

Chapter 8

LCP Based Polymer Blend Nanocomposites

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8.1 Polymer Blends

Polymer blends are macroscopically homogeneous mixture of two or more different species of polymers. The advantages of polymer blends includes (1) production of materials with full set of desired properties at the lowest price, (2) improvement of engineering resins' performance, (3) enhancement of specific properties, (4) improved processibility, product uniformity, and scrap reduction, (5) quick formulation (6) high productivity, (7) reduction of the number of grades that needs to be manufactured and stored and (8) Inherent recyclability, etc. (Utracki 2002a). Polymer blends can be formed at various states of miscibility between the blend partners like completely miscible, phase separated and partially miscible and the properties of these blends can vary in line with the percentage of miscibility. Polymer blends properties, like mechanical, optical, rheological, dielectric, and barrier properties, depends on two major parameters: the control of the interface and the control of the morphology. Due to this, study and control of morphology of polymer blends has emerged as an area of continuous interest to polymer material scientists in the last few decades (Cahn and Hilliard 1958; Siggia 1979; Kessler et al. 1986). Miscible polymer blend is a polymer blend which is homogeneous down to the molecular level and associated with the negative value of the free energy of mixing and domain size is comparable to the dimensions of macromolecular statistical segment. The most important factor leading to miscibility in low molecular weight materials is the combinatorial entropy contribution which is very large compared to high molecular weight polymers. A miscible blend of two

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polymers is going to have properties somewhere between those of the two unblended polymers. In partially miscible blends both the interacting phases are homogeneous. An example is the PC/ABS blends. In these blends, PC and the SAN phase of ABS partially dissolve in one another. In this case, the interphase is wide and the interfacial adhesion is reasonable. In immiscible blends the constituent polymers do not mix, but remain in separate phases, leading to the formation of a dispersion of one of the polymers in a continuous matrix of the other resulting which leads to the phase separation between the interacting polymers resulting in poor bonding but the immiscible materials upon blending are turned out to be nifty and useful.

8.2 Thermodynamics of Polymer Blends

If two polymers are mixed, the most expected result is a system that exhibits a complete phase separation due to the repulsive interaction between the polymeric components i.e. the chemical incompatibility between the polymers. The phase separation generally takes place when a single-phase system suffers a change of composition, temperature or pressure that forces it to enter either the metastable or the spinodal region. When the system enters from single-phase region into the metastable region, the phase separation occurs by the mechanism resembling crystallization—slow nucleation followed by growth of the phase separated domains. By contrast, when the system is forced to jump from a single-phase into the spinodal region of immiscibility the phases separate spontaneously by a mechanism called spinodal decomposition. The situation can be better explained by considering Fig. 1.1.

As shown in the Fig. 1.1a, the miscibility increases with temperature, and at the Upper Critical Solution Temperature (UCST), the blend forms a single phase. Similarly in Fig. 1.1b the polymers form a single phase at low temperatures, and phase separate as the temperature is increased above the LCST. This can occur if there are specific interactions between the polymers (such as hydrogen bonds), or if mixing results in a decrease in volume. As the temperature is increased, these attractive interactions eventually become disrupted, and the blend begins to phase-separate.

8.3 Factors Controlling the Miscibility of Polymer Blends

Generally mixing of two polymers lead to a two-phase system because polymers are thermodynamically immiscible and incompatible, this leads to high interfacial tension and poor interface adhesion. Consider a system of two polymers, A and B. If a small amount of B is added to pure A, the blend will be miscible and form a single phase. As more B is added, the blend becomes unstable and separates into

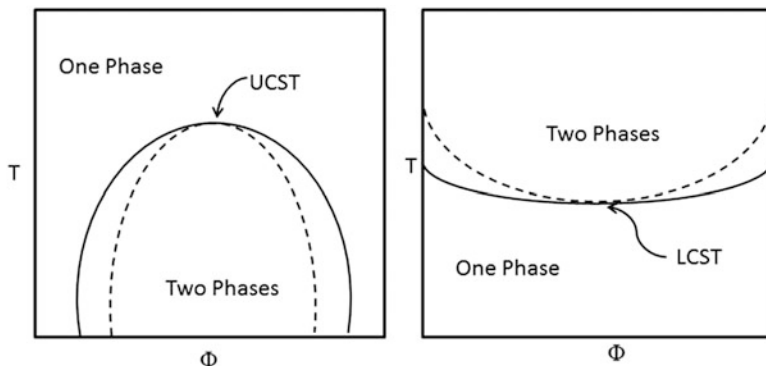


Fig. 1.1 (a) UCST type phase diagram, (b) LCST type phase diagram. *Solid lines* show the binodal curve, *broken lines* show the spinodal curve (Utracki 2002a, b; Siggia 1979)

