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REVIEW

Biodegradable Polymer Blends and Composites: An Overview[1]

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Abstract—Biodegradable polymers belong to a family of polymer materials that found applications ranged from medical applications including tissue engineering, wound management, drugs delivery, and orthopedic devices, to packaging and films applications. For broadening their potential applications, biodegradable polymers are modified utilizing several methods such as blending and composites forming, which lead to new materials with unique properties including high performance, low cost, and good processability. This paper reviews the recent information about the morphology of blends consisting of both biodegradable and non-biodegradable polymers and associated mechanical, rheological, and thermal properties of these systems as well as their degradation behavior. In addition, the mechanical performance of composites based on biodegradable polymers is described.

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INTRODUCTION

Oil-based polymer materials have been known for more than 90 years and a lot of applications have been found for them, ranging from simple packaging to heavy constructions, and they play an important role in the improvement and quality of human modern life. On other hand, the wide using of polymer materials brings danger problems to ecosystem. The rising oil prices and increasing activity in regards to environmental pollution prevention have pushed research and development of biodegradable polymers.

The academic researches on properties and applications of biodegradable polymers including polylactic acid (PLA), polybutylene succinate (PBS), polybutylene succinate adipate (PBSA), poly(butyleneadipate-*co*-terephthalate) (PBAT), polycaprolactone (PCL) and thermoplastic starch (TPS) cause a lot of interest since the first synthesis of these materials [1]. The most important property of mentioned polymers is their biodegradability. Other properties, such as mechanical, thermal, rheological, and processing properties related to the structure of the polymer are generally competitive to those of the traditional polymers, e.g. PE, PP, polystyrene, and PET, for example good strength, stiffness, and gas barrier characteristics of PLA [2], water, oil and chlorine resistance of PCL [3], high ductility of PBSA and PBAT [4], fast biodegradability of TPS [5]. In addition, the wide ability of these materials to be fabricated using traditional processing technologies [6] broadened their applications.

However, some disadvantages of biodegradable polymers including low viscosity and poor toughness in PLA [7], low modulus in PBAT [8], and thermal sensitivity in PCL (the melting point less than 60°C) [2] were reported previously. Also, the high cost of these polymers comparing with that of traditional polymers is another disadvantage (Fig. 1). To overcome these drawbacks, various methods such as copolymerization, compositing and blending are com-

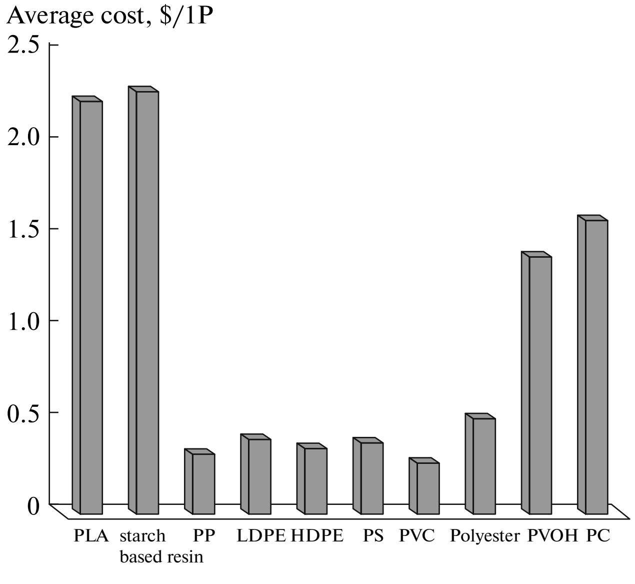

Fig. 1. Cost comparison between some biodegradable and traditional polymers.

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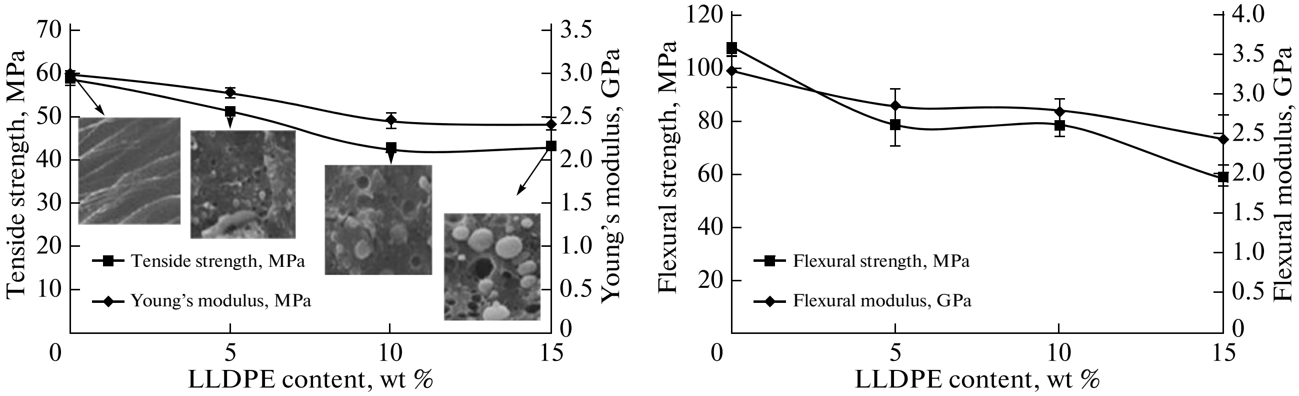

Fig. 2. Mechanical and morphological properties of PLA/PE polymer blends. Reprinted with permission from Reference [9]. Copyrights 2014, Wiley Periodicals, Inc.

monly used. Among them, blending is the most popular because of its low cost comparing to preparing copolymers. Most of commercial plastic materials are polymer blends, such as polycarbonate/poly(acrylonitrile-butadiene-styrene) blend (PC/ABS) (*Triax*$^{\text{TM}}$), PP/ ethylene-propylene-diene monomer rubber (PP/EPDM) (*Santoprene*$^{\text{TM}}$, and polyvinyl chloride/polyamide (PVC/PA) (*Cylon*$^{\text{TM}}$).

The fabrication of materials containing both biodegradable and non-biodegradable polymers can be effective method to reduce the total amount of polymer waste, which cannot be degraded in nature. In this paper, the recent works reporting the preparation, properties and biodegradation behavior of polymer blends and composites containing biodegradable and non-biodegradable polymers are reviewed.

Polylactic Acid Systems

PLA/PE blends. The first works documented the properties of PLA/PE blends were reported by Raghavan and Emekalam [9], where the effect of starch additives on the degradation of blend was investigated. The results showed that the starch additives enhance the acid degradability of the blend. The effect of cotton by-products as fillers on the mechanical properties of PLA/LDPE blends was investigated in order to reduce the high cost production of PLA [5], and it was found that the addition of the filler materials to PLA/LDPE blend increased the Young modulus whereas it decreased the strength and elongation.

Balakrishnan et al. [10] prepared PLA/LLDPE polymer blends with low content of LLDPE (<20 wt %), and determined their mechanical and thermal properties. In this case poor compatibility in the blend and decrease of tensile properties of the blend comparing to pure PLA were observed (Fig. 2). The poor compatibility of PLA/PE blends was also reported by Hamad et al. [11], where blends of PLA and LDPE were prepared using a single screw extruder. The compatibility between PLA and LDPE was determined through the effect of PLA content on the mechanical and rheological properties of the fabricated blends (Fig. 3). For improving the compatibility of PLA/PE blends and related mechanical performance, various compatibilizers including PLA-*co*-PE [11], PE-*g*-glycidyl methacrylate (PE-*g*-GMA) [12], styrene/ethylene-butylene/styrene grafted maleic anhydride (SEBS-*g*-MA) [13] and PE-*g*-MA [13, 14] were used. In general, the compatibilizers reduce the domain size of dispersed phase and give the strongest interfacial adhesion between phases, which can result in enhancing the mechanical properties of the blend.

Anderson and Hillmyer [12] studied the mechanical properties of PLA/PE blends compatibilized by PLA-*co*-PE. Blending of PLA with PE improves the impact strength of the material comparing to pure PLA and it was more pronounced, when compatiblizers were used, whereas the tensile properties including the tensile strength, elongation, and Young's modulus in both compatiblized and non-compatiblized materials were less than those of pure PLA. In another work reported by Kim et al. [13], PE-*g*-GMA was used for improving mechanical (tensile) properties of PLA/LDPE blends due to chemical reaction between PLA and PE-*g*-GMA, which contributes to strengthen the interface between PLA and LDPE. Recently, Singh et al. [14] used PE-*g*-GMA as a compatibilizer for a blend contained 20 wt % PLA and 80 wt % LLDPE and found that optimum tensile strength and elongation at break were achieved at 4 wt % of the compatibilizer, which was attributed to the specific interaction between the blend and compatibilizer.

PLA/PP blends. The first report on the preparation and characterization of PLA/PP polymer blends belongs to Reddy et al. [15]. Thermal and morphological properties of the prepared blends showed their partial compatibility even in the melt phase. The morphology of the blend having 50 wt % PLA showed ill-defined interfaces, which are similar to those obtained in the compatibilized PLA/PE systems. Besides,

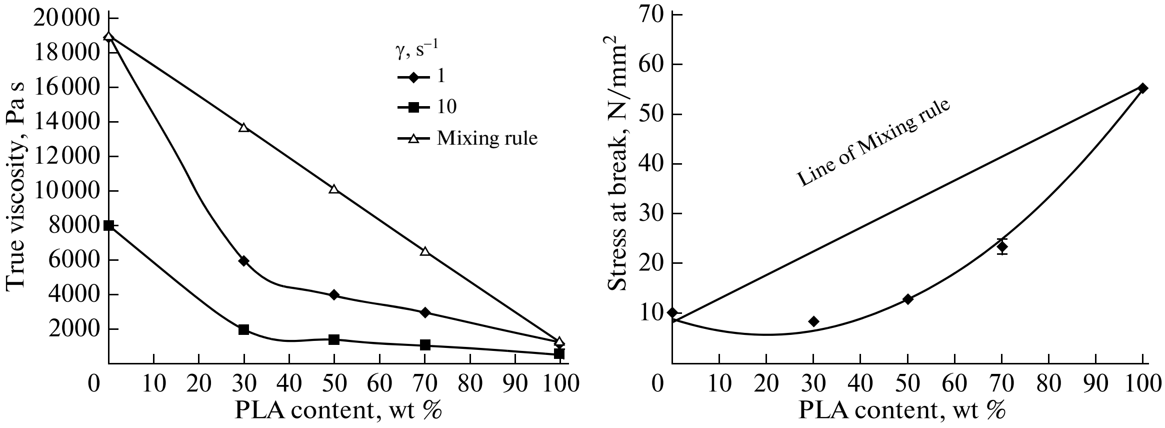

Fig. 3. Effect of PLA content on the rheological and mechanical properties of PLA/LDPE polymer blends. Reprinted with permission from Reference [10]. Copyright 2010, SAGE Publications.

