Effectiveness of Compatibilizers and Filler on the Performance of the Blends of Thermoplastic Polyurethane/Polyolefins

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Abstract

Thermoplastic Polyurethane (TPU) is a highly versatile material with superior physical properties but high cost. Melt blending of TPU with Polyolefins (PO) can lower the cost and improve mechanical and chemical properties. Since TPU and PO are completely immiscible polymers, property enhancement cannot be attained. Effect of incorporation of Polypropylene Copolymer (PPCP) as compatibilizer on the miscibility of the blends and effect of calcium carbonate as filler to enhance the mechanical properties were studied. Blends were produced by melt mixing using a single screw extruder. Miscibility studies were done using Scanning Electron Microscope (SEM) and thermal characteristics were determined using Differential Scanning Calorimeter (DSC). Mechanical properties like tensile strength, impact strength, flexural strength and hardness were also studied using Universal Testing Machine (UTM). The results show that the blend having 20% loading of polyurethane (PU) with suitable compatibilizers and calcium carbonate gives excellent performance in all aspects.

Keywords: Polymer blends; compatibilizer; polyurethane; filler; SEM.

1. Introduction

Blending of polymers is an economically attractive approach to development of new materials since it combines the desirable properties of more than one polymer. Blends of TPU and PO are highly incompatible because of large difference in polarities and high interfacial tension [1]. Since most immiscible blends are thermodynamically unstable, the copolymer must be added to stabilize the morphology. This process of stabilizing polymer blends is commonly called compatibilization [2]. The incorporation of particulate fillers into polymer matrices has been an extended technique to improve or modify some properties of neat polymers [3]. It is well-known that blending is important not only for obtaining polymer materials with excellent properties, but improving their processing capabilities and reducing the product costs. Owing to the needs of academic research and industrial application, most polymer materials are not homogeneous systems any longer, but multiphase complex systems obtained through blending [4]. We studied the effects of fillers on the mechanical, dynamic mechanical and aging properties of rubber-plastic binary and ternary blends derived from acrylic rubber, fluorocarbon rubber, and multifunctional acrylates [5]. Nowadays, requirements for the production of new polymers with the best cost/performance balance are increasing; thus, research based on the study of polymer blends and polymer-filler composites is extensive [6]. Calcium carbonate ($CaCO_3$) is one of the inorganic materials most widely used as filler in polymers [7-11]. The incorporation of calcium carbonate in thermoplastics is used to modify the mechanical properties and morphology of the polymers. This filler improves Young´s Modulus, but it also decreases impact strength, toughness and elongation at break, it is generally accepted that compatibilizers serve as polymeric surfactants for immiscible blends by migration to the interface and thereby lowering the interfacial tension. In the present work, a study was performed on the morphological, mechanical and thermal properties of blends of TPU and PO in various proportions after incorporating PPCP as compatibilizer and calcium carbonate as filler.

2. Methods

2.1. Materials and characterization

Low density polyethylene (LD), high density polyethylene (HD), polypropylene (PP) and PPCP (Grade: MI 1530) were supplied by Reliance India Ltd, Vadodara. TPU with medium shore hardness no. 85 was supplied by DuPont, Savli.

2.2. Blending process

The TPU and PO were preheated for three hours. The blends of TPU and PO with and without compatibilizer were made using single screw extruder. Composition of the TPU/PO blends were 95/5, 90/10, 85/15, 80/20, 75/25 and 70/30, and mixed with 20 parts of calcium carbonate ($CaCO_3$) on a two roll mill. These blends were grinded and used for making test specimen. Specimens for different mechanical testing were prepared using injection moulding machine.

2.3. Analysis of mechanical properties

The tensile strength and tensile modulus of all the blends were carried out at room temperature according to ASTM D-638.The flexural strength and flexural modulus of blends were done according to ASTM D-790.The izod impact strength test of all blends were carried out at room temperature according to ASTM D-256. Shore D hardness of the blends was determined according to ASTM D-2240.

