

## Studies on the recycling of glycolized nylon 66 using novel chain extenders

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### Abstract

Nylon 66 (NY66) polymer based products widely used in automotive applications undergo deterioration in their mechanical properties when repeatedly exposed to ethylene glycol (EG) solution. In this study, recycling of glycolized NY66 (g-NY66) samples was carried out through melt-compounding with novel isocyanate based chain extenders namely hexamethylene 1,6-dicarbamoyl dicaprolactam (HDC) and tolylene 2,4-dicarbamoyl dicaprolactam (TDC). The recycling efficiency of HDC and TDC on g-NY66 was compared with two commercially available chain extenders 1,1-carbonyl biscaprolactam (CBC) and 1,3-phenylene bis(2-oxazoline) (PBO), and the resultant changes in molecular weight, melt flow, and crystallization behavior in the modified NY66 samples were confirmed from intrinsic viscosity, rheology, and differential scanning calorimetry measurements, respectively. The active ingredients (isocyanate and  $\epsilon$ -caprolactam) liberated from HDC and TDC during the melt-compounding process reacted efficiently with the end groups of g-NY66 ( $-\text{OH}$  and  $-\text{NH}_2$ ) resulting in improved molecular weight compared to g-NY66 and the results are reported in detail.

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**Keywords:** Glycolysis; Nylon 66; Recycling; Chain extenders; Dicarbamoyl dicaprolactam

### 1. Introduction

Among the commercially produced polyamides, Nylon 66 (NY66) is an important semi-crystalline thermoplastic polymer having good mechanical, thermal, and chemical properties. In the automobile industry, NY66 is widely used in high performance molded applications such as in radiator end tank, engine cover, intake manifold, dipstick caps, thrust washer, liners for sheathed cables, etc. [1]. According to a recent industrial estimate, an average car uses nearly 30 times of NY66 in underhood applications alone compared to that used in 1960s [2].

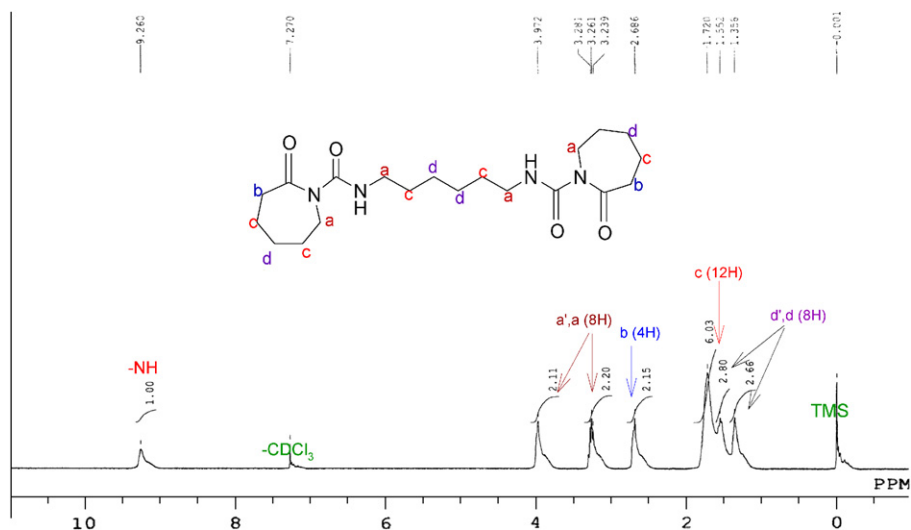
Extended exposure of nylon based products to physical factors such as thermal-oxidation, radiation, etc. [3–6] and chemical factors such as mixture of ethylene glycol/water (used as cooling liquid), calcium chloride (used for melting ice during winter), methanol (used as washing solvent), etc. [7–16] is unavoidable and can lead to side reactions producing low molecular weight degradation products. This is a problem of industrial significance because these changes can adversely affect the performance of nylon based products. Many researchers have focused on the degradation of NY66 by chemical agents in the past [7–14,16] and more recently, our group has focused on studying the glycolysis of NY66 and its degradation mechanism [14,15].

Recycling of used/degraded polymers is an important process to practice industrial economy and to maintain environmental safety. Some of the routes followed for recycling the

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Fig. 1.  $^1\text{H}$  NMR spectrum of HDC.