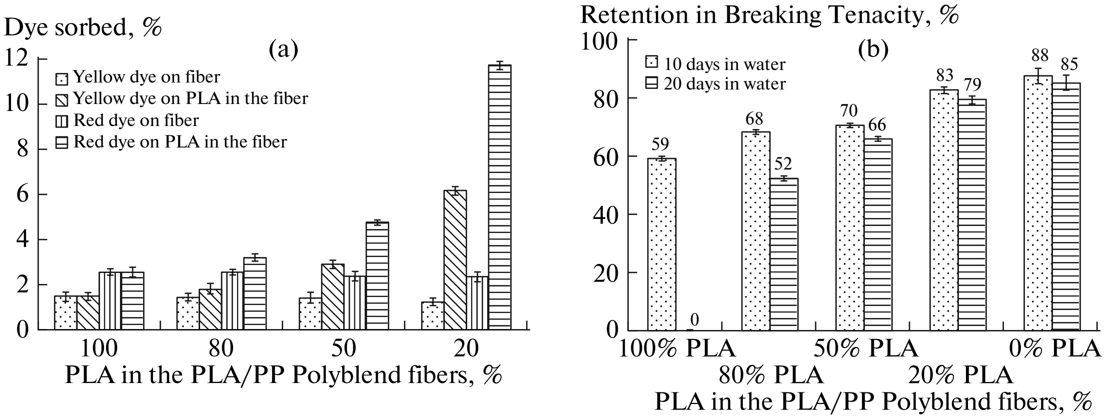

Fig. 4. (a) Dye-ability of PLA/PP polymer blend, (b) breaking tenacity of PLA/PP (50/50) blend after hydrolysis. Reprinted with permission from Reference [15]. Copyright 2008, Elsevier.

PLA/PP blend fibers are more resistant to hydrolysis than pure PLA, and PP improves the dye-ability of PLA (Fig. 4).

The partial compatibility in PLA/PP blends prepared using a single screw extruder was confirmed by Hamad et al. [16], where the calculations of the interfacial tensions showed higher compatibility of blend comparing to other PLA/synthetic polymer systems. Rheological study revealed that fabricated blend possesses low viscosity compared to that of pure PP, which resulted in improving the extrusion ability of PLA.

For improving the compatibility in PLA/PP polymer blends, various compatibilizers were used. Choudhary et al. [17] used PP-*g*-MA and PP-*g*-GMA as compatibilizers for a blend containing 90 wt % PLA and 10 wt % PP and investigated the effect of the compatibilizers on thermal, mechanical, and morphological properties. Thermal stability of PLA/PP/PP-*g*-MA blend is better than that of pure PLA, uncompatibilized blends, and another compatibilized blend (PLA/PP/PP-*g*-GMA); this behavior was attributed to finer and more homogenous distribution of PP phase in PLA matrix, as shown in Fig. 5.

In other works [18, 19], the effect of SEBS-*g*-MA and PP-*g*-MA as compatibilizers for PLA/PP (80/20 wt %) blend prepared using a twin screw extruder in different ratios was compared. The results showed that PP-*g*-MA is more effective for improving tensile strength of the blend, whereas the impact strength of the blend was significantly enhanced by addition of SEBS-*g*-MA. From the above results of tensile and impact strengths of the PP/PLA (80/20) blends, it is suggested that the PP-*g*-MAH acts as an effective compatibilizer to increase the tensile strength of the blends, while the SEBS-*g*-MAH is an effective impact modifier to increase the impact strength of the PP/PLA blends. Lee and Kim [20] used hybrid compatibilizers composed of PP-*g*-MA and PE-*g*-GMA in the presence of an impact modifier. The blend compatibilized by PE-*g*-GMA had the highest impact strength comparing with the other compositions (PLA/PP/PP-*g*-MA and PLA/PP/PP-*g*-MA/PE-*g*-

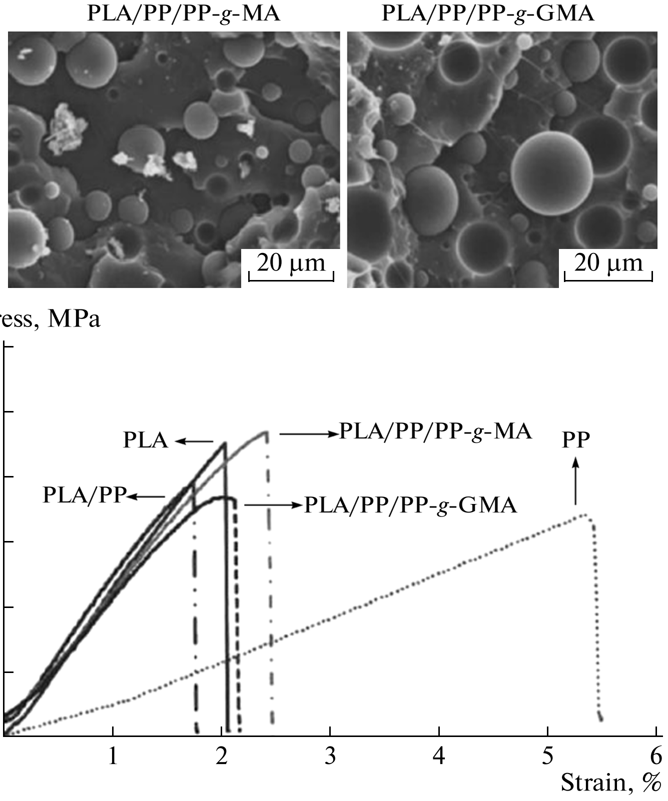

Fig. 5. Morphology and mechanical properties of PLA/PP/PP-*g*-MA and PLA/PP/PP-*g*-GMA blends. Reprinted with permission from Reference [17]. Copyrights 2011, Wiley Periodicals, Inc.

GMA) due to role of PE-*g*-GMA as an effective compatibilizer between PLA and the toughening modifier leading to enhance the impact strength of the blend.

The fabrication of nanocomposite blends containing PLA/PP and sepiolite, and the effect of the latter on the rheological and mechanical properties of PLA/PP blend was investigated by Nunez et al. [21]. The nanocomposite blends exhibited lower tensile strength and Young's modulus values and an increase in elongation at break, tensile toughness, complex viscosity, and storage modulus compared to those of the nanocomposite of PLA without PP [22]. Chen et al. [23] used bamboo fiber (BF) for preparing composite blends based on PLA/PP blends in the presence of PP-*g*-MA and they found that good rheological, morphological and thermal properties could be achieved at ratio of PP/PLA/BF/PP-*g*-MA equal to 48.75/13/35/3.25 wt %.

PLA/PS blends. PLA/PS blends are described in numerous publications; among them the first was reported by Biresaw and Carriere on interfacial tension of PLA/PS blends determined using different theoretical and experimental methods [24]. Thereafter, Mohamed et al. [25] studied the compatibility and thermal properties of PLA/PS blend and found a kind of interaction between PLA and PS, which was attributed to the physical bond between unshared pair of electrons (n) of the carbonyl groups in PLA and π-electrons of aromatic rings in PS (n–π bond) that was detected by shift of carbonyl absorption band (near 1760 cm^{-1}) of pure PLA toward the less wavenumbers in the blend (Fig. 6a and 6b). This interaction resulted in a kind of poor compatibility, which led to higher thermal stability of the blend compared to that of pure PLA (Fig. 6d). The same result was reported by Hamad et al. [26], who studied recycling of PLA/PS blends.

Compatibility of PLA/PS polymer blends was estimated by study of tensile properties and compared with that of other PS/biodegradable systems including PCL/PS and PBS/PS [27] prepared using extrusion process. A good compatibility in PCL/PS and PBS/PS blends was found compared to that of PLA/PS. The investigation of rheological behavior of PLA/PS blends reported by Hamad et al. [28] exhibited a typical shear-thinning behavior over the range of the studied shear rates, and the viscosity of the blend decreased with increasing of PLA content.