2.4. Thermal and morphological properties

Thermal properties of the blends were studied using with Perkin-Elmer, DSC-PYRIS-I differential scanning calorimeter (DSC). The fracture surface of the blend samples were analyzed with a Philips, Scanning Electron Microscope (SEM). The surface morphology of the TPU/PO's blends with or without compatibilizer was examined in scanning electron microscopic in the inert atmosphere of nitrogen gas.

3. Results and Discussion

3.1. Analysis of mechanical properties

Addition of PPCP as compatibilizer was found to increase the tensile strength and tensile modulus of all TPU/PO blends such as TPU/LD, TPU/HD and TPU/PP (Table 1 and 2). Addition of filler such as calcium carbonate increases the tensile and tensile modulus of the blends while the elongation was found to decrease (Table 3).

Flexural strength and flexural modulus of the blends with and without compatibilizer and filler are shown in Table 4 and 5. The addition of compatibilizer and the $CaCO_3$ into blends increases the flexural strength and flexural modulus. The Phase morphology and the interfacial adhesion between components influenced the mechanical properties of the polymer blends, because the morphology of two phases that lack of adhesion between the components polymers may lead to premature failure and reduced mechanical properties such as tensile, flexural strength. As PPCP was mixed in to blends it helped to increase the adhesion between two phases, hence improved the mechanical properties [1].

Table 1: Tensile strength of TPU/PO blends (effect of PPCP compatibilizer and calcium carbonate filler)

Blends	Tensile Strength (Kg/cm^2)					
	% of PO added					
	5	10	15	20	25	30
TPU/LD	73.03	79.37	84.03	82.03	82.70	84.03
TPU/LD/PPCP	73.36	76.03	81.36	86.70	86.70	86.03
TPU/LD/PPCP/$CaCO_3$	77.03	78.03	84.03	94.70	90.04	89.37
TPU/HD	75.03	76.70	78.03	87.37	90.04	86.70
TPU/HD/PPCP	78.70	82.03	84.70	86.70	90.04	86.03
TPU/HD/PPCP/$CaCO_3$	78.70	84.03	91.04	103.37	98.04	89.37
TPU/PP	74.03	78.70	80.70	84.70	89.37	94.04
TPU/PP/PPCP	74.36	78.70	86.03	109.71	104.71	100.71
TPU/PP/PPCP/$CaCO_3$	74.03	82.70	92.04	112.71	94.04	93.37

Table 2: Tensile modulus of TPU/PO blends (effect of PPCP compatibilizer and calcium carbonate filler)

Blends	**Tensile Modulus (Kg/cm^2)**					
	% of PO added					
	5	**10**	**15**	**20**	**25**	**30**
TPU/LD	16.53	18.54	18.76	18.31	19.41	21.01
TPU/LD/PPCP	12.23	12.67	14.03	15.26	15.94	16.29
TPU/LD/PPCP/$CaCO_3$	14.16	14.78	16.16	18.79	18.15	18.62
TPU/HD	17.05	18.80	19.51	22.06	22.74	22.23
TPU/HD/PPCP	16.26	18.48	20.17	21.68	22.51	21.73
TPU/HD/PPCP/$CaCO_3$	17.57	19.19	22.53	26.10	25.53	23.52
TPU/PP	18.32	20.18	20.38	22.29	22.92	24.49
TPU/PP/PPCP	16.90	18.39	20.48	27.43	27.55	26.50
TPU/PP/PPCP/$CaCO_3$	26.44	31.33	41.83	50.32	50.56	56.53

Table 3: Elongation of TPU/PO blends with and without calcium carbonate.

Blends	**Elongation (%)**					
	% of PO added					
	5	**10**	**15**	**20**	**25**	**30**
TPU/LD	460	428	448	448	426	400
TPU/LD/PPCP	600	600	580	568	544	528
TPU/LD/PPCP/$CaCO_3$	544	528	520	504	496	480
TPU/HD	440	408	400	396	396	390
TPU/HD/PPCP	484	444	420	400	400	396
TPU/HD/PPCP/$CaCO_3$	448	438	404	396	384	380
TPU/PP	404	390	396	380	390	384
TPU/PP/PPCP	440	428	420	400	380	380
TPU/PP/PPCP/$CaCO_3$	280	264	220	224	186	164

Table 4: Flexural strength of TPU/PO blends with and without calcium carbonate.