## 2. Experimental

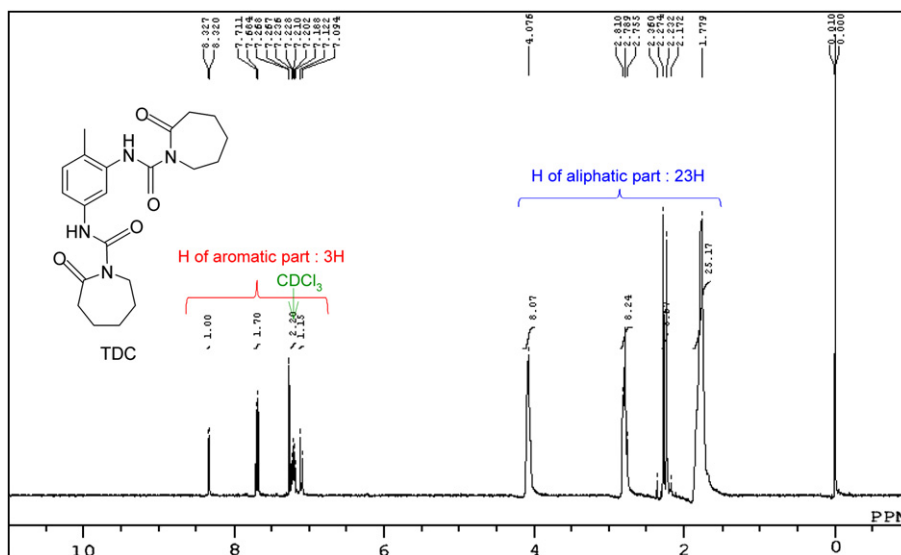
### 2.1. Materials

Virgin nylon 66 (NY66) chips and ethylene glycol (EG) were purchased from Du Pont (USA) and SK Chem. (Korea), respectively. Two commercially available chain extenders, CBC and PBO were received from DSM, the Netherlands. For the synthesis of HDC and TDC,  $\epsilon$ -caprolactam (CL) from Kolon Co. (Korea), tolylene diisocyanate (TDI), hexamethylene diisocyanate (HDI), acetone, and toluene from Sigma Aldrich Co. (USA) were used. All the above chemicals were used without further processing or purification. The chemical structures of chain extenders used in this study are shown in Table 1.

### 2.2. Synthesis of chain extenders (HDC and TDC)

#### 2.2.1. Hexamethylene 1,6-dicarbamoyl dicaprolactam (HDC)

CL (0.73 mol) and HDI (0.33 mol) were reacted in a three-necked round-bottomed flask at 75 °C for 6 h under dry  $\text{N}_2$  atmosphere. The product was diluted with 90 ml of acetone and the solution was added dropwise into an excess of distilled water under vigorous stirring. The precipitate was filtered and repeatedly washed with distilled water to obtain the pure product (HDC). It was then dried in an air oven maintained at 50 °C for a day and further dried in a vacuum oven (ca. 1–2 mm Hg) at 80 °C for 3 days to form a fine powder.

Fig. 2.  $^1\text{H}$  NMR spectrum of TDC.

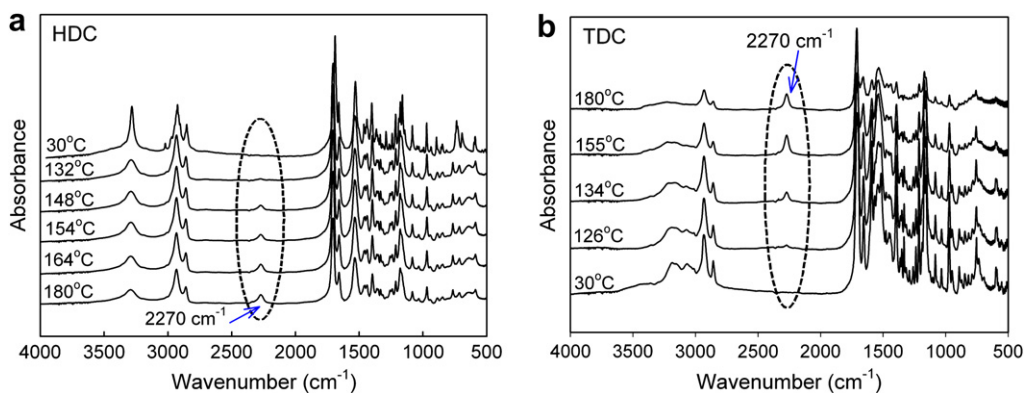


Fig. 3. FT-IR spectra of (a) HDC and (b) TDC during heating from 30 to 180 °C.

### 2.2.2. Toluene 2,4-dicarbamoyl dicaprolactam (TDC)

CL (0.73 mol) and TDI (0.33 mol) were dissolved in 100 ml dry toluene in a three-necked round-bottomed flask at room temperature and then refluxed for 8 h under dry  $N_2$  atmosphere. The product was concentrated using a rotary vacuum evaporator. The precipitation of the concentrate (TDC) and its drying were performed in the same manner as in the case of HDC. During the synthesis of both HDC and TDC, samples were taken at regular intervals of time to check for the disappearance of free  $-NCO$  stretching vibration at  $2270\text{ cm}^{-1}$  peak using FT-IR absorption spectroscopy in order to optimize the reaction time. The synthesis routes for (i) HDC and (ii) TDC are illustrated in Scheme 1. The products were stored in a vacuum desiccator for further use.