The compatibilization process of this blend was reported by Zuza et al. [29]. PS was functionalized by copolymerization of styrene and hydroxystyrene (HS). Compatibility of PLA with P(S-*co*-HS) increased due to formation of hydrogen bonds –OH···O=C; besides it was noted that the blend has a

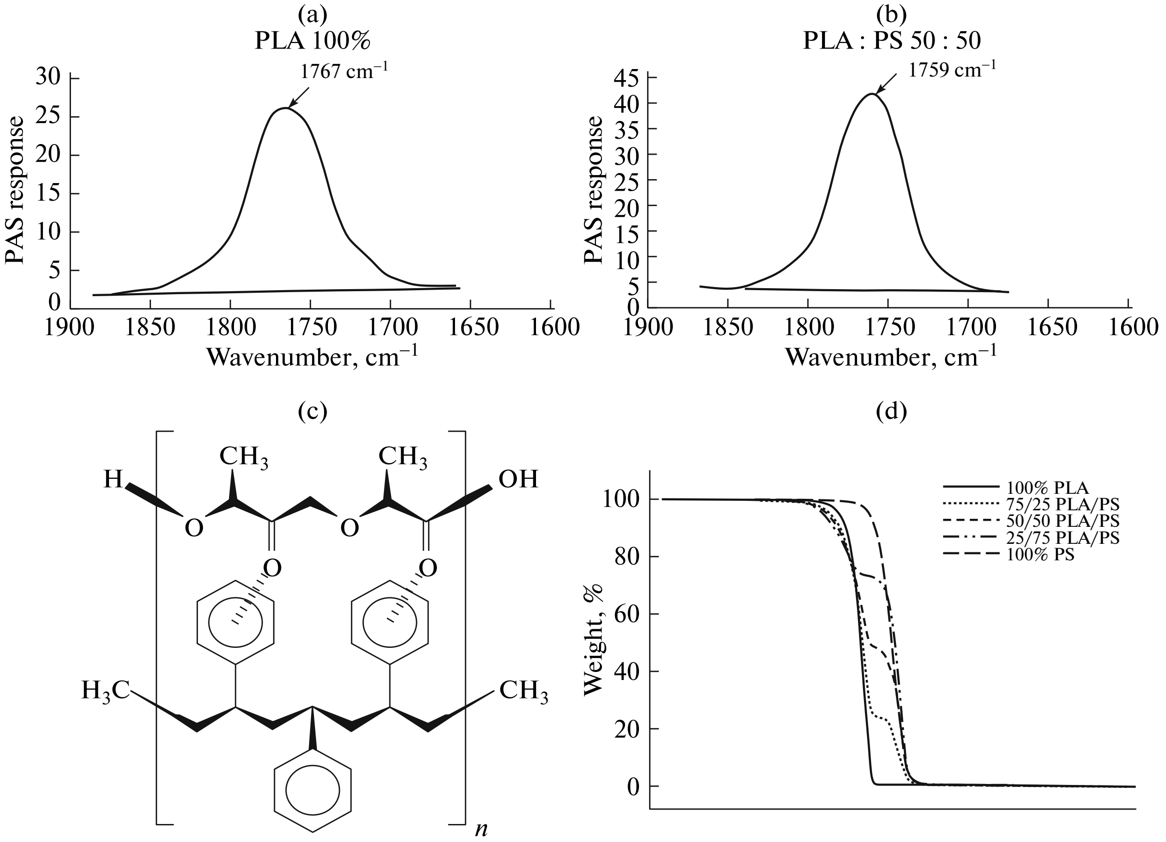

Fig. 6. FTIR spectra of (a) PLA and (b) PLA/PS blend, (c) n–π bond between PLA and PS (d) thermal stability of PLA and PLA/PS blends. Reprinted with permission from Reference [25]. Copyrights 2007, Wiley Periodicals, Inc.

single glass transition temperature (T_g) in whole composition range and a single-phase morphology. SEM observations also confirmed phase separation in the uncompatibilized PLA/PS blends (Fig. 7a), whereas The SEM picture of the compatibilized PLA/PS blends confirmed its single-phase morphology (Fig. 7b).

PLA/ABS blends. Due to good mechanical properties of ABS including impact strength, tensile strength, and tensile modulus, it was used extensively in the blending technology for preparing new materials with unique properties. PLA/ABS polymer blends were also prepared, compatibilized using styrene/acrylonitrile/glycidyl methacrylate copolymer (SAN–GMA) by incorporating with ethyltriphenylphosphonium bromide (ETPB) as catalyst, and characterized by Li and Shimizu [30]. The results summarized in Fig. 8 revealed that uncompatibilized blends of PLA and ABS have morphologies with big second-phase size and weak interface leading to poor mechanical properties with low elongation at break and impact strength. SAN–GMA in the presence of ETPB was an effective reactive compatibilizer for PLA/ABS blend that was confirmed by significant improvement in dispersion of rubber particles and improved impact strength and elongation at break with a slight loss in modulus and tensile strength compared to pure PLA.

ABS–GMA synthesized by emulsion polymerization was also incorporated for toughening PLA [31]. ABS–GMA was found an effective toughening agent, as impact strength of PLA/ABS–GMA with 1 wt % GMA was 27 times higher than that of pure PLA and the elongation at break of the blend was also higher.

Recently [32], effect of various compatibilizers including PE-*g*-epoxy, SAN-*g*-MA, SAN-*g*-GMA and maleic anhydride grafted ethylene propylene rubber (EPR-*g*-MA) on mechanical performance of PLA/ABS blend was studied and for improving thermal stability of PLA, Songsorb–3270 was added to the blend. Mechanical properties of the blend were further improved by addition of SAN-*g*-GMA and Songsorb–3270. The impact strength and tensile strength of the blend containing SAN–GMA and Songsorb–3270 made it suitable to apply in car console boxes.

PLA/PC blends. Kanzawa and Tokumitsu [33] prepared PLA/PC blends and used PBAT in the presence of dicumyl peroxide (DCP) as a radical initiator to improve the elongation at break, tensile strength, and impact strength of the blend. It was found that DCP induces the reaction between PBAT and PLA resulting in a good dispersion. On the other hand, PC tends to

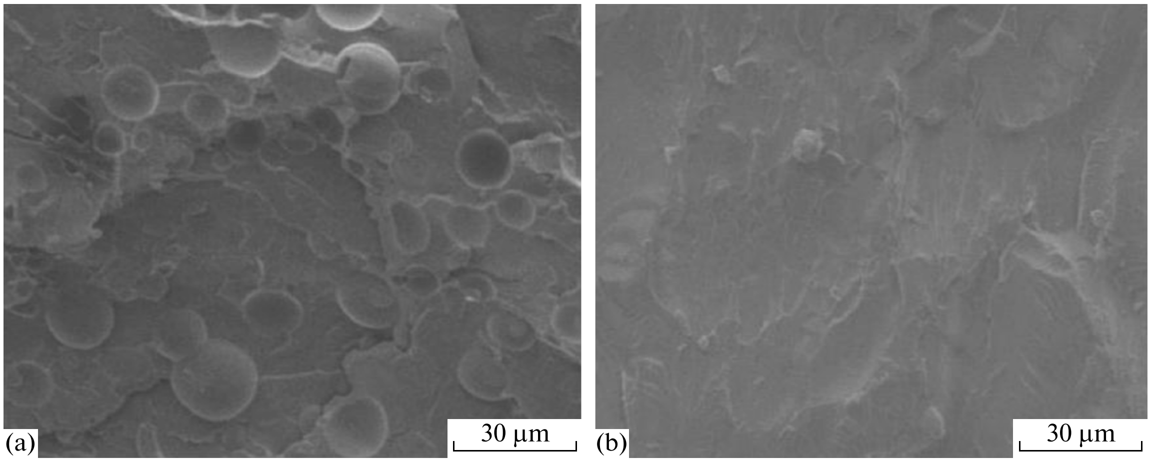

Fig. 7. SEM morphology of (a) PLA/PS blend and (b) PLA/PS-*co*-HS blend. Reprinted with permission from Reference [29]. Copyright 2008, American Chemical Society.

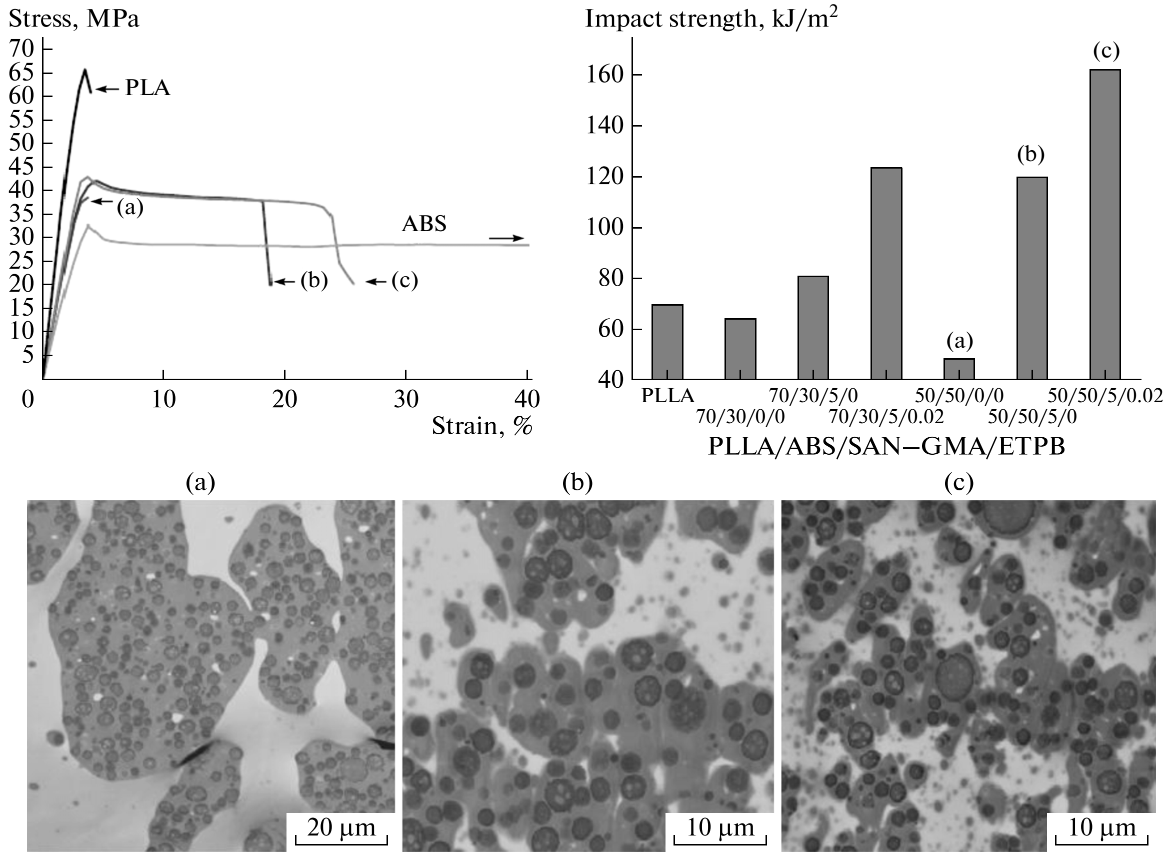

Fig. 8. Mechanical properties and TEM morphology of PLA/ABS/SAN–GMA/ETPE blend: (a) 50/50/0/0, (b) 50/50/5/0, and (c) 50/50/5/0.02. Reprinted with permission from Reference [30]. Copyright 2009, Elsevier.

locate near the new phase (PBAT–PLA) due to its good compatibility leading to a multi-dispersed phase of PLA/PBAT/PC. The new developed morphology contributed to enhance the ductility of the fabricated material. Figure 9 shows the role of DCP in the improving the tensile properties of PLA/PBAT/PC.