Blends	**Flexural Strength (Kg/cm^2)**					
	% of PO added					
	5	**10**	**15**	**20**	**25**	**30**
TPU/LD	17.64	18.90	20.16	22.68	16.38	17.64
TPU/LD/PPCP	20.16	25.20	26.46	31.51	27.72	22.68
TPU/LD/PPCP/$CaCO_3$	30.25	25.20	27.72	32.77	32.77	37.81
TPU/HD	18.90	21.42	23.94	23.94	22.68	30.25
TPU/HD/PPCP	23.94	21.42	26.46	31.51	27.72	35.29
TPU/HD/PPCP/$CaCO_3$	25.20	27.72	32.77	40.33	42.85	36.55
TPU/PP	16.38	20.16	18.90	21.42	25.20	25.20
TPU/PP/PPCP	10.08	22.68	30.25	37.81	31.51	37.81
TPU/PP/PPCP/$CaCO_3$	18.90	25.20	35.29	46.63	41.59	41.59

Table 5: Flexural modulus of TPU/PO blends with and without calcium carbonate.

Blends	Flexural Modulus (Kg/cm^2)					
	% of PO added					
	5	10	15	20	25	30
TPU/LD	22.82	25.49	29.72	32.67	22.57	24.31
TPU/LD/PPCP	27.78	38.03	38.12	43.41	38.20	33.43
TPU/LD/PPCP/$CaCO_3$	45.64	37.15	42.86	51.92	53.25	63.06
TPU/HD	29.95	32.33	37.94	38.91	35.94	50.45
TPU/HD/PPCP	34.49	33.95	40.91	49.92	42.86	58.85
TPU/HD/PPCP/$CaCO_3$	38.03	43.93	50.65	67.26	71.46	64.34
TPU/PP	24.15	31.17	30.72	33.95	40.96	39.94
TPU/PP/PPCP	13.89	34.23	47.92	59.90	52.55	66.56
TPU/PP/PPCP/$CaCO_3$	28.53	39.94	55.91	82.09	77.52	87.86

Table 6: Impact strength of TPU/PO blends with and without calcium carbonate.

Blends	Impact Strength (Kg/cm^2)					
	% of PO added					
	5	10	15	20	25	30
TPU/LD	0.087	0.120	0.152	0.130	0.163	0.196
TPU/LD/PPCP	0.087	0.120	0.152	0.174	0.185	0.196
TPU/LD/PPCP/$CaCO_3$	0.239	0.239	0.272	0.304	0.304	0.174
TPU/HD	0.087	0.109	0.130	0.152	0.130	0.174
TPU/HD/PPCP	0.109	0.152	0.152	0.130	0.152	0.152
TPU/HD/PPCP/$CaCO_3$	0.109	0.130	0.174	0.217	0.196	0.185
TPU/PP	0.087	0.130	0.120	0.120	0.109	0.109
TPU/PP/PPCP	0.120	0.130	0.120	0.163	0.174	0.196
TPU/PP/PPCP/$CaCO_3$	0.152	0.185	0.207	0.261	0.239	0.207

Table 7: Hardness of TPU/PO blends with and without calcium carbonate.