### 2.3. Glycolysis of NY66

Virgin NY 66 chips were grounded into fine powder, added to aqueous EG (50/50 v/v) at the liquor ratio of 1/5 in a custom-made glass vessel and refluxed under constant stirring for 312 h. Samples were taken from this batch at every 24 h in order to study the degradation rate during the glycolysis reaction. The samples thus collected were Soxhlet extracted with distilled water for 24 h to remove EG, dried in an air oven at 50 °C for a day, and further dried in a vacuum oven (ca. 1–2 mm Hg) at 90 °C for 24 h. Another batch of glycolyzed NY66 (g-NY66) samples was also prepared with an extended

glycolysis time of 700 h and both the batches were used for melt-compounding.

### 2.4. Melt-compounding

The chain extension reaction was carried out in a Haake Rheomix 600 batch intensive mixer at 280 °C for 5 min with a motor speed of 50 rpm.

### 2.5. Characterization

$^1H$  NMR spectra of the synthesized chain extender adducts were obtained with a 300 MHz FT-NMR (JNM-AL300, Jeol, Japan) using  $CDCl_3$  as a solvent. FT-IR-transmission spectra were obtained using Bruker IFS66v FT-IR spectrometer in the range between 4000 and  $400\text{ cm}^{-1}$  with a resolution of  $2\text{ cm}^{-1}$  and 32 scans during heating from 30 to 180 °C. Simultaneous DSC–TGA curves were obtained using DSC–TGA Q600 (TA Instruments Inc., USA, scan rate  $10\text{ °C/min}$ ). Intrinsic viscosity was measured using Schott AVS-260 auto viscometer at 25 °C with formic acid (85%) as a solvent. Samples were filtered with  $0.45\text{ }\mu\text{m}$  Teflon filter before the viscosity measurement. Circular disks (25 mm diameter and 3 mm thick) were prepared using a Carver press by melt-fast cooling method and their rheological studies were carried out using Rheometric Scientific Inc. (USA) at 280 °C.

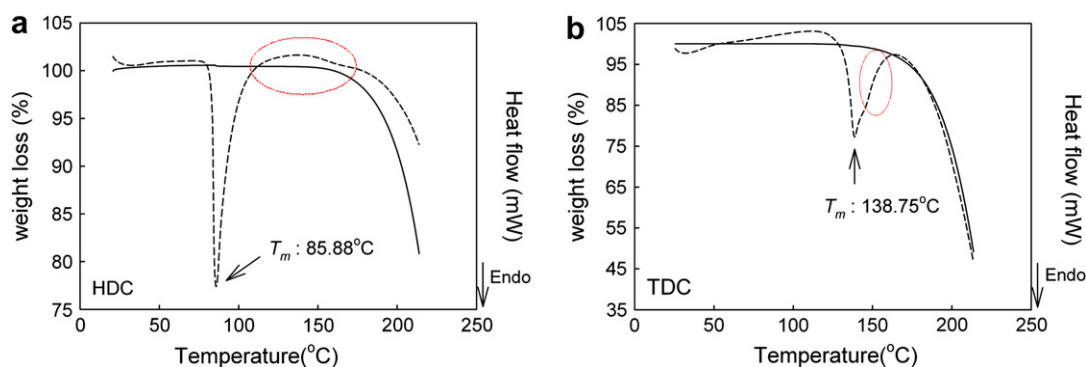
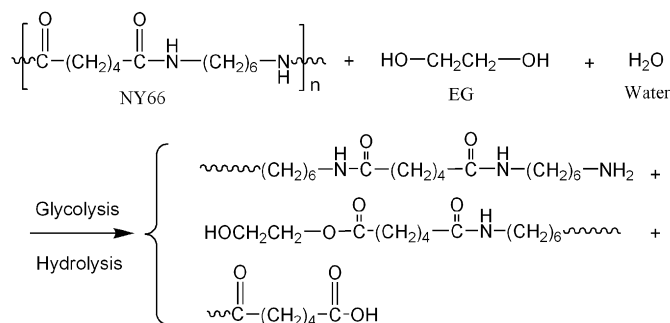


Fig. 4. DSC–TGA plots of (a) HDC and (b) TDC.



Scheme 2. Overall glycolysis and hydrolysis reaction of NY66 with aqueous EG solution.