Lee et al. [34] used three types of compatibilizers SAN-*g*-MA, poly(ethylene-*co*-octene) rubber grafted by maleic anhydride (EOR-*g*-MA), and poly(ethylene-*co*-glycidyl methacrylate) (EGMA) for enhancing the properties of blends containing 30 wt % PLA and 70 wt % PC. The blends were prepared using a

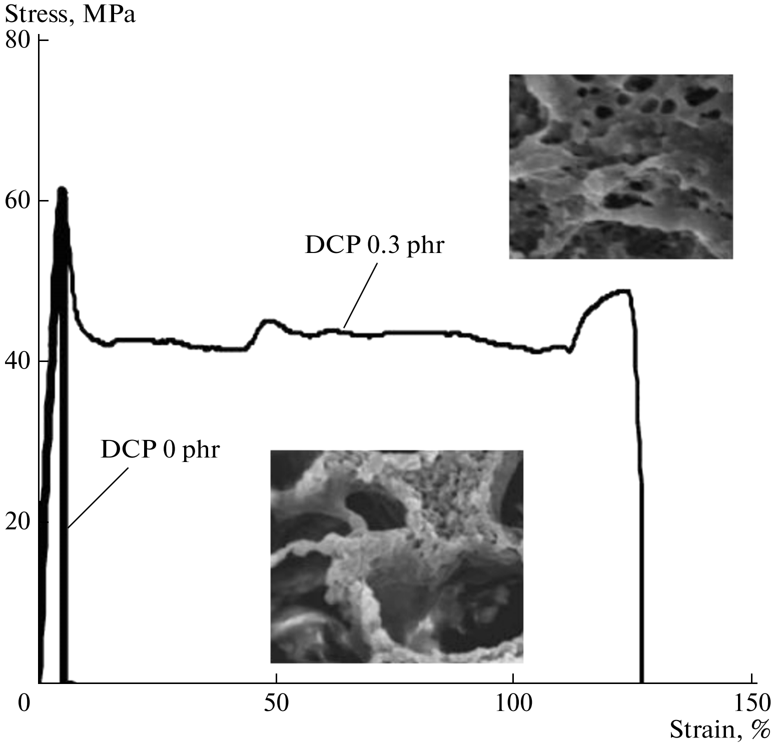

Fig. 9. Stress—strain curves of PLA/PBAT/PC blends with without DCP and the associated SEM images of the blends after impact tests. Reprinted with permission from Reference [33]. Copyrights 2011, Wiley Periodicals, Inc.

twin screw extruder and characterized in term of mechanical properties, rheology, and biodegradability. The analysis of mechanical properties showed that SAN-*g*-MA is the most effective compatibilizer for improving the performance and properties of PLA/PC blend. Biodegradability of the compatibilized blends was determined through the hydrolysis ability; it was found that PLA/PC/SAN-*g*-MA is most resistant to hydrolysis comparing to other compositions, which was attributed to the good compatibility between the components of the blend due to decrease of PLA phase size dispersed in PC matrix (Fig. 10).

Recently, Wang et al. [35] used poly(butylene succinate-*co*-lactate) (PBSL) and epoxy (EP) as compatibilizers for PLA/PC polymer blends prepared by twin screw extruder. The effect of compatibilizers on the thermal and mechanical properties of the blend showed that this combination could facilitate both the toughness and heat resistance of PLA/PC blend.

Thermoplastic Starch (TPS) Systems

Starch is a natural polymer with the advantages of being renewable, biodegradable, abundant, and low cost. Firstly, starch was used extensively in plastic industry as a filler material [36] to produce eco-friendly and low cost plastic materials. Due to the decreasing in mechanical properties and difficulties of processing highly filled polymer materials, granular starch composites are generally limited to starch contents of 40 wt % or less.

In the last ten years starch was used in plasticized form, so-called thermoplastic starch (TPS), as main component in polymer blends. Various plasticizers were used to prepare TPS such as glycerol, formamide, and urea [37]. TPS is generally fabricated by compounding starch/plasticizer mixture in extruders or internal batch mixers under high sharing conditions, where both plasticizer and shear deformation induced to the mixture during the compounding change starch granular morphology through disrupting *H-bonds* between starch chains and forming new *H-bonds* between plasticizers molecular and starch chains. A number of works reporting preparation and the application of TPS in the plastic industries were devoted in the last ten years, where polymer blends having different contents of TPS plasticized by various plasticizers were fabricated and investigated [37]. In addition, the rheological behavior of TPS revealed a good processability of TPS by traditional technologies used for processing of conventional plastics such extrusion and injection. Kaseem et al. [38] prepared TPS materials with different contents of glycerol ranging from 20% to 35% using a single screw extruder provided by a slit die for determining the rheological properties. The results showed that TPS melts were pseudoplastic in manner similar to other polymer systems, and the shear viscosity decreases with increasing shear rate at different

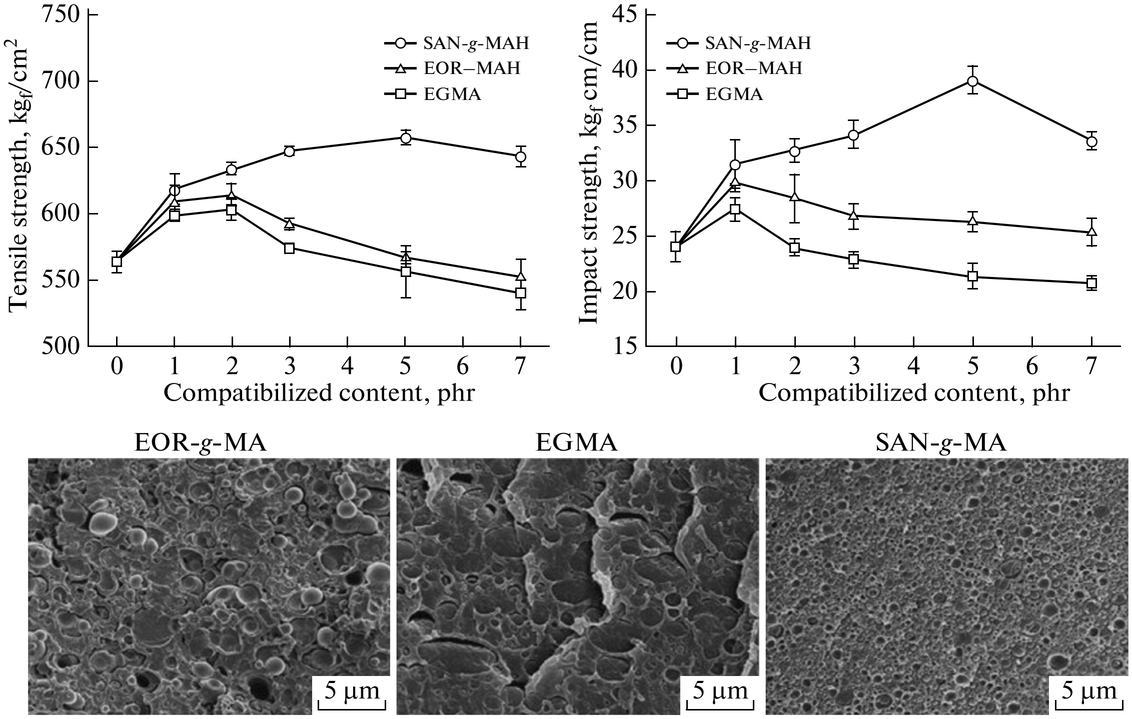

Fig. 10. Mechanical properties and morphologies of PLA/PC (30/70) blend compatibilized by EOR-*g*-MA, EGMA, and SAN-*g*-MA. Reprinted with permission from Reference [34]. Copyright 2012, Elsevier.

temperatures and with increasing glycerol content in the material (Fig. 11).

TPS/PE blends. The first work investigated the properties of blends containing PE and TPS was reported by Pierre et al. [39]. Glycerol plasticized TPS and the blends were prepared on step using a single screw extruder for TPS fabrication connected to a twin screw extruder, which was used for blends preparation. The mechanical, thermal and morphological properties of prepared blends were determined. The incompatibility between two components of the blend led to less thermal stability comparing with pure PE. The mechanical properties showed that the elongation at break of blend is similar to that of PE, while the modulus was less than that of PE. Prinos et al. [40] studied the effect of ethylene/vinyl acetate (EVA) copolymer on the mechanical and thermal properties of TPS/LDPE polymer blends; also glycerol was used as plasticizer. The results showed that mechanical properties and thermal stability improved with increasing EVA content in the blend.

Ning et al. [41, 42] prepared high performance TPS/LLDPE polymer blends using one step extrusion process in the presence of two plasticizers; citric acid (CA) and glycerol in the absence of any compatibilizer. The effect of plasticizer type and its content on rheological and mechanical properties of the blend was studied. The results showed that viscosity of the blend decreases with increasing of CA content that was attributed to the acidity hydrolysis effect of CA on the TPS, which resulted in decreasing of TPS molecular weight. Good compatibility between TPS and PE was achieved when CA was used as a plasticizer and led to improvement of mechanical properties of the blend, while tensile strength and elongation at break reached the levels of the conventional plastics at certain compositions.