Blends	Shore D Hardness					
	% of PO added					
	5	10	15	20	25	30
TPU/LD	23	24	27	29	28	30
TPU/LD/PPCP	28	29	30	30	31	30
TPU/LD/PPCP/$CaCO_3$	31	32	32	34	35	36
TPU/HD	25	28	30	32	33	34
TPU/HD/PPCP	29	29	30	32	30	31
TPU/HD/PPCP/$CaCO_3$	34	37	41	43	40	41
TPU/PP	28	29	30	35	33	35
TPU/PP/PPCP	26	32	32	36	38	44
TPU/PP/PPCP/$CaCO_3$	38	42	45	48	49	46

The impact strength of the blends such as TPU/LD, TPU/HD, TPU/PP with and without compatibiliser and calcium carbonate as filler was measured and shown in Table 6. Addition of the compatibilizer such as PPCP was found to increase the blend miscibility and toughness of TPU/LD, TPU/HD and TPU/PP blends. The shore D hardness of the PU/PO's blends with and without compatibilizer and filler was measured (Table 7). The shore hardness of the blends was found to increase with the addition of the compatibilizer and filler.

3.2. Morphology

Figures 8a-8f show SEM photographs of TPU/PO's blends with and without compatibilizer. The presence of cryogenic fracture along the boundaries of the blends without compatibilizer indicates that the immiscibility of the two polymers blends. When PPCP and calcium carbonate were added into the TPU/PO's blends, the blends display significantly finer morphology. When filler is introduced into a polymeric material, the ideal is that it has regular granulometry and that its particles are sufficiently small to enable good distribution in the matrix [13]. It gives the evidence that the above compatibilizers give better results for miscibility of the blends.

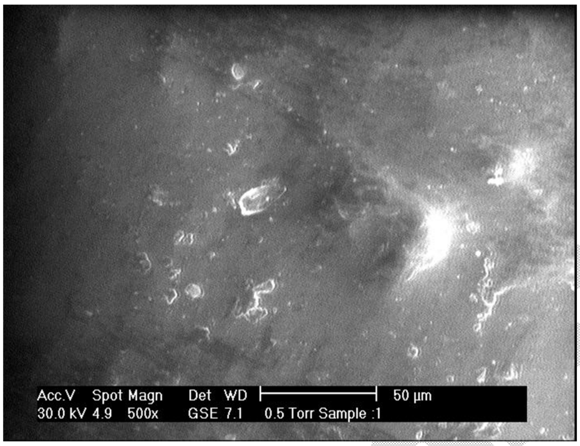

Figure 8a: SEM for PU/LD/PPCP.

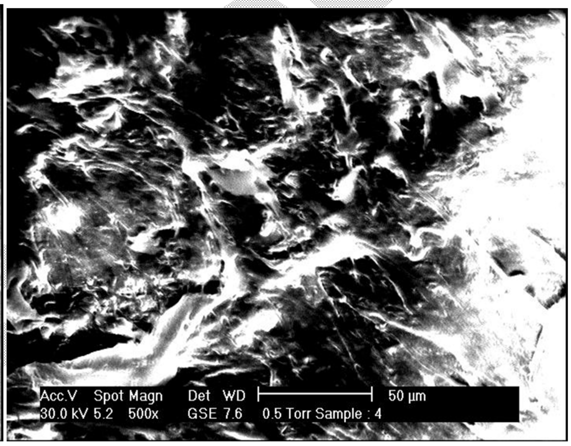

Figure 8b: SEM for PU/LD/PPCP/$CaCO_3$.

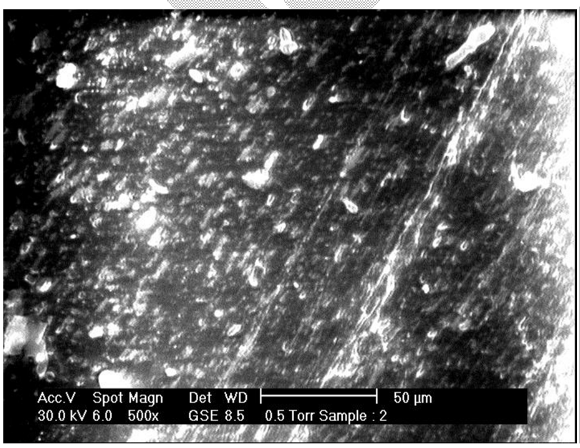

Figure 8c: SEM for PU/HD/PPCP.