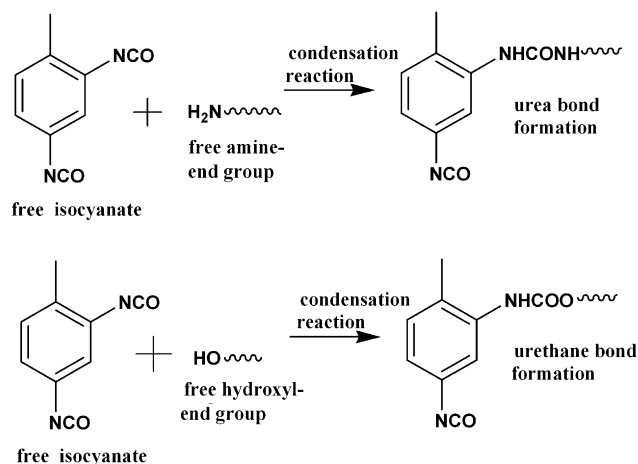
### 3. Results and discussion

#### 3.1. Characterization of chain extenders

The synthesis and structural characterization of CBC and PBO are described in detail elsewhere [26,27,29–32]. In this study, the structures of the synthesized chain extenders (HDC and TDC) were identified using  $^1\text{H}$  NMR spectroscopy. Fig. 1 shows the  $^1\text{H}$  NMR spectrum of HDC, in which the chemical shifts at  $\delta = 2.69$  and 9.26 ppm correspond to the  $-\text{CH}_2$  group of CL ring and  $-\text{NH}$  group of the open chain, respectively. The peaks at  $\delta = 1.36$ , 1.52, 1.72, 3.26, and 3.97 ppm correspond to the methylene groups in the CL ring and in the open chain. Fig. 2 shows the  $^1\text{H}$  NMR spectrum of TDC in which the chemical shifts at  $\delta = 4.07$  and 2.78 ppm correspond to  $-\text{CH}_2$  and  $-\text{N}-\text{CH}_2$  groups of CL ring. Chemical shifts at around  $\delta = 7.18$ , 7.68, and 8.32 ppm correspond to the protons of the aromatic ring. In addition to this, the aliphatic protons in the open chain also exhibited the characteristic peaks as shown in Fig. 2.

For the proposed chain extension method, it is important to ascertain the temperature at which the de-blocking of isocyanates and CL occurs. In order to predict the suitable conditions for the formation of active ingredients, FT-IR spectra of HDC and TDC were recorded in the temperature range during heating from 30 to 180  $^\circ\text{C}$  as shown in Fig. 3. In HDC (Fig. 3(a)), the  $2270\text{ cm}^{-1}$  (free  $-\text{NCO}$ ) peak started to appear at around 132  $^\circ\text{C}$  and in the case of TDC (Fig. 3(b)), it was observed at around 126  $^\circ\text{C}$ . In both the cases, the peak intensity increased with further increasing temperature.

To confirm the FT-IR results, the chain extenders (HDC and TDC) were further studied using simultaneous DSC–TGA as



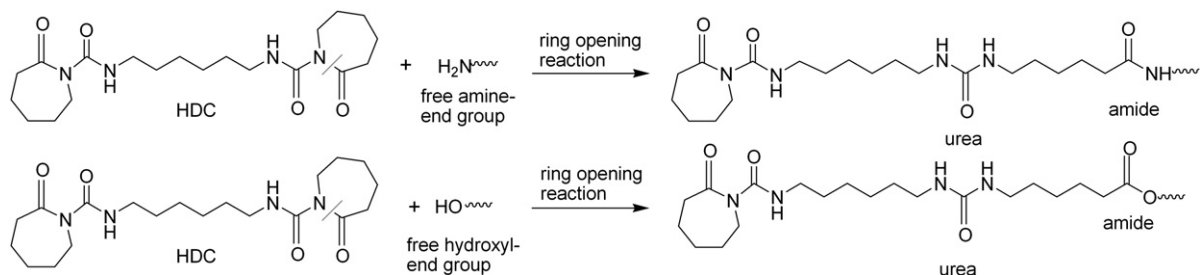
Scheme 4. Proposed condensation reaction between free isocyanates in TDC/HDC with amine/hydroxyl end groups in g-NY66.

shown in Fig. 4. HDC (Fig. 3(a)) showed the characteristic melting endothermic peak at 85.88  $^\circ\text{C}$  and in the case of TDC (Fig. 3(b)), at 138.75  $^\circ\text{C}$ . The interesting point to be noted is the appearance of endothermic shoulder at around 152  $^\circ\text{C}$  which may be attributed to the thermal dissociation of chain extenders to liberate isocyanates and CL. Among HDC and TDC, the comparative weight loss (%) due to thermal dissociation was higher in the case of TDC which may be due to faster rate of de-blocking and subsequent vaporization of the active ingredients (CL and isocyanates) than in HDC.