two phases, one rich in polymer A, and the other rich in B. The miscibility of the system is also affected by temperature. Some blends phase separate on heating, while others phase-separate as the temperature decreases. This can occur if there are specific interactions between the polymers (such as hydrogen bonds), or if mixing results in a decrease in volume. As the temperature is increased, these attractive interactions eventually become disrupted, and the blend begins to phase-separate. A numbers of other factors also play role in the miscibility and immiscibility of polymer blends and alloys. Similar structured polymers or with similar polarity are likely to form miscible blends whereas different polarities produce immiscibility. Polymers of low molecular weight permits greater randomization on mixing and therefore greater gain of entropy, results in miscibility, while polymers of different molecular weight result in immiscibility. Polymers that are attached to each other by hydrogen bonds, ion-dipole, donor-acceptor adduct, transition metal complexes, etc. are likely to impart miscibility in blends and alloys. Separate phase is developed when a polymer is crystallized. When polymer in blend crystallize they will form two separate crystalline phases, it is rare for the two polymers to co-crystallize in a single crystalline phase. In immiscible or incompatible polymer blends, the phase rule explains quantitatively the extent to which they separate and the extent to which each phase are actually not pure polymer I and II, but rather solution of I in II and solution of II in I. The major phase will form the continuous matrix and control the properties, while the minor phase will form dispersed domain and it contributes certain specialized properties to the blend. The simplest shape of dispersed domain with minimum surface energy is spherical, as the attraction between the immiscible phases increases the size of sphere decreases and compatibility increases. When two polymers repel each other then they separate into different phases (incompatible) and the interface could be very weak and can fail under any kind of mechanical or thermal stress. Thus compatible blends must therefore have a strong interface which allows the stress to transfer. This shows that the compatible blends must have a broad transition region, which has the

ability to resist stress. This transition phase is referred as interphase. Difference between compatibility and incompatibility can be explained by broad strong interphase and sharp weak interface.

8.4 Compatibilization of Immiscible Polymer Blends

The compatibilization of immiscible polymers is one of the most important, widespread and difficult problems in contemporary applied polymer science. The compatibilization of immiscible blends can be accomplished by the optimization of the interfacial tension (to achieve the desired degree of dispersion), stabilization of the morphology against high stresses during blending (to get optimum structure) and enhancement of adhesion between the blend partners in the solid state (facilitating the stress transfer from one phase to other and hence improves the performance). There are several approaches adopted for making the incompatible polymer blends compatible, which includes:

1. Incorporation of specific interactive groups
2. In-situ polymerization
3. Addition of graft copolymer
4. Reactive compatibilization
5. Addition of Block copolymer
6. Nanoparticle compatibilization

Among these approaches co-polymer compatibilizer is widely adopted. Addition of a small amount of copolymer (block-, graft-, random-copolymer) mainly affects the interfacial tension coefficient and hence the size of dispersed phase. However, it has little effect on either the shear sensitivity of the blends morphology or their solid-state behavior. While the addition of di-block copolymer efficiently reduced the interfacial tension, the tri-block copolymer leads to better mechanical properties (Utracki 2002b). The morphology of immiscible blend depends on many factors, among which the flow history and the interfacial properties are the most important. Thus, the interfacial and rheological properties are the keys to morphology. Polymer blends with low interfacial tension tend to form co-continuous morphologies over a wider composition range than those with high interfacial tension. Several studies have investigated the effect of block copolymer on the boundaries of the region of co-continuity (Bourry and Favis 1998; Jorgensen 1999; Li et al. 2002; Chuai et al. 2003; Dedecker and Groeninckx 1998). In contrast to the expansion of co-continuity region, addition of block copolymer actually narrowed it. This result is surprising because the addition of block copolymer is expected to reduce the effective interfacial tension and thereby promote the formation of elongated domains, making co-continuous morphologies easier to generate. The possible cause for this observation could be the effect of block copolymer on the coalescence of domains i.e. the block copolymer stabilizes the droplet morphology of the polymer blends by reducing the coalescence tendency of the dispersed phase and hence cause the region of co-continuity to narrow down.