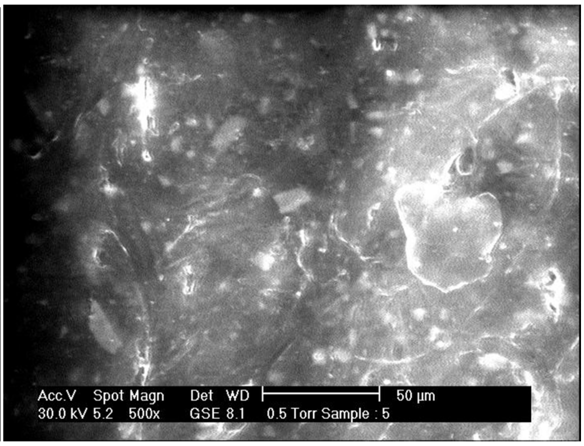

Figure 8d: SEM for PU/HD/PPCP/$CaCO_3$.

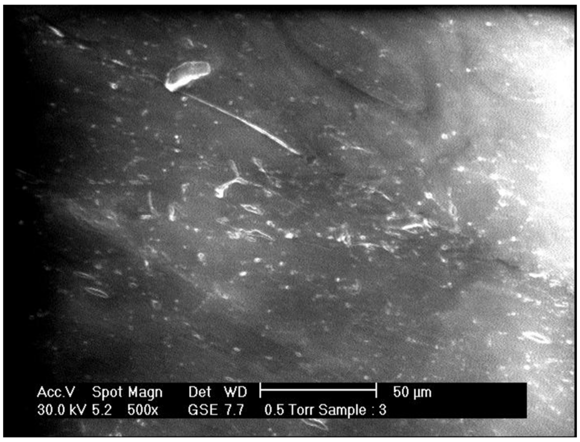

Figure 8e: SEM for PU/PP/PPCP.

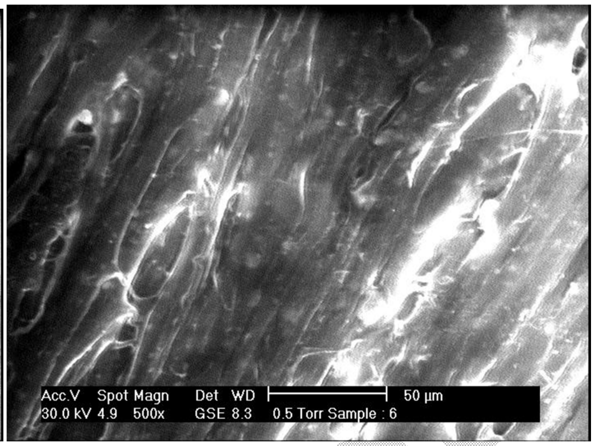

Figure 8f: SEM for PU/PP/PPCP/$CaCO_3$.

3.3. Thermal properties

DSC was used to evaluate the thermal property of the TPU/LD, TPU/HD and PU/PP blend with and without PPCP and calcium carbonate (Figure 9a-9f). Thermal analytical curve shows as endothermic peak of all the blends shows the slight increases thermal behavior of the filler filled blends. The increasing in melting temperature was due to the increasing crosslink between calcium carbonate and blend matrix that increased the nucleation activity of calcium carbonate [14].

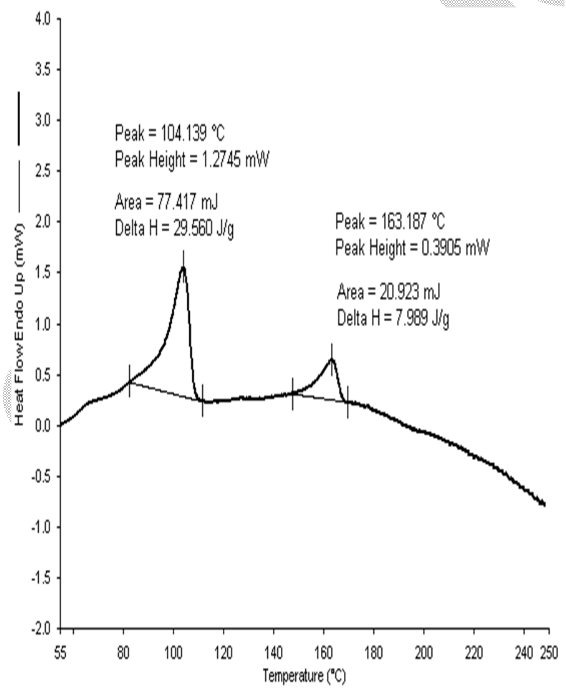

Figure 9a: DSC for PU/LD/PPCP.

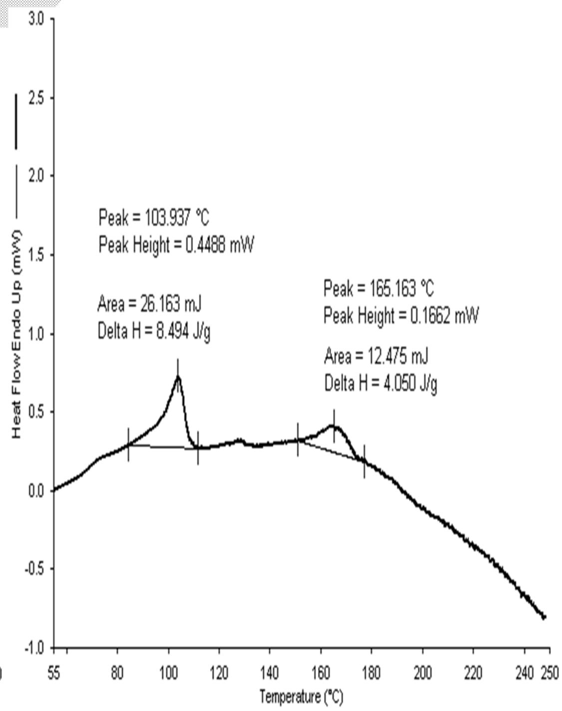

Figure 9b: DSC for PU/LD/PPCP/$CaCO_3$.

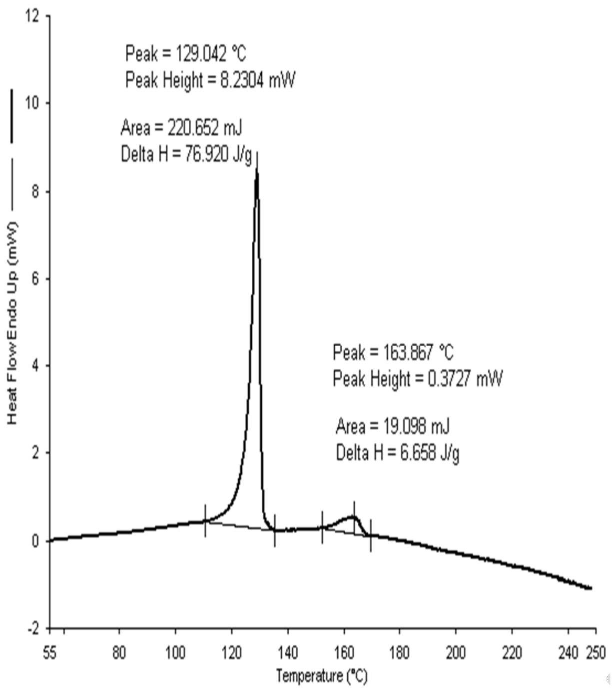

Figure 9c: DSC for PU/HD/PPCP.

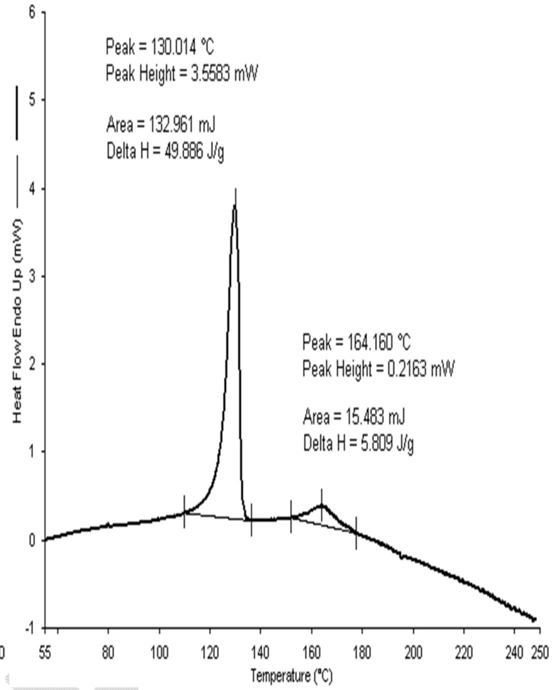

Figure 9d: DSC for PU/HD/PPCP/$CaCO_3$.

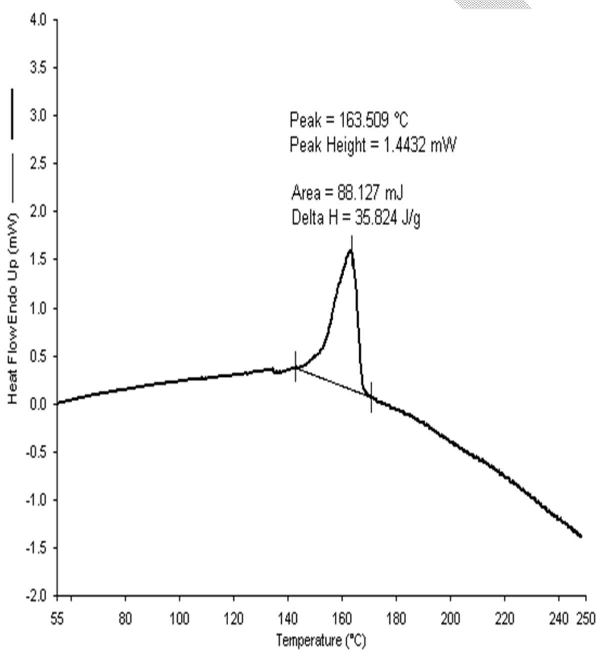

Figure 9e: DSC for PU/PP/PPCP.

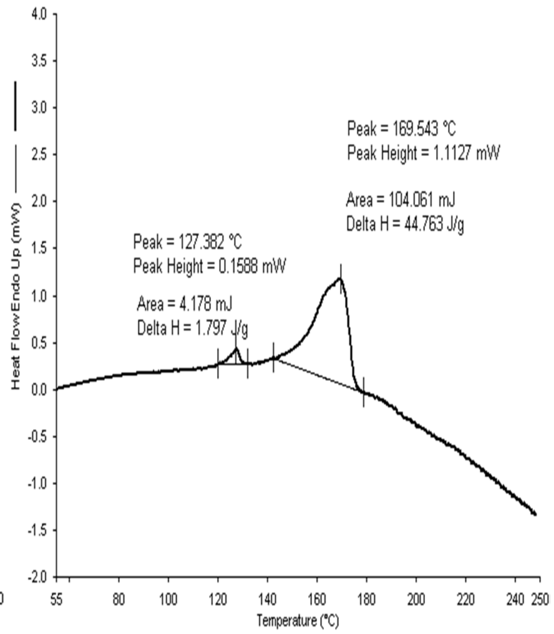

Figure 9f: DSC for PU/PP/PPCP/$CaCO_3$.

4. Conclusion

PPCP was found to be a good compatibiliser for TPU/LD, TPU/HD and TPU/PP blends. Addition of calcium carbonate as filler was found to increase the mechanical properties such as tensile strength, impact strength, and hardness, but decreases the elongation. SEM images show that the addition of small quantities of compatibiliser and filler are required to improve the mechanical properties of the blends studied.

Competing Interests

Authors declare that they have no competing interests.

Authors' Contributions

All authors contributed equally to this work.

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