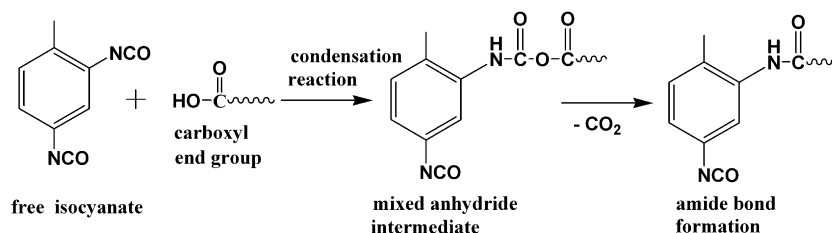
FT-IR and DSC–TGA were quite helpful in fixing the temperature range of the thermal dissociation reaction in HDC (132–164  $^\circ\text{C}$ ) and TDC (126–155  $^\circ\text{C}$ ) during which the active ingredients were liberated. Regarding CBC and PBO, previous reports have confirmed that the chain extension reaction in CBC occurs in the temperature range between 100 and 150  $^\circ\text{C}$  [27] and for PBO in the range between 140 and 220  $^\circ\text{C}$  [30] without any noticeable side reactions.

#### 3.2. Glycolysis and hydrolysis of NY66

In our earlier report [14], we have observed the presence of amino and hydroxyl end groups in g-NY66 and the overall glycolysis reaction can be summarized as shown in Scheme 2. In addition, we must also consider the possibility of carboxyl and amino end group formation during hydrolysis of NY66 as reported in previous publications [1,10].



Scheme 3. Proposed ring opening reaction between HDC and amine/hydroxyl end groups in g-NY66.



Scheme 5. Possible condensation reaction between free isocyanates in TDC/HDC and carboxyl end groups in hydrolyzed NY66.

The possible chain extension reactions (ring opening and condensation) between the active ingredients in HDC/TDC and the g-NY66 end groups during melt-compounding are shown in Schemes 3–5. In the case of HDC, the most preferred chain extension pathway among the two is the ring opening of CL portion at elevated temperatures followed by its reaction with free  $-\text{NH}_2$  and  $-\text{OH}$  end groups in g-NY66 leading to the formation of urea/amide and urea/ester bonds, respectively (Scheme 3). In the case of TDC, chain extension through condensation (Scheme 4) is highly preferred than ring opening due to the following reasons: compared to HDC, the amount of CL liberated in TDC is higher at elevated temperatures as observed earlier from the DSC–TGA data. Consequently, the amount of free  $-\text{NCO}$  groups available for chain extension process is also higher in the case of TDC when compared to HDC which may have resulted in a preferential condensation reaction involving free  $-\text{NCO}$  groups in TDC with free  $-\text{NH}_2$  and  $-\text{OH}$  end groups in g-NY66 to form urea and urethane bonds, respectively. Though we have mainly focused on the chain extension of g-NY66 end groups in this study, we should also consider the presence of hydrolyzed NY66 products, though lesser than g-NY66 and their possible chain extension pathway. The carboxyl end groups present in hydrolyzed NY66 react preferentially with the free  $-\text{NCO}$  groups in TDC resulting in the formation of amide bond as shown in Scheme 5.

The possible reactions between CBC/PBO chain extenders with  $-\text{OH}$ ,  $-\text{NH}_2$ , and  $-\text{COOH}$  end groups are shown elsewhere [26,27,29–32]. CBC reacts more preferentially with

$-\text{OH}$  and  $-\text{NH}_2$  end groups and PBO reacts preferentially with  $-\text{COOH}$  end group. The mixture of these two chain extenders can also be very effective for the chain extension of NY66 degraded by both hydrolysis and glycolysis [29].

### 3.3. Intrinsic viscosity studies

Fig. 5 shows the intrinsic viscosity (IV) data of g-NY66 as a function of glycolysis time. IV values decreased gradually with increasing glycolysis time and it was correlated with the decrease in both and as reported in our previous publication [14]. Compared to virgin NY66, IV values decreased by around 20% after 310 h of glycolysis time which further decreased to around 50% after 700 h of treating time.

Fig. 6 and Table 2 show the IV data of g-NY66 (310 h) samples after melt-compounding with 3 wt.% of chain extenders used in this study. As-glycolyzed NY66 was taken as the ‘control’ sample and melt compounded without the addition of any chain extenders. The observed decrease in the IV value for the ‘control’ sample may be due to further degradation of g-NY66 during the melt-compounding process. The incorporation of TDC and HDC to g-NY66 (310 h) increased the IV values by around 15% compared to ‘control’ sample, whereas the addition of CBC and the mixture of CBC/PBO (1.5/1.5 wt.%) increased the IV value of g-NY66 only to a lesser extent than that observed for HDC and TDC. Compared to CBC, the mixture of CBC/PBO decreased the IV value and this may be due to the presence of lesser amount of  $-\text{COOH}$  end groups which can react with PBO. The appreciable increase in IV values observed for both HDC and TDC may be due to their respective preferential chain extension