8.5 Liquid Crystalline Polymer

A liquid crystal, or mesophase, is a state of matter between the liquid and crystal states. Liquid crystals are ordered like crystals but flow like liquids. Liquid crystalline polymers (LCP) are usually classified into two groups: lyotropic LCPs and thermotropic LCPs, based on the conditions for the formation of their liquid crystalline state. Lyotropic LCPs are processed to high-strength, high-modulus fibers by a solution spinning technique whereas thermotropic LCPs can be processed and molded to structural parts of different shapes by means of conventional processing techniques for thermoplastics, such as extrusion and injection molding. The temperature at which phase transition from liquid crystal to melt state occurs is called the isotropization (T_i) or clearing temperature (T_c). Liquid crystals are classified according to the shape of the mesogens and the structure and appearance of the mesophases. Mesogens are either rod-like or disk-like and they are divided into three main classes: nematic, smectic, and cholesteric. The mesogenic units in a liquid crystalline polymer may be in the main chain or the side chain of the polymer. Polymeric liquid crystals are also classified according to their chemical structure and the conditions under which the LC state is formed. Main-chain LCPs may be either fully aromatic or built up of rigid mesogens and flexible spacers. In side-chain LCPs, the rigid mesogenic units usually are present in pendant side chains (Percec 1997). The potential applications of LCP includes: production of high-strength and high-modulus fibers, precision molded small components, films exhibiting excellent barrier properties, novel composites, processing aids in the melt, reversible information storage, electro-optical displays, and non-linear optical devices. Their applications arise directly from a number of interesting properties they exhibit, which typically include: low melt viscosity, fast cycle time in molding, very low mold shrinkage, excellent mechanical properties, good solvent resistance, low thermal expansion coefficient, low water absorption, excellent barrier properties, ferroelectric properties, and high continuous use temperatures (Han and Bhowmik 1997).

8.6 Polymer Blends Based on Liquid Crystalline Polymer

Polymer blends, containing liquid crystalline polymer, is a special class of composite, known as in-situ composites, where the reinforcement have been provided by the in-situ generated LCP fibers. These types of polymer blends were studied intensively by different research groups mainly due to two advantages; (1) in-situ fibrillation and reinforcement and (2) improved processibility. Both LCP and thermoplastics show shear-thinning behavior which promotes the fibrillation of the LCP to form rigid and highly oriented LCP fibers. Thermotropic LCPs can also function as a processing aid and a reinforcing agent to improve both the processibility and performance of thermoplastics. Because of its high cost, LCP is

used as the minor component in these types of blend systems. From a scientific viewpoint, several aspects of basic understanding are involved in order to develop marketable technology: the rheological behavior of LCP blends, orientation and crystallization of blend systems, interfacial interaction and compatibilization in LCP blends, microstructure development, and the processing-structure-property relationship in these LCP blends. There are several factors to be fine-tuned to achieve the in-situ fibrillation but the major road block is the incompatibility between the blend partners, containing LCP, which decreases the interfacial adhesion, enhances the interlayer slippage and hence restricts the fibrillation. To overcome this obstacle compatibilizers are being used which can restricts the interlayer slippage and enhance the fibrillation.

The research on LCP containing in-situ composite was started in the early 1980s. Siegmann et al. reported reduced melt viscosity of the polyamide/LCP blend, with only 5 % of LCP, and superior mechanical properties as compared to the individual components (Siegmann et al. 1985). They also analyzed the phase morphology of the polymer blends with various LCP contents and found that the domain structure changed from spherical to fibrillar with increasing LCP content. This was the first paper reporting in detail the LCP blends that were named later as “in-situ composites”. The fibrillation of LCPs in thermoplastic melts is influenced by several parameters, including the thermal characteristics of the component polymers and their compatibility, and processing parameters such as viscosity ratio, melt temperature, flow mode, and shear rate.

8.7 Major Factors Controlling the LCP Fibrillation

The morphological development of LCP containing polymer blends, during processing, depend on several factors like processing device, flow field, viscosity and viscosity ratio, processing temperature, interfacial tension, domain deformation, coalescence, breakup, and relaxation of the dispersed phase.

8.7.1 Viscosity Ratio

Viscosity ratio of the blend partners plays a crucial role in the LCP domain deformation and coalescence, under the shear flow. La Mantia and Valenza (1992) proposed that if the viscosity of TLCP was higher than matrix, large droplets of TLCP were formed, whereas fibrillation could only occur when the viscosity of the matrix was higher than that of the TLCP. Hence the viscosity ratio of TLCP to polymer matrix should be less than one in order to facilitate the deformation of LCP droplets to fibrillar form. In an extruder, the shear flow, before the die, could result in the domain deformation and fibrillation of LCP, if the viscosity ratio is 0.01 or smaller. Similarly at die entrance the coalescence and further deformation of the

LCP domains lead to the increase in volume and aspect ratio of the fibrils. In general, viscosity ratio, less than unity, is a necessary condition for the fibrillation of LCPs. Deformation of the droplet is dependent on the interaction between the viscous force and interfacial force. When the disruptive stress due to viscous drag of the medium is capable of overcoming the cohesive effect of surface tension, the suspended phase would be deformed and elongated into cylindrical shape (Lee et al. 2003a). Even though the viscosity ratio effect is a necessary condition for the fibrillation of LCP, it is not always sufficient condition. There are many LCP containing blends studied by several groups for the exploration of suitable conditions for the fibrillation of LCP.

Table 1.1 summarizes the effect of viscosity ratio on the LCP droplet morphology, in various polymer matrices along with their viscosity ratios. It can be seen that, viscosity ratio lower than unity, although necessary but not always a sufficient condition for the fibrillation of LCP.

8.7.2 Capillary Number

According to Taylor, droplets were deformed as spheroids under shearing, and the deformation of these droplets depended on dimensionless parameters such as the capillary number and the viscosity ratio (Taylor 1932, 1934; Heino and Seppala 1993). The Capillary number (Ca) is a dimensionless number that predicts fibrillation originated from the hydrodynamic theorem. The capillary number can be defined as the ratio of the shear stress acting on the LCP droplet by an external flow field to the interfacial tension which resists the deformation of the spherical droplet: The Ca can be measured by following the (1.1), which is represented as:

$$Ca = \eta_m \left[1 - (4\phi_d\phi_m)^{0.8} \right] \frac{d\gamma(16\lambda + 16)}{2\sigma(16\lambda + 16)} \quad (1.1)$$

where γ is the shear rate; d is the diameter of the dispersed phase droplet, σ is the interfacial tension, ϕ_d is the volume fraction of dispersed phase (LCP), ϕ_m is the volume fraction of the matrix phase, η_m is the viscosity of the matrix and $\lambda = \eta_{\text{LCP}}/\eta_m$ is the viscosity ratio. So the magnitude of Ca was affected by many factors such as shear rate (affects the size and shape of LCP fibers), interfacial tension (affects the drag force of viscous media upon LCP), LCP content (affects the coalescence and particle breakup), material properties, viscosity ratio and processing conditions which in turn influence the droplet-fibril transition. Generally the droplet-fiber transformation favored if the Ca exceed the critical limit by many fold. Heino et al. investigated various types of LCP/PP blends and noticed that, while fibrillar LCP was formed at viscosity ratios ranging from 0.5 to 1, spherical or cluster like morphology was exhibited for ratios above unity (Heino et al. 1994).

Table 1.1 Morphology of LCP containing polymer blends reported in the literature

System	Extrusion Temp (°C)	η_{LCP}/η_{matrix}	Morphology (with LCP concentrations indicated)	Ref.
LCP (PHB/HNA)/PC	310	<1	2.5 %, 5 %, 10 % fibrils; 25 %, 50 % droplets	Isayev and Modic (1987)
LCP (PHB/PET)/PC	240	<1	5 %, 10 % droplets	Nobile et al. (1989)
	260	<1	50 % thick fibers	
LCP (PHB/HNA)/PET	280–288	<1	20 %, 40 %, 60 % no fibril; 80 % fibrils; at high shear rates, 30 % fibrils	Ko and Wilkes (1989)
LCP (PHB/HNA)/PEEK	350	<1	2.5 %, 5 % no fibril; >10 % fibrils	Mehta and Isayev (1991)
LCP (PHB/PET)/PET	280	<1	Large L/D of die, no fibril; small L/D, lightly fibril	(Sukhadia, et al. 1990)
LCP (PHB/HNA)/PPO	310	<1	Most fibrils in skin, >50 % fibrils in core	Limtasiri and Isayev (1991)
Polyester/PC	270	<1	Fibrils at very high shear rates and small L/D	Kohli et al. (1989)
LCP (PHB/PET)/PA66	275	<1	No fibril in stable shear	Blizard and Baird (1987)
LCP (PHB/PET)/PC	260	<1	Extruding, 10 % droplets, 30 % fibrils, >50 % continuous	Blizard and Baird (1987)
LCP (PHB/HNA)/PC	260	Cross	Fibrils at high shear rates	Beery et al. (1991)
LCP (PHB/HNA)/PBT	260	>1	Droplets	Beery et al. (1991)
LCP (PHB/HNA)/PA66	260	>1	Droplets	Beery et al. (1991)
LCP (PHB/HNA)/PPS	285	>1	Droplets	Subramanian, and Isayev (1991)
LCP (PHB/HNA)/PS	295	>1	Spherical form	Choi et al. (1996)
LCP (PHB/PET)/PS	295	<1	Fibrils	Choi et al. (1996)

8.7.3 *Critical LCP Content*

The LCP content has critical effect on the geometry of LCP, in the polymer blend system. In the uncompatibilized blend system low concentration of LCP, below 5 wt%, results in geometry like spheroids or ellipsoids of LCP, regardless of the shear rate during mixing or extrusion (Song and Isayev 2010). However, higher LCP concentration, in excess of 20 wt%, gives rise to long LCP fibers. This is related to the magnitude of force exerted by the matrix phase on to the dispersed phase during blending. According to Taylor's theory (Taylor 1934), higher force is needed to deform a small particle as compared to a large particle. At lower concentration of LCP, the droplet size will be obviously smaller than that with the higher concentration, which makes it difficult to deform the smaller droplets into fibrillar form. Moreover, at low volume fraction of the LCP, the size of dispersed LCP phase may be too low such that the small and sparsely distributed LCP particles could not coalesce to any significant extent to form larger particles that were required for deformation to occur. This demonstrates that a lower limit of LCP concentration is essential for the development of in-situ fibrillation.

8.7.4 *Processing Equipment*

Extrusion has been the preferred method for the processing of LCP containing polymer blends over the conventional internal mixture. The extensional flows, such as melt drawing, are most effective to produce LCP micro-fibrils and the effectiveness increases with draw ratio. Drawing promotes fibrillation especially with high LCP content because it facilitates the deformation of the large LCP domains into fibrils under the applied extensional flow. It was determined that as draw ratio increased, the tensile modulus increased due to the improvement in the molecular orientation and the higher aspect ratio of the LCP fibrils. Kyotani et al. (1992) showed that addition of LCP to a polymer like PET, produced excellent molecular orientation, at a draw ratio of 80, which was not possible for the draw ratio of 120 in pure PET. This molecular alignment was reflected in the stiffness of the blend where the tensile modulus almost tripled. A schematic diagram of the post extrusion process adopted by Lee et al. (2003b) is shown in Fig. 1.2. In this mixing process, a post draw force has been exerted by few rollers which draw the fibers coming out of the extruder. The fibers are being passed through the water trough to cool them. They showed that the aspect ratio of the in situ LCP fibers can be controlled by the draw ratio.

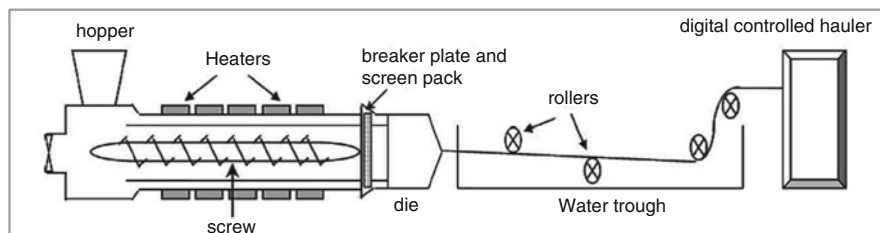


Fig. 1.2 Schematic setup for extrusion process (Lee et al. 2003b)

8.7.5 Interfacial Adhesion

Interfacial adhesion at the matrix-LCP interface has a significant role to play in the formation of in situ fibrillation of LCP. Generally, LCP/thermoplastics blends consist of two separate phases, which in most cases are immiscible. The poor adhesion between the components of the blends gives rise to polyblends having lower tensile modulus and strength than expected from the law of mixtures. In addition to that absence of interfacial adhesion promotes the interlayer slippage at the LCP matrix interface and restricts the LCP domain deformation and hence the fibrillation. Such situation can be resolved by the addition of suitable compatibilizer into the polymer blend system which can promote the interfacial adhesion. Better interfacial adhesion also helps in the stress transfer from matrix to dispersed LCP phase. The mechanical and thermal properties of the polymer blends can be enhanced by the addition of compatibilizer.

8.8 Carbon Nanotube

The CNT has gained tremendous momentum from the scientific community in the present decade because of their wide range of potential applications in several areas since its invention by Iijima in the year of 1991. MWCNT is considered to be the most promising nanomaterial due to its high flexibility, low mass density, high aspect ratio (typically $>10^3$), and exceptional mechanical, thermal, and electrical properties. The CNT is an allotropic modification of carbon and the extraordinary properties of the CNT are attributed to the unique tubular structure of the graphitic sheets, which is in the order of nanometers in diameter and microns in length. The carbon-carbon (C-C) chemical bond present in CNTs is completely formed by sp^2 hybridized bonding orbitals, which is comparatively stronger than the sp^3 types bonding structure located in diamond as a result it exhibits extremely high mechanical properties. The CNTs are mainly divided into two types depending on the reaction conditions of fabrication techniques; such as single-walled CNT (SWCNT) and multi-walled CNT (MWCNT). The SWCNT is made up of a single sheet of graphene layer, which is perfectly folded to form a hollow cylinder with a diameter

in order of 1 nm and up to few centimeters in length. The MWCNT consists of more than single concentric nested cylindrical graphene layers with an interlayer spacing of 0.35 nm (equal to the basal plane separation in turbostratic graphite), which are coaxially assembled around the central main hollow core by the van der Waals force of attraction between the adjacent graphene layers. MWCNT has diameters ranging from 2 to 10^2 nm and lengths in tens of microns. The whole families of CNTs are classified into three types of tubes of different diameters based on the rolling up of the graphene sheets along one of the symmetry axis (armchair and zigzag tubes) or in a direction that differs from a symmetry axis (chiral tubes). The functionalization of carbon nanotubes are carried out by different conventional (covalent, non-covalent exohedral, and endohedral functionalization) (Hirsch and Vostrowsky 2005) and non-conventional radiation induced graft polymerization (RIGP) (Jung et al. 2009), plasma treatment (Felten et al. 2005), and γ -irradiation (Skakalova et al. 2004) methods to improve its solubility, wetting, dispersion, processibility and properties. The covalent modification of CNTs is generally a successful and adopted technique to introduce some defects on the CNT surface where polar chemical functional groups like carboxyl, derivative of carboxyl, hydroxyl, amine, halogens etc. can be placed. The pristine CNTs has enormous prospect for extensive application in conducting plastics, energy storage, sensors, electronic devices, electron microscope tips, electron emission devices, structural materials, catalyst supports, biological applications, air and water filtration, ceramics and so on (Thostenson et al. 2001). The MWCNT is an ideal reinforcing nanofiller for the development of new generation high strength, lightweight, and multi-functional polymer nanocomposites for electromagnetic shielding, antistatic coatings, high strength low density corrosion resistant components, and lightweight energy storage applications (Coleman et al. 2006).

Carbon nanotubes are widely used as nanofillers for the fabrication of advanced polymeric nanocomposites due to its superior properties like high mechanical strength, excellent electrical and thermal conductivity. However, uniform dispersion of CNTs in the polymer matrix is the major obstacle for development of high performance nanocomposites. To improve the dispersion of CNTs in the polymer matrix, functionalization of CNTs has been done by several research groups. However chemical modification of CNTs introduces defective sites in CNTs and breaking of CNTs and thus property improvement of the nanocomposites falls below expectation. Non-covalent modification of CNTs, like ceramics coated CNTs, overcomes the above limitations of breaking and defective sites in CNTs which are developed by covalently bonded functional groups.

8.9 Effect of Compatibilizers on the Properties of LCP Containing Blends

Polymer blends, having LCP as minor components, are being studied extensively for the production of high performance materials with superior properties. However, as we know, most polymer blends are immiscible, i.e. simply mixing these polymer pairs cannot produce practically useful materials. With regard to this, improving the compatibility and controlling the phase separation and morphologies of polymer blends turn out to be most important parameters in polymer blending. In addition to this, the condition of blending must be optimized for the in-situ generation of LCP fibers, which not only improve the processibility of the polymer blends but also reinforce the base matrix. Many researchers have analyzed the effect of Compatibilizer on LCP based polymer blends with respect to different compatibilizers.

Seo et al. (1999a) demonstrated that addition of functionalized polypropylene (maleic-anhydride-grafted polypropylene, MA-PP) in TLCP (poly (ester amide))/nylon 6,6 blend facilitate the structural development of the TLCP by acting as a compatibilizer at the interface. Addition of MA-PP improved the mechanical properties of the resulted blend. From morphological observations it was evident that the interfacial adhesion was superior and the reduced particle size enables finely dispersed liquid crystalline polymer to be deformed by shear flow without strong elongation, even when the viscosity of the matrix is much lower than that of the liquid crystalline polymer. Krishnaswamy et al. (1999) investigated the influence of reactive terpolymer on the properties of in situ composites based on polyamides and thermotropic liquid crystalline polyesters. Small amounts of a reactive terpolymer added to a binary blend of polyamides and thermotropic liquid crystalline polyesters prior to injection molding yielded in situ composites with significantly higher modulus and strength along the reinforcement direction and substantially higher strength and toughness along the transverse direction of injection molded parts. Miller et al. (1995) observed that acrylic acid-functionalized polypropylene (PP-AA) was assessed as compatibilizers for polypropylene/liquid-crystal polymer (PP/LCP) blends. Incorporation of PP-AA increased the fiber crystallinity and fibers were oriented in the direction of flow field. This was attributed to the promotion of specific polar interactions between the blend components. Seo et al. (1999b) established the relationships between the properties of ternary blends of nylon 6, a thermotropic liquid crystalline polymer and a compatibilizer (maleic-anhydride-grafted polypropylene) under various processing conditions. The compatibilizer provides extrudate surface stability, thus enabling high drawing. The fibrillation of dispersed TLCP phase was evident.

The rheological, mechanical properties and micro-structural development during capillary flow of maleic anhydride compatibilized PA6 (MAP)/liquid crystalline polymers (LCPs) blends were studied by Meng and Tjong (1998). From SEM observations long and fine fibrils formation was evident. The rheological measurements showed that the viscosity ratio between the Vectra A950 and (PA6 (MAP))

matrix was much larger than unity. Chiou et al. (1996) used ethylene-glycidyl methacrylate copolymer (EGMA) as a reactive compatibilizer for the immiscible and incompatible blends of polypropylene (PP) and a liquid crystalline polymer (LCP). The epoxy functional groups of the EGMA copolymer reacted with the carboxylic acid and/or hydroxyl end-groups of LCP. The in situ-formed EGMA-g-LCP copolymer tends to reside along the interface of the PP/LCP and reduces the interfacial tension during melt processing. The lowering of crystallinity of the compatibilized blends was reflected in a substantial reduction in stiffness (in terms of the tensile modulus). However, the improved adhesion of the compatibilized blends resulting in an improvement in the toughness. As mentioned by Li et al. (2002), random styrene–maleic anhydride copolymer (RSMA) could be used as an effective compatibilizer in polyamide-6/liquid crystalline copolyester blend. The mechanical measurements illustrated that the stiffness, tensile strength, and toughness of the in situ composites were generally improved with increasing RSMA content. The results also showed that the maximum impact force (F_{\max}) and crack-initiation energy (E_{init}) tend to increase with increasing RSMA contents. From these results, it appeared that RSMA prolongs the crack-initiation time and increases the energies for crack initiation and impact fracture, thereby leading to toughening of LCP/PA6 in situ composites. Vallejo et al. (2000) reported the effect of an ionomer as a compatibilizer in PP/LCP blend system. The ionomer used as compatibilizer was an ethylene–methacrylic acid copolymer where methacrylic acid was partially neutralized with Zinc. The fibers of uncompatibilized blend were pulled out from the matrix, but those of compatibilized blends were mostly fractured. The improved morphology, gave rise to increase in modulus by 20 % and tensile strength by 32 %. Chin et al. (1996) investigated that solid epoxy had been demonstrated to be an effective compatibilizer for the incompatible PET/LCP blends. The LCP fibril formation was also enhanced after compatibilization and resulted in substantial improvement on both stiffness and toughness. Huang et al. (2001) reported the usefulness of styrene–acrylonitrile–glycidyl methacrylate (SAG) copolymers with various contents of glycidyl methacrylate (GMA) as compatibilizer for incompatible blends of styrene–acrylonitrile (SAN) and a liquid crystalline polymer (LCP). These SAG copolymers contain reactive glycidyl groups that are able to react with the carboxylic acid and/or hydroxyl end groups of the LCP to form the SAG-g-LCP copolymers during melt processing. Compatibilized SAN/LCP blends were observed with finer fibrils than those of the corresponding uncompatibilized blends.

The morphology, compatibility and mechanical properties of the blends of a co-polyester type LCP and ABS were studied by Xie et al. (2003). LCP fibrils were formed and distinct skin/core morphology was observed in the injection molded samples. At higher LCP concentration (50 wt%), phase inversion took place, where the dispersed LCP phase became a co-continuous phase. The blend modulus was lower than the values predicted by the rule of mixtures, suggesting a poor interface between the LCP droplets and ABS matrix. However, copolymer of styrene and maleic anhydride (SMA) used as compatibilizer, resulted in improvement in mechanical properties as well as interfacial adhesion.

8.10 Effect of Fillers on the Properties of LCP Containing Ternary Blends

From the above discussion it is clear that compatibilizer can significantly affect the ultimate properties of the LCP containing polymer blends. However, selection of compatibilizers for polymer blends consisting of engineering thermoplastics, having very high melting temperature, and LCP has been an area of concern because the compatibilizers must have sufficient thermal stability to sustain the processing temperature. In addition to this the dispersion of nanofillers, uniformly, in the blend matrix also presents separate problem. In order to overcome these problems, different research groups studied the effect of nanofillers as compatibilizers for these types of polymer blends, where the nanofillers act both as reinforcing agent and compatibilizer and also enhance the LCP fibrillation. This process produced a dual reinforcement effect on the polymer matrix where the LCP (in micro phase) and nanofillers (in nano phase) enhanced the mechanical properties of polymer blends. Some of the important works are cited in the following section. Jun et al. (2006) described the hydrodynamic effects arising from the presence of fillers in in-situ PSF/LCP hybrid composites. They showed that in presence of fillers the flow field changed from shear flow to elongational flow. So, in in-situ hybrid composites, containing LCP droplets and filler particles, extra hydrodynamic effects arise from the presence of filler particle and act on the morphological evolution of the LCP droplets. The study confirmed that the presence of rigid CaCO_3 whiskers altered the flow field and enhanced the vortex in the converging flow area at the entry of the capillary. It is this vortex enhancement that resulted in the increase of the elongational stress and promoted the fibrillation of the LCP droplet in PSF/LCP/whisker systems. They found that mainly spherical domains of LCP formed along with some ellipsoids in PSF/LCP binary blends. However, after the whisker was added into the binary blends, LCP fibrils with large aspect ratios were generated in all the hybrid composites; and with the incorporation of more whiskers, the larger aspect ratio of LCP was obtained. Incorporation of 2.1 vol% of whisker to the binary PSF/LCP blend increased the aspect ratio of LCP to three times, suggesting an enhanced fibrillation of LCP. At the maximum content 11.5 vol% of whiskers studied, the LCP average aspect ratio increases to 12.4. Similarly they found that addition of a small amount of whiskers to the PSF/LCP blend increased the volume-average diameter of LCP particles. Tjong and Meng (1999a, b) explored the effect of potassium titanate whiskers ($\text{K}_2\text{Ti}_6\text{O}_{13}$) on the properties of PA6/LCP blend system. The whisker was surface treated with tetrabutyl orthotitanate in order to improve the compatibility. They observed that the tensile modulus and tensile strength increased with the whisker content but impact strength varied up to 10 wt% of whisker after which it starts to decrease. LCP fibers were formed in the skin section of composite up to 10 wt% of whisker content but spherical domains of LCP were identified beyond the whisker content of 15 wt%. They also reported an enhancement of thermal stability with the addition of whisker. In another study they showed that incorporation of potassium titanate

whiskers in the maleic anhydride compatibilized PP/LCP blend system improved the fibrillation of LCP (Tjong and Meng 1999a, b). Due to the dual reinforcement of LCP fiber and whisker, the mechanical properties of the hybrid composites were found to be superior to the binary blend system. They ascribed this enhancement, in the mechanical properties, to the compatibilizing effect of maleic anhydride, which step up the interfacial adhesion to promote the LCP fibrillation and incorporation of whisker.

Lee et al. (2003c) studied the effect of nanosilica on the PP/LCP blend systems and found that the mixing sequence, the filler size, and the filler surface nature affected the rheology of the composites and the morphology of the LCP phase in the ternary composite. They have demonstrated that the droplet-fibril transition of LCP depends strongly on the compatibility between the filler and the PP matrix. According to this study, hydrophobