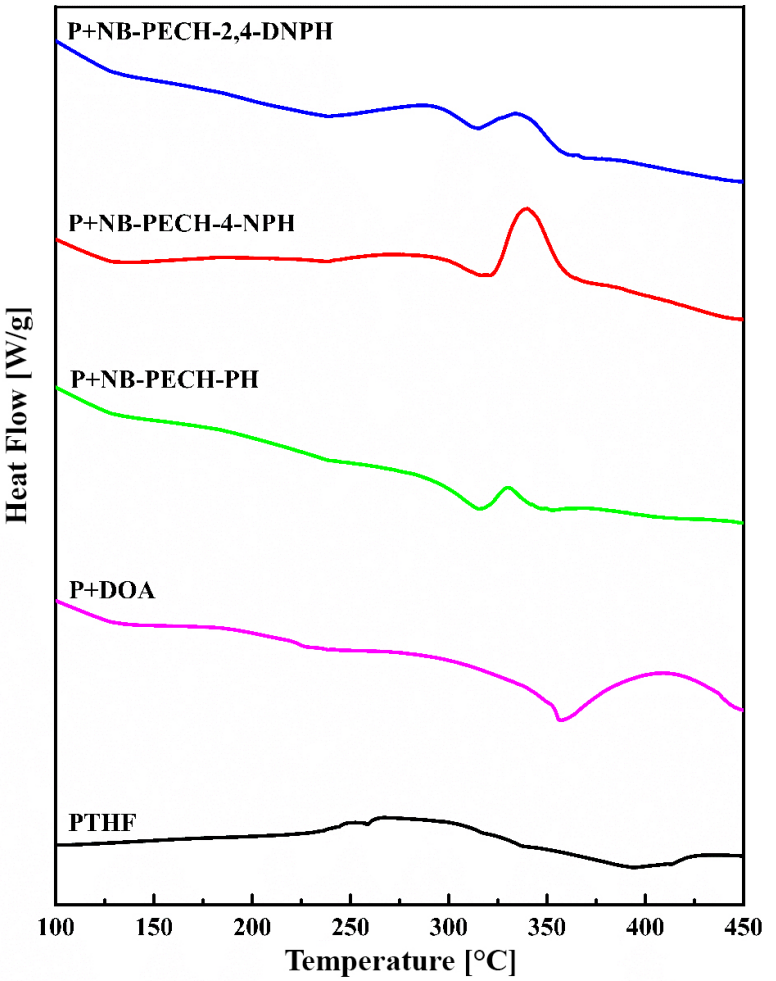


Figure 10. DSC chart for PTHF, P/DOA, P/NB-PECH-PH, P/NB-PECH-4-NPH and P/NB-PECH-2,4-DNPH

4.4 Measuring the enthalpy of the heated polymers

To compare the energy content of the synthetic polymers, the enthalpy of the heated polymers has been measured, and the thermal enthalpies obtained from the heated polymers are listed in Table 6. According to Table 6, the least amount of energy is exhibited by heated PTHF and the highest amount is exhibited by P/NB-PECH-2,4-DNPH.

Table 6. Enthalpy value and residue yields for PTHF, P/DOA, P/NB-PECH-PH, P/NB-PECH-4-NPH and P/NB-PECH-2,4DNPH

Sample	ΔH [J/g]	Residue yield [%]
PTHF	–430	0
P/DOA	–179	
P/NB-PECH-2,4-DNPH	93	10
P/NB-PECH-4-NPH	82	
P/NB-PECH-PH	20	9

5 Conclusions

Initially, poly(epilchlorohydrin) was reacted with 3-nitrobenzoyl chloride, which led to the formation of 3-nitrobenzoyl-terminated poly(epichlorohydrin) (NB-PECH). NB-PECH was subsequently modified by reaction with phenylhydrazine (PH), 4-nitrophenylhydrazine (4-NPH) and 2,4-dinitrophenylhydrazine (2,4-DNPH), and the resultant products were studied as plasticizers. The polymers PECH, NB-PECH, NB-PECH-PH, NB-PECH-4-NPH and NB-PECH-2,4-DNPH were investigated by UV-VIS, FT-IR, CHN, ^{1}H NMR and thermal analysis. The results obtained from the structural analysis confirmed the capping of the PECH polymer ends by 3-nitrobenzoyl groups, as well as the replacement of the chlorine atoms by phenylhydrazine and its derivatives. The synthesized samples were examined by thermal analysis. The TGA tests showed that the highest thermal stability was exhibited by NB-PECH and that NB-PECH-2,4-DNPH has the least thermal stability. The thermal behaviours of the two polymers NB-PECH-PH and NB-PECH-4-NPH were somewhat similar to each other. The glass transition temperatures for the plasticizers were determined from their DSC graphs, and the T_g value was negative for all of them. The results of the DSC tests indicated the energy of the plasticizers, and the highest amount of energy was associated with NB-PECH-2,4-DNPH, with its two nitro groups.

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