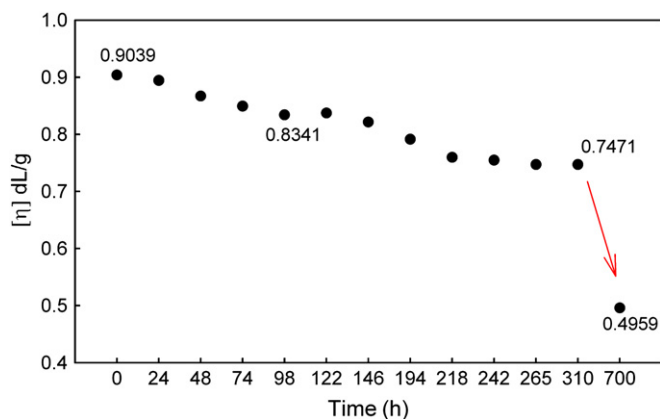


Fig. 5. Changes in intrinsic viscosity  $[\eta]$  of virgin NY66 as a function of glycolysis time.

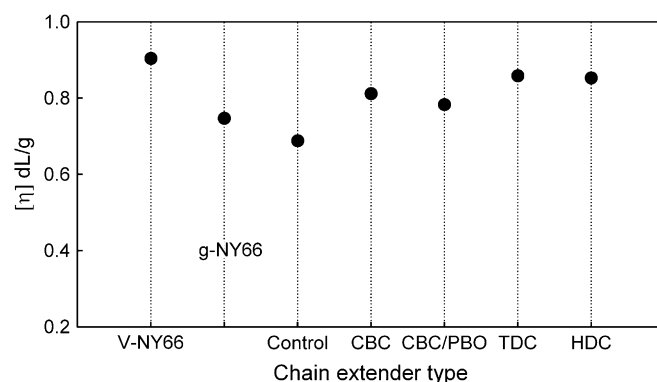


Fig. 6. Changes in intrinsic viscosity  $[\eta]$  of melt-compounded g-NY66 (310 h).

Table 2  
Intrinsic viscosity values of melt-compounded g-NY66 as a function of varying glycolysis time and chain extenders

Glycolysis time	Chain extender	Wt.%	IV [ $\eta$ ]	Glycolysis time	Chain extender	Wt.%	IV [ $\eta$ ]
–	NY66	–	0.9039	–	NY66	–	0.9039
310 h	g-NY66	–	0.7471	700 h	g-NY66	–	0.4959
	Control	–	0.6881		Control	–	0.5681
	HDC	3	0.8528		HDC	3.85	0.7006
	TDC	3	0.8583		TDC	3.85	0.8171
	CBC	3	0.8119		CBC	6.98	0.9613
	PBO	3	0.7664		PBO	6.08	0.5507
	CBC/PBO	1.5/1.5	0.7828		CBC/PBO	1.22/1.05	0.5303
			HDC/PBO		1.95/1.05	0.5122	
			TDC/PBO		1.95/1.05	0.7077	
			TDC/PBO		3.77/2.03	0.8130	

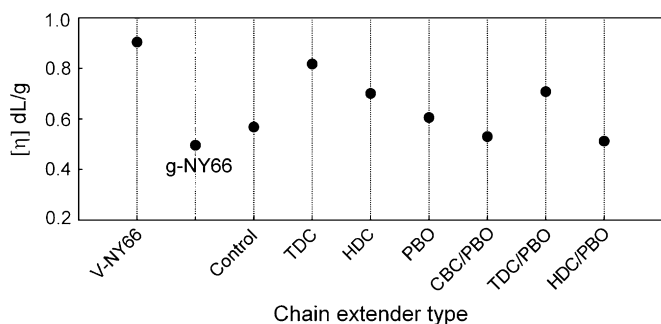


Fig. 7. Changes in intrinsic viscosity [ $\eta$ ] of melt-compounded g-NY66 (700 h).

pathways followed when reacted with end groups in g-NY66 as discussed earlier.

Fig. 7 shows the IV values of melt-compounded products from the g-NY66 (700 h). The amount of chain extenders added to g-NY66 was varied as shown in Table 2 in order to assess the requirement as well as efficiency of the melt-compounding process. The incorporation of TDC and HDC (3.85 wt.%) led to an appreciable increase in IV almost comparable to that of virgin NY66. The addition of CBC (6.98 wt.%) increased the IV value to little higher than virgin NY66 but only after the addition of around 1.8 times higher quantity than that added for TDC and HDC. The lower increase in IV value for the addition of PBO compared to CBC in both the batches (310 and 700 h) may be due to the presence of very small amount of carboxyl groups in the g-NY66 as well as

less possibility of hydrolysis during the artificial degradation (glycolysis) process. The IV of ‘control’ sample increased compared to the g-NY66. This indicates that condensation polymerization is more dominant than thermal degradation during the melt-compounding process due to the higher concentration of other functional end groups like amine, carboxylic acid, and hydroxyl in the highly degraded polymer (700 h) compared to 310 h g-NY66 sample. We also attempted to improve the chain extension properties of PBO by using mixtures with other chain extenders. The order of increasing activity was observed to be as follows: HDC/PBO < CBC/PBO < TDC/PBO.