Pushpadass et al. [43] studied the effect of processing method on mechanical, thermal and morphological properties of films fabricated from TPS/LDPE blend that was prepared by either single-step twin screw extrusion or by two-steps process involving compounding of the ingredients before film formation. Tensile strength and water vapor permeability of film prepared using a single-step approach are impaired, while decreasing of TPS viscosity during compounding in the two-steps process enhances the compatibility between two components and improves tensile strength and decreases water vapor permeability. Gonzalez et al. [44] prepared high performance TPS/LDPE polymer blends using single-step combined with twin screw and single screw extrusion process in the presence of different ratios of glycerol as a plasticizer. The unique mechanical properties of the blend containing 45 wt % TPS and 55 wt % LDPE were obtained through controlling processing conditions. Tensile strength, elongation at break, and modulus of the blends are nearly higher or similar to those of pure PE. Also, high performance TPS/PE polymer blend was prepared by Cercle et al. [45] through controlled emulsification.

The effect of TPS on mechanical and thermal properties of TPS/HDPE blends during UV-accelerated aging was studied in [46]. The presence of TPS in the blend resulted in increasing of tensile modulus of TPS/HDPE blends, which was attributed to increasing of crystallinity produced by starch retro-gradation.

The compatibilization process of TPS/PE blends was reported in various works [47–53]. Although, the most popular compatibilizer is PE-*g*-MA [53], additives of MA and DCP were used during blend compounding to achieve compatibilization [53]. The presence of a compatibilizer resulted in improvement of mechanical properties including tensile strength, elongation at break, modulus, impact strength, thermal stability, and gas barrier (O_2, N_2 and CO_2). However, the incorporation of compatibilizers can result in increasing the viscosity of the materials and decreasing biodegradability due to the rise of compatibility.

TPS/PP blends. Kaseem et al. [54] prepared and studied properties of TPS/PP polymer blends containing glycerol as plasticizer; TPS and blends were prepared separately using a single screw extruder. The blends showed a shear thinning behavior leading to good processability of the blends by traditional processing machines. In addition, the lubrication effect of the glycerol acting between material and capillary rheometer die resulted in decreasing the viscosity of the blend as the glycerol content increased. Mechanical properties of the blend showed that Young's modulus increased sharply with increasing TPS and glycerol content, whereas the strain at break decreased. Rosa et al. [55] compared the plasticization effect of a biodiesel glycerol and commercial glycerol used for preparing TPS/PP blends. The results obtained were almost similar: tensile strength of the blend decreased by the increasing of TPS content. For producing TPS/PP blends that have a high renewable and biodegradable content with good mechanical properties, montmorillonite clays (MMT) and cloisite 30B (30B), which is MMT that has been organically modified with methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium salts, were incorporated [56]. Figure 12 shows TEM morphology of the blend with different compositions. As is seen the unmodified MMT was primarily located in the TPS phase due to its affinity and hydrogen bonding with TPS, whereas the organically modified 30B was both dispersed in TPS phase and located at the interface between TPS and PP, which leads to improving mechanical properties of the TPS/PP blends with high content of TPS.

TPS/PS blends. The thermal degradation of blends containing TPS plasticized by glycerol or buriti oil and PS was reported by Schlemmer et al. [57]. It was found that the blend having buriti oil-plasticized TPS was more thermal stable comparing with plasticized by glycerol. However, biodegradability tests showed that the former is more biodegradable than the later [58].

Buriti oil was also used for preparing TPS and PS waste blends [59]. Morphology of the blend showed good dispersion of the TPS in the PS matrix with distinct domains but poor thermal stability comparing with pure PS (Fig. 13). Oliveira et al. [60] studied the interfacial adhesion in blends between TPS plasticized by glycerol and PS treated with MA during melt mixing of blend components. Also, the effect of TPS content on degradation behavior during soil burial test determined by sample weight loss was investigated. Increasing of TPS content leads to the rise of total weight loss, which was attributed to role of TPS phase in easing the rate of bacterial growth during degradation process.

TPS/ABS blends. Preparation and study of properties of TPS/ABS blends were reported by Kaseem et al. [61, 62]. Thus, TPS plasticized by glycerol and ABS were blended using a single screw extruder and rheological and mechanical properties were determined. TPS/ABS blends are shear-thinning materials, in which the viscosity decreases with increasing shear rates, and viscosity of the blend decreased with increasing glycerol content indicating good processability of material utilizing the injection molding process. Poor mechanical properties of the blend in various compositions including stress at break and ductility were obtained, which indicated to the incompatibility between the components of the blend.

Polycaprolacton Systems

Polycaprolacton (PCL) is linear polyester manufactured by ring-opening polymerization of ε-caprolactone; it may be referred to biodegradable and nontoxic materials. It is a promising candidate for medical applications such as controlled release, especially for long-term drug delivery. Several works studying blends of PCL and synthetic polymers such as PE, PP, PS, PVC, and PC were reported [63–90].

PCL/PE blends. Ratnagifu and Scott [63] prepared PCL/PE blend using an internal mixer and studied the phase inversion during compounding. The results showed that the blend is incompatible in the studied range of the compositions.

Tjong and Bei [64] prepared PCL/LDPE blends in the presence of MA and compared them with poly(capro1actone)-*block*-poly(ethylene glycol) blends. Although the mechanical properties of the latter were higher than those of PCL/LDPE blends, the first were more compatible.

Matzinos et al. [65] studied the effect of PCL content and processing technique (injection molding and film blowing) on mechanical properties of TPS/LDPE blends. The morphology and some mechanical properties of the blends with 50 wt % PCL processed by two methods are shown in Fig. 14. In blown films there was a fine dispersion of PCL phase in LDPE/TPS matrix in the form of droplet-like particles with a mean size less than 2.5 μm resulting in

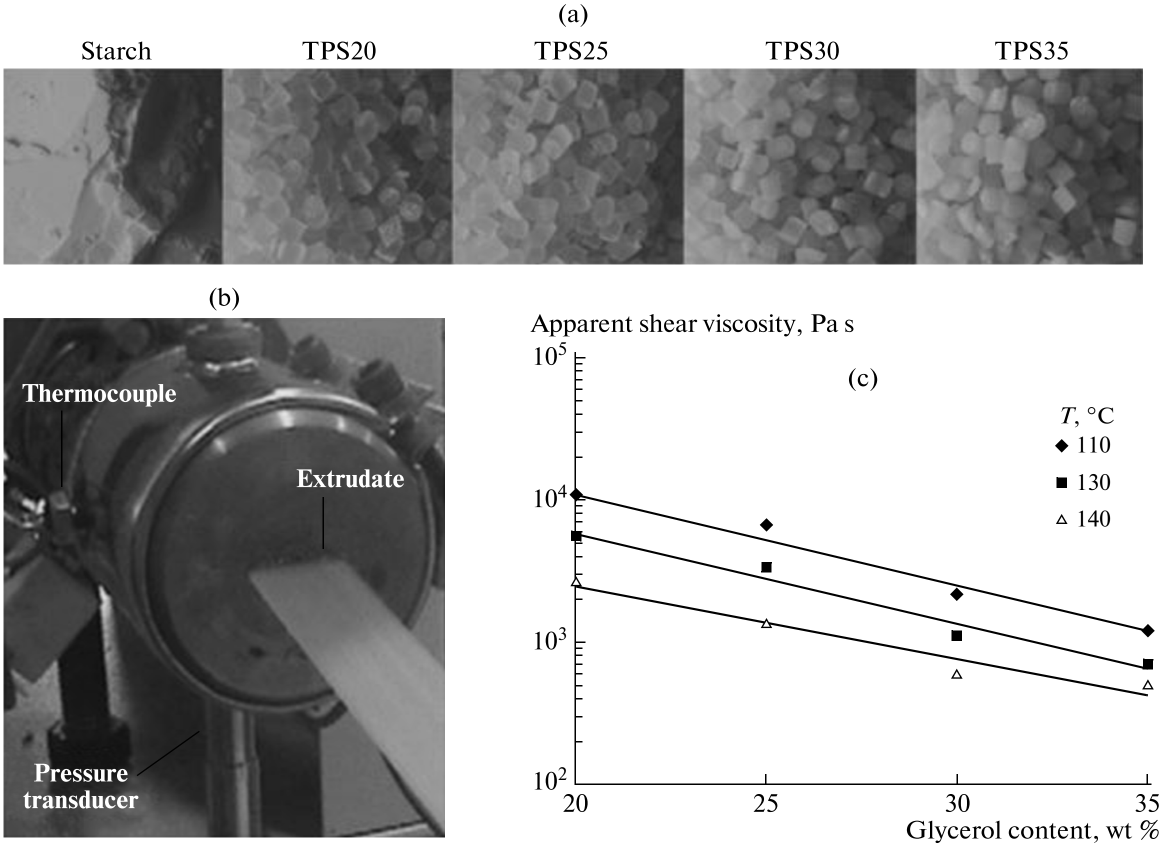

Fig. 11. (a) TPS samples, (b) slit die used for determining the rheological properties of TPS samples, (c) effect of the processing temperature and glycerol content on the viscosity of TPS samples. Reprinted with permission from Reference [38]. Copyright 2013, Central Institute of Plastics Engineering and Technology.

good mechanical properties compared to those obtained for the injection-molded blend samples where the inter-dispersion between the LDPE/TPS and PCL phases is very poor.

PCL/PP blends. Balsamo et al. [66] studied the compatibility of PCL/PP polymer blends prepared using the extrusion process. Morphology of the blends showed incompatibility between two components in the blend and coarse distributions of the dispersed phase in the matrix (indicted by arrows in Fig. 15). Also, it was found that PP acts as a nucleating agent for PCL.

In the work of Krucinskaet al. [67] rheological and thermal properties of PCL/PP/multiwall carbon nanotubes (MWCNTs) blend composites were studied, the results showed that the incorporation of MWCNTs into PCL resulted in a slight increase in both crystallinity degree and thermal resistance, but PP presence in the composite caused a decrease in the thermal stability of the blends. Also, PCL/PP/MWCNTs blend composites and the effect of MWCNTs on electrical properties of the resultant materials was reported by Ptschke et al. [68]. Morphological observations showed good MWNTs dispersion and distribution in the polymer matrix, thus yielding the formation of a conductive MWNTs network structure at low MWNTs contents.

PCL/PS blends. Good compatibility in PCL/PS blends was reported by Biresaw and Carriere [27] through the mechanical properties of prepared blends in various ratios, which were between the values of the corresponding pure components (PCL and PS). In addition, the compatibility of PCL/PS blends was investigated by Mohamed et al. [69]. Differential scanning calorimetry results showed good compatibility between two components, which was attributed to the intermolecular n–π interactions between PCL and PS. Thermal stability of these blends is higher than that of pure PCL; the same result was obtained in the case of PLA/PS blend [25, 26].

PLC/PVC blends. The first report describing experiments on PCL/PVC polymer blends was documented by David el al. [70], where the effect of dibasic lead phthalate and dibutyltindilaurate as thermal stabilizers on diffusion of PCL phase in PCL/PVC blends was investigated. Thereafter, solution rheology of PCL/PVC polymer blends was studied [71]. Complete compatibility was observed between PCL and PVC in the blend, and it was attributed to the *H–bond*

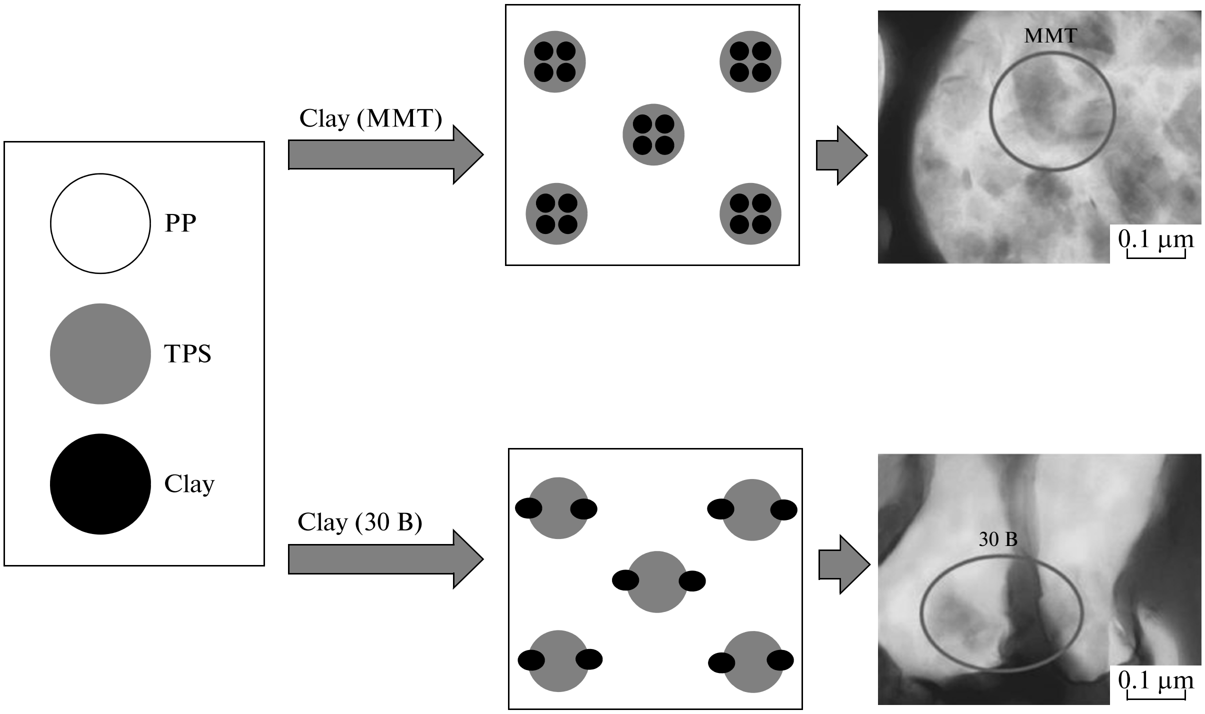

Fig. 12. Morphology of TPS/PP/clay nanocomposites. Reprinted with permission from Reference [56]. Copyright 2011, Springer Science + Business Media New York.

between the chains of two components. Their good compatibility was also confirmed by Chiu et al. [72]; study of thermal properties revealed that blend has a single T_g, and this result was consistent with the mechanical properties of the fabricated blend, where the elongation at break of blend increases with increasing the PCL content (Fig. 16).

Christensen et al. [73] studied the photo-degradation of PCL/PVC blend by determination of carbon dioxide emission during UV exposure. They found that PCL/PVC blend is more resistance to photo-degradation than PVC or PCL due to compatibility between two components. Gordin et al. [74, 75] reported the use of poly(caprolactone)-*b*-poly(dimethylsiloxane) (PCL-*b*-PDMS) as a third component in PCL/PVC blend, and they found that its addition resulted in interesting properties such as hemocompatibility, anti-adhesive behavior, and resistance to oxidation. Franchett et al. [76] studied the effect of biodegradation on morphology of PCL/PVC blend; they found that blend became more crystalline after the biodegradation. Recently Shi et al. [77] compared plasticization efficiency of PCL modified with octanoate and benzoate-terminal groups with that of di(ethylhexyl) phthalate (DEHP). The results showed that most of the PCLs tested were readily biodegraded and none of them resulted in the accumulation of metabolites. In general, these properties were much better than those of the control plasticizer DEHP.

PCL/PC blends. The first work reported this system was performed by Don et al. [78], where the antiplastization behavior of the system was studied. In addition, the biodegradation behavior of PCL/PC blends treated by O_2-plasma and Ar-plasma was studied by Hirotsu et al. [79, 80] using burial in soil tests. The results showed that PCL becomes less degradable when it blended with PC, and the oxidative treatments by O_2–plasma increase the enzymatic biodegradation whereas the Ar–plasma treatments rather decrease the degradation.

Thermal properties and compatibility of PCL/PC blends were studied by Balsamo et al. [81]; these blends are compatible in a wide range of compositions. For blend containing 40 wt % or more PCL, either one or both components can crystallize. The isothermal crystallization process of the blend with 10 wt % of PCL was studied by Laredoet al. [82]; they found that the existence of a rigid amorphous phase in the blend is established in non-negligible amounts as isothermal crystallization of PC develops.

Hong et al. [83] studied the effect of PCL content (up to 5 phr) on the properties of PC/ABS (30/70 wt/wt) blend. The results are summarized in Fig. 17, which showed that mechanical properties have maximum values at 0.5 phr content of PCL that were higher than those of binary blend, indicating that PCL could be used as a compatibilizer for PC/ABS blend. The fine distribution of PC phase (indicated by arrows in Fig. 17) at 0.5 phr of PCL was confirmed by

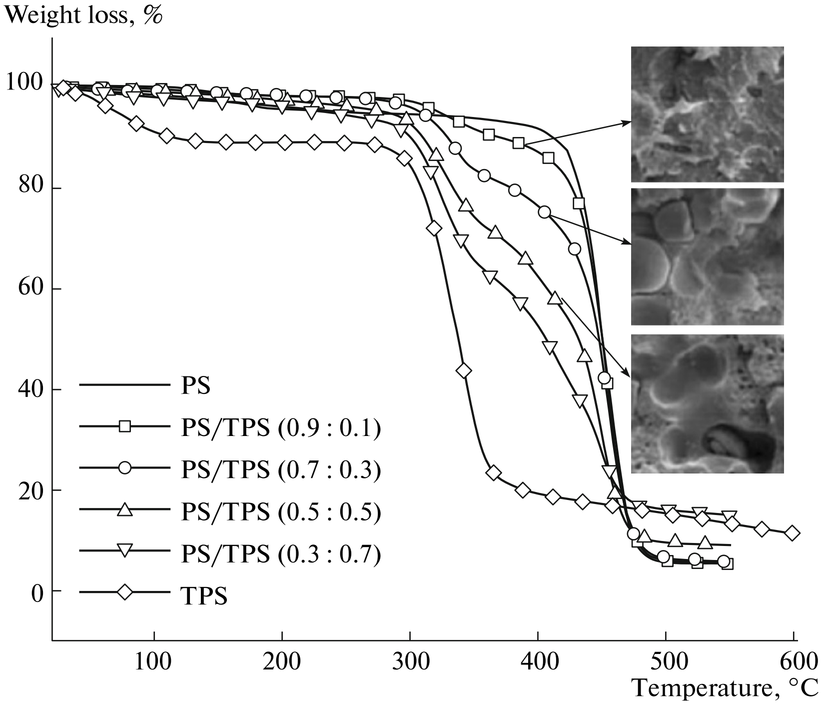

Fig. 13. Thermal degradation of TPS/PS waste blends. Reprinted with permission from Reference [59]. Copyright 2007, Springer Science + Business Media, LLC.

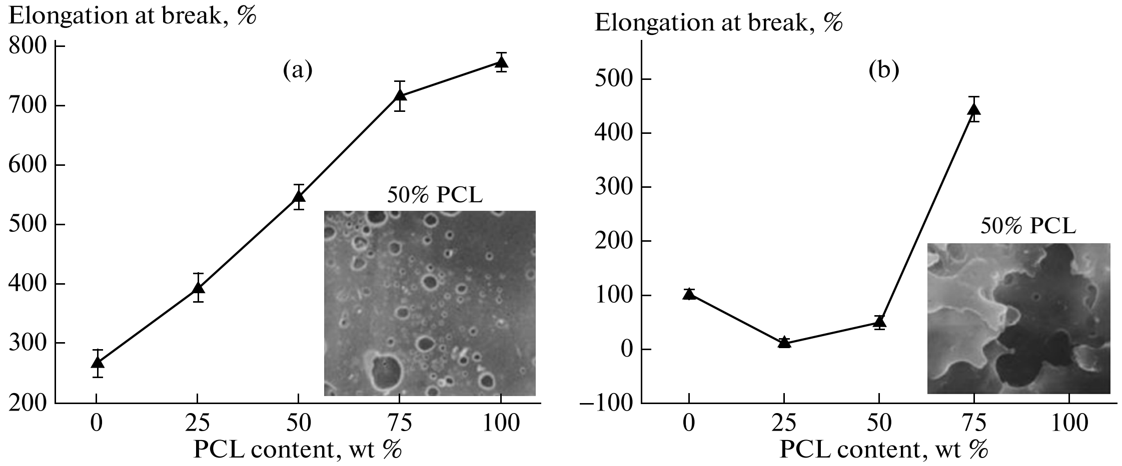

Fig. 14. SEM morphology and elongation at break of PCL/LDPE/TPS blends fabricated by (a) film blowing and (b) injection molding. Reprinted with permission from Reference [65]. Copyright 2002, Elsevier.

SEM. The high viscosity of blend compatibilizied by 0.5 phr PCL also confirmed the role of PCL in forming co-polymers, which act as bridges between two main phases in the blend.

PCL/SAN blends. Various works reporting preparation and application of PCL/SAN polymer blends have been documented since 1982 [84–87]. The compatibility of PCL/SAN polymer blends has been investigated by various research groups. Chiu and Smith [84] have reported compatibility of PCL/SAN blends over the entire range of blend compositions using DSC and a dynamic mechanical analyzer. They have found that PCL is compatible with SAN containing AN contents which are greater than 8 wt % but less than 28 wt %. Fernandes et al. [85] estimated the segmental interaction parameters in the PCL/SAN blends from melting point depression analysis. Jo et al. [87] studied the effect of AN content (0–30 wt %) on rheological properties of PCL/SAN polymer blends prepared using solution method, in which solutions of polymers

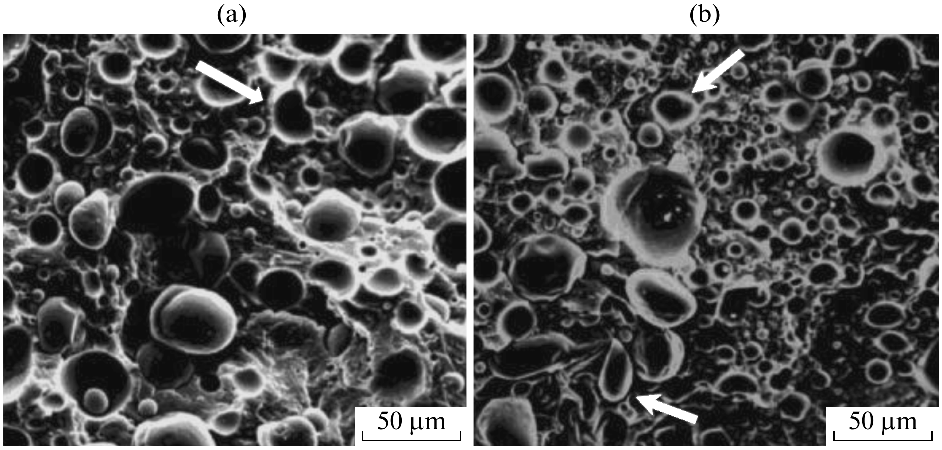

Fig. 15. SEM morphology of PCL/PP blends: (a) 70/30 and (b) 30/70. Reprinted with permission from Reference [66]. Copyright 2007 Wiley Periodicals, Inc.

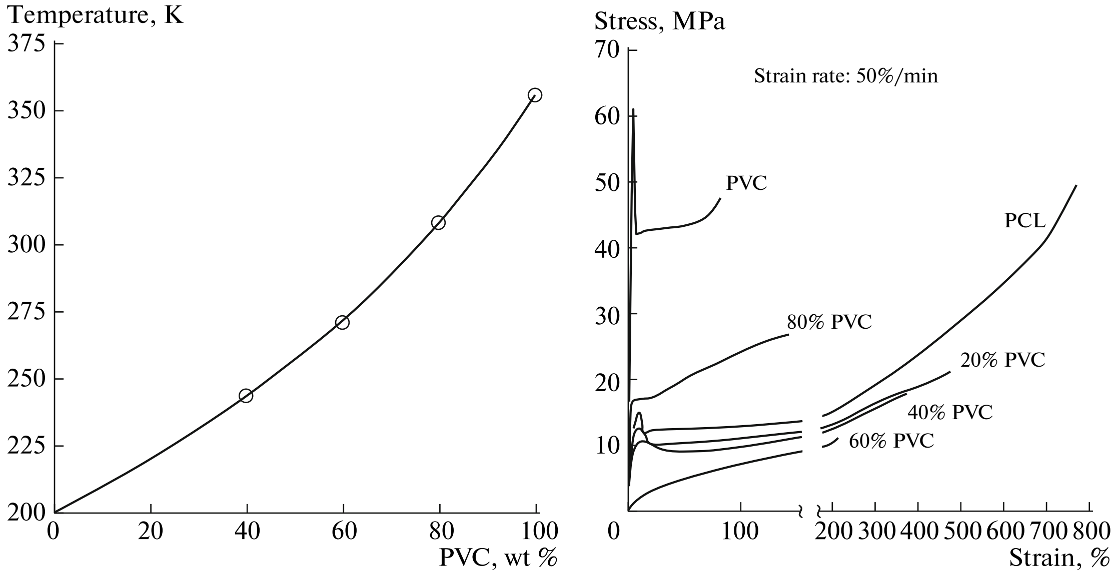

Fig. 16. T_g values and tensile curves of PCL/PVC polymer blends. Reprinted with permission from Reference [70]. Copyrights 1996, Wiley Periodicals, Inc.

are mixed and then precipitated. The results showed that blend is compatible in the studied range of compositions and its viscosity reaches minimum values at 15 wt % AN.

The biodegradation of PCL/SAN blend was studied by Choi and Park [88]. The weight loss and decrease in molecular weight of PCL with time in tested samples was observed in the compositional range above 50 wt % of PCL, where PCL degraded completely after 3 months and PCL/SAN blend (50/50 wt/wt) degraded to 80%.

Crystallization kinetics of PCL/SAN blend was also studied [89]. The isothermal crystallization kinetics of PCL in the blend was greatly affected by the presence of SAN, where the crystallization halftime ($t_{0.5}$) in the case of PCL/SAN (80/20) blend was much longer than corresponding value for pure PCL due to favorable interaction between of PCL and SAN. This interaction between PCL and SAN was also investigated by Princi and Vicini [90]; they found that PCL/SAN blend is compatible in whole composition range due to the repulsive interaction between styrene and acrylonitrile segments in SAN.

Poly(butylene succinate adipate) Systems

PBSA is commercial synthetic polyester with excellent biodegradability, its properties are very similar to those of linear low-density polyethylene such as high ductility [3], excellent processability using con-

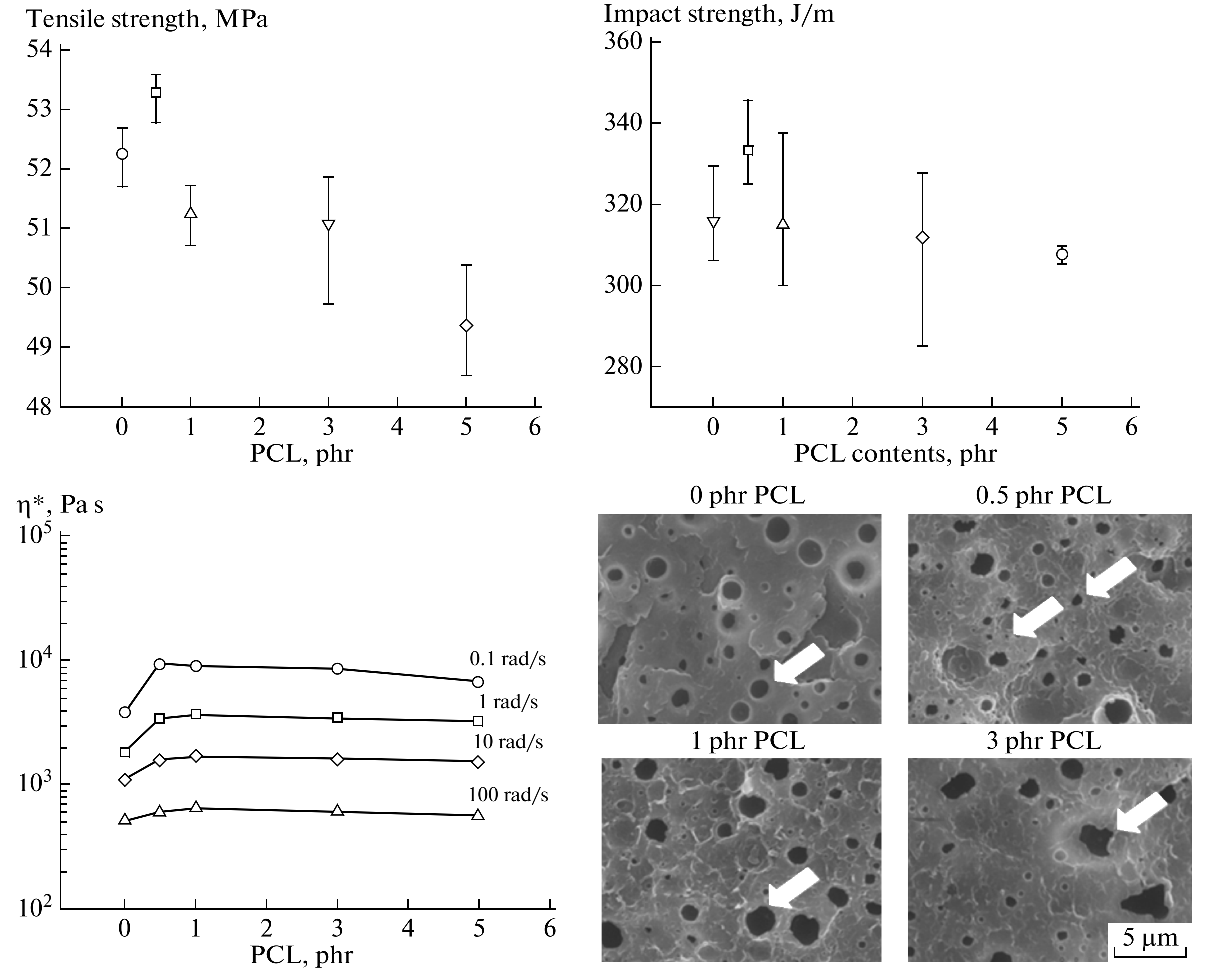

Fig. 17. Effect of PCL content on the properties and morphology of PC/ABS (30/70) blend. Reprinted with permission from Reference [83]. Copyright 2005, Elsevier.

ventional equipment's commonly used for polyolefin. However, poor tensile strength and high thermal sensitivity are main disadvantages of this polymer. For overcoming these problems, different fillers were used to fabricated PBSA composites and nanocomposites having high tensile strength and good thermal stability without any losing the ductility of the fabricated material. Ray et al. [91, 92] prepared PBSA/organically modified montmorillonite (OMMT) nanocomposites and studied the effect of OMMT structure on mechanical, morphological and thermal properties of the fabricated composites. The results showed that tensile strength, modulus, thermal stability, and elongation at break of PBSA were improved (Fig. 18). This effect was more pronounced by use of OMMT with diols chemical structure (C30B).

In another work reported by Ray and Bousmina [93], crystallization behavior of PBSA/organically modified synthetic fluorine mica (OSFM) nanocomposites was studied; the nanocomposites were prepared by melt-blending using aninternal batch mixer. In this case incorporation of OSFM decelerates the mechanism of nucleation and crystal growth of PBSA.

Poly(butylene succinate) Systems

PBS is biodegradable aliphatic polyester, which is commercially available as thermoplastic polymer and possesses biodegradability, melt processability, and thermal and chemical resistance. For further improvement of its properties and reduction of its production cost, PBS is mixed with plant fibers (reinforcing) and fillers. Zhao et al. [94] prepared PBS/rice straw fiber (RSF) composites in the presence of amino coupling agents. Excellent mechanical strength was obtained in the presence of coupling agent containing amino groups. Nam et al. [95] studied the effect of alkali treatment by 5 wt % NaOH solution on mechanical properties of PBS/coir fiber composites, the results showed that tensile strength and modulus of the composites increased with increasing fiber content while elongation at break decreased. Tan et al. [96] studied the non-isothermal crystallization kinetics of

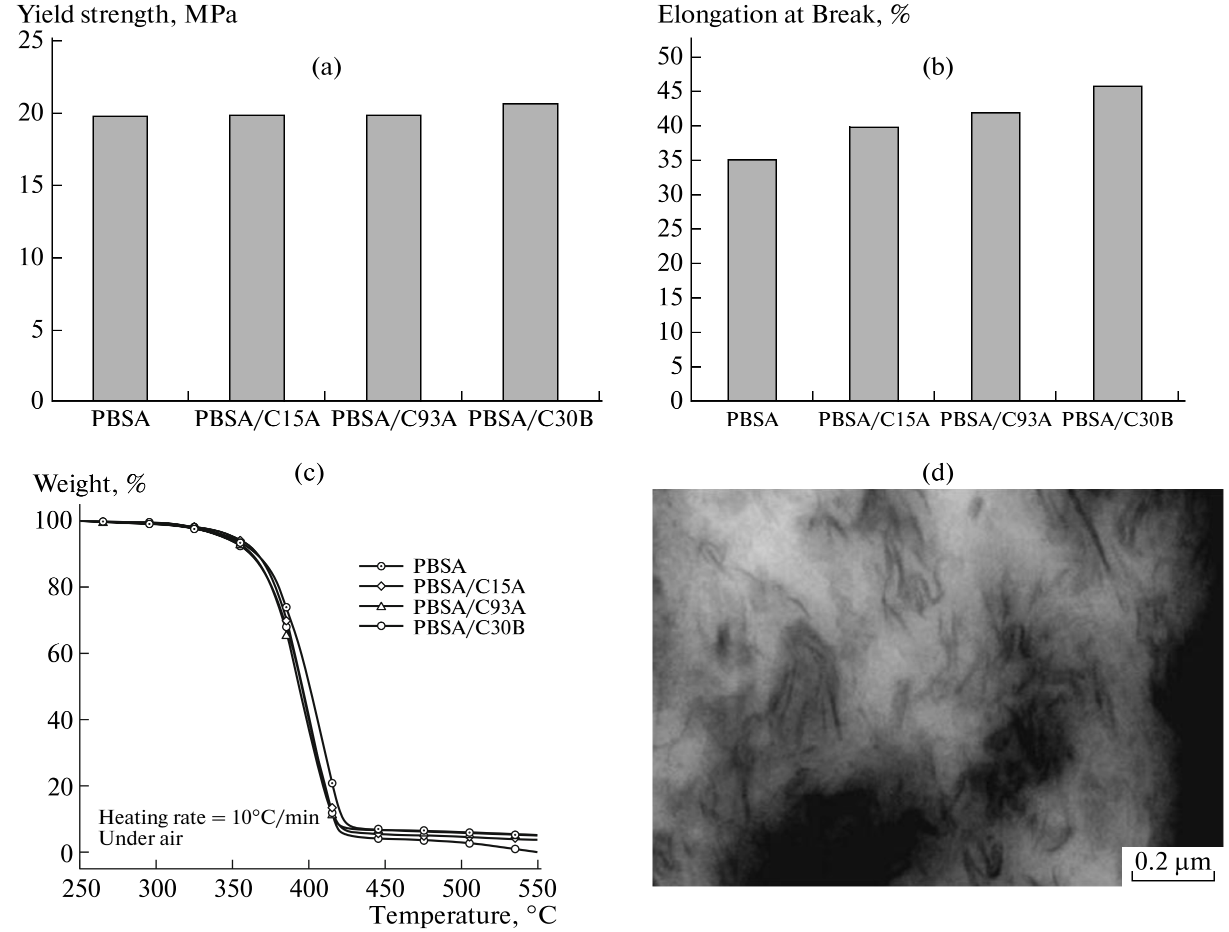

Fig. 18. (a) and (b) mechanical properties and (c) thermal stability of PBSA/OMMT's nanocompsoites, (d) morphology of the PBSA/C30B nanocomposite. Reprinted with permission from Reference [91]. Copyrights 2005, Wiley Periodicals, Inc.

PBS/cotton stalk bast fibers (CSBF) composites; they found that CSBF played a dual role for acting as both nucleating agents to promote nucleation and physical hindrances to retard the transport of chain segments during crystallization. Nie et al. [97] prepared PBS/bamboo fiber (BBF) composites using melt mixing, the effect of microencapsulated ammonium polyphosphate (MCAPP) as a flame retardant on thermal properties of the composites was studied and compared with other flame retardants such as $Mg(OH)_2$ and $Al(OH)_3$. MCAPP showed the best flame retardant property comparing with $Mg(OH)_2$ and $Al(OH)_3$. Hong et al. [98] studied the effect of sisal fibers (SFs) content on the rheological properties of PBS/SFs composites; the composites are shear thinning in behavior where the viscosity decreased with increasing shear rate. In addition, it was found that the non-Newtonian index (n) of the composites decreases with increasing fiber content indicating that viscosity of the composites is stable in a wide range of shear rates.

In addition, single-walled carbon nanotubes (SWCNTs) were incorporated for improving the mechanical strength and thermal stability of PBS [99]. In another work [100], hydrolytic stability of PBS was enhanced using OMMT, where PBS/OMMT nanocomposites were prepared in the molten state using an internal batch mixer. Recently [101], the biodegradation of PBS/OMMT nanocomposites under controlled composting conditions was studied and compared with that of pure PBS. PBS nanocomposites showed lower biodegradability than that of neat PBS due to improved barrier properties of the composites, which were further improved by the using of PBS-*g*-MA as a compatibilizer.

Poly(butylene adipate-co-terephthalate) Systems

PBAT, aliphatic-aromatic co-polyester, is able to degrade in the environment by intervention of microbial lipases. PBAT has excellent properties for film extrusion and coatings, and high elongation at break. Several works focused on preparation and characterization of PBAT composites using various materials such as talc and OMMT.

Raquez at al. [102] prepared PBAT/talc composites using extrusion process, and to improve the interfacial adhesion in composite PBAT was grafted with MA. The interfacial adhesion between PBAT-*g*-MA and talc was improved as evidenced by SEM images and selective extractions of polyester part from composites. Improvement of tensile properties of PBAT including tensile strength, modulus, and elongation at break were observed. The melt viscosity of composites showed that viscosity of PBAT/talc composites increases with increasing talc content.

Yang and Qiu [103] prepared PBAT/OMMT nanocomposites and studied their non-isothermal crystallization. OMMT enhanced the crystallization of PBAT apparently due to the heterogeneous nucleation effect of OMMT, which was consistent with the results obtained by Chivrac et al. [104]. In another work reported by Mohanty and Nayak [105], PBAT was grafted with MA and blended with sodium montmorillonite (Na^+MMT) in the presence of a reinforcing agent and the effect of MA and the reinforcing agent on the properties of PBAT/Na^+MMT composites was studied. Mechanical results showed an increasing in tensile modulus of PBAT nanocomposites in the grafted samples comparing with pure PBAT and non-grafted samples and thermal stability of the pure PBAT increased by incorporation of Na^+MMT. The biodegradation of PBAT/Na^+MMT nanocomposites was studied also by Mohanty and Nayak [106].They found that the incorporation of Na^+MMT resulted in faster biodegradation than pure PBAT.

CONCLUSIONS

The growing price of petroleum and consumer demand for sustainable products led to more interest in blends and composites based on biodegradable polymers [107]. In this review, recent developments in preparation and properties of blends consisting of biodegradable and non-biodegradable polymers were summarized.

It could be concluded that the commercial success of these systems depends on several factors, which are price, market demand, performance, composting infrastructures, and legislation. Most of the papers discussed in the present review have revealed that it is possible to fabricate these systems with unique properties and low price through creating of new fabrication methods and procedures.

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