It is important to emphasize that all melt-compounded products exhibit better solubility in 85% formic acid during the IV measurement which essentially proves the absence of cross-linking and highly branched structure. In an earlier report by Perry and Savory [34], the insolubility of NY66 chain extended with diisocyanates and diacid chlorides was explained as due to the cross-linking arising from the reaction between the isocyanate and amide groups. In our case, it can be predicted that the isocyanates had only reacted with the end hydroxyl, amine, and carboxyl groups and not with the amide groups.

### 3.4. Melt viscosity studies

Fig. 8(a) shows the shear viscosity behavior of g-NY66 (700 h) compounded with varying chain extenders. At lower

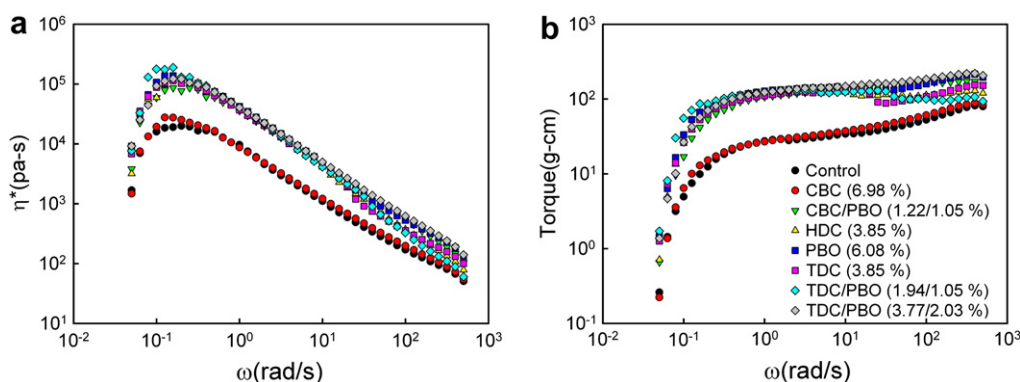


Fig. 8. Changes in (a) shear viscosity and (b) torque values in g-NY66 (700 h) melt compounded with varying chain extenders.

shear rates, the absolute shear viscosity values of the chain extended samples were significantly higher (except CBC) compared to control sample. With increasing shear oscillatory frequency, the curves display a shear-thinning behavior which is in agreement with the behavior expected for long chain materials. Among the chain extenders used in this study, the synthesized TDC and HDC exhibited higher shear viscosity than the commercially available CBC and PBO. Among the combination of chain extenders used, the TDC/PBO combination performed much better than CBC/PBO, a trend similar to that observed earlier in IV studies.

Fig. 8(b) shows the changes in torque during melt viscosity measurement. Increasing torque at lower shear rates and subsequent stabilization of torque values at higher shear rates show that chemical reactions between the end groups of g-NY66 and the chain extenders take place very fast. In this case too, CBC containing sample showed different behaviors with less increase in torque compared to other chain extenders and thereby indicate that the liberated isocyanates from HDC and TDC are more reactive toward the end groups of g-NY66 than carboxyl groups in CBC under the experimental conditions employed in this study.

### 3.5. DSC studies

The effect of varying chain extenders on the melting and crystallization behaviors of melt-compounded g-NY66 (700 h) was analyzed using DSC studies as shown in Fig. 9. After melt-compounding, the melting point ( $T_m$ ) of chain extended g-NY66 samples was slightly shifted toward lower temperature compared to g-NY66 (Fig. 9(a)) probably due to the decrease in sequence length of nylon chains along with decrease in their chemical regularity caused by the presence of chain extender [35]. Among the chain extenders, CBC exhibited relatively reduced  $T_m$ , whereas the other chain extenders exhibited almost same  $T_m$  peak position. However, during the second heating (Fig. 9(c)), the shapes of the g-NY66 and chain extended g-NY66  $T_m$  peaks resembled almost similar and the two-peak behavior became more obvious. In earlier studies, the dual melting transition of crystalline polymers has been explained as due to one among the following reasons: the presence of two crystal modifications [39], the presence of two populations of crystal lamellae of different thicknesses [40] or the simultaneous melting, recrystallization, and remelting of the lamellae initially formed at the crystallization conditions [41]. Since the dual melting transition in g-NY66 and chain extended g-NY66 samples was observed at almost same temperature, the origin of the dual melting transition must be the same for the samples used in this study.

The crystallization rate increased with the chain extension process as observed from slightly increased melt-crystallization peaks ( $T_{cm}$ ) for chain extended g-NY66 samples compared to unmodified g-NY66 (Fig. 9(b)). Since the rate of crystallization from the melt is controlled by the rate of nucleation rather than the rate of diffusion of amorphous phase to crystalline phase, this higher shifting of  $T_{cm}$  indicates that the chain extenders used in this study possibly functioned as a nucleating

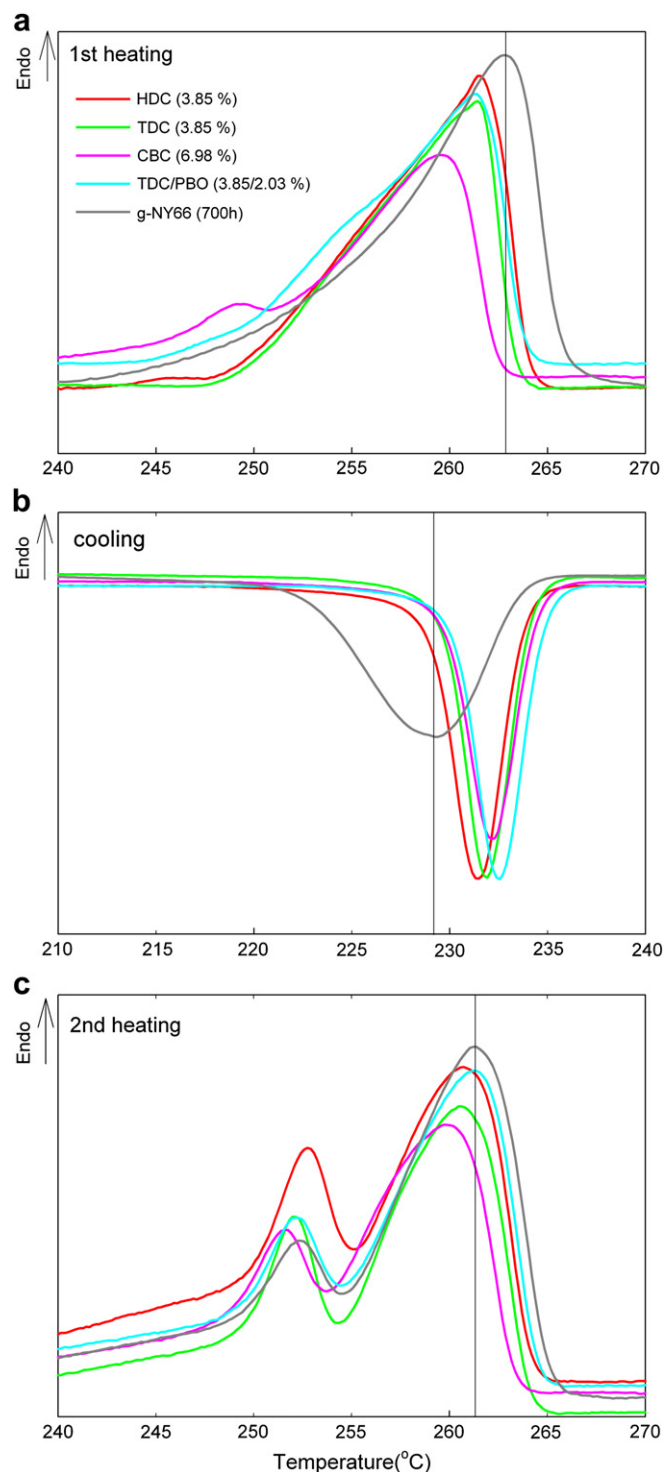


Fig. 9. DSC thermograms for g-NY66 (700 h) melt compounded with varying chain extenders. (a) First heating, (b) cooling, and (c) second heating.

agent and thereby increased the crystallization rate in chain extended samples compared to unmodified g-NY66.

## 4. Conclusions

The lab-scale glycolyzed NY66 (g-NY66) was effectively recycled through melt-compounding process using novel chain



extenders. The structure of synthesized chain extenders (TDC and HDC) was confirmed using  $^1\text{H}$  NMR. Thermal conditions for melt-compounding were estimated after analyzing the chain extenders using FT-IR and DSC studies and the release of active ingredients (free NCO and CL) at elevated temperatures was confirmed. g-NY66 samples exhibited decreasing IV values due to their degradation behavior, whereas the chain extended g-NY66 samples using melt-compounding process increased IV values thereby suggesting the effectiveness of chain extension method. Among the chain extenders used in this study, TDC, HDC, and TDC/PBO mixture were found to improve the molecular weight of g-NY66 as observed from their improved viscosity and thermal properties compared to CBC and PBO. The absence of cross-linking in g-NY66 was confirmed by its rather easier solubility in 85% formic acid during IV measurement. If the cross-linking was formed after the melt-compounding process, their recycling may have become very difficult. Overall, the results obtained from this study suggest that the recycling of g-NY66 by melt-compounding using chain extenders results in linear NY66 (recycled) polymer which can be formed into new products using the existing manufacturing lines employed for virgin NY66. Moreover, they can also be recycled many times using the above melt-compounding process with properties almost comparable to those of virgin NY66 and hence has significant industrial applications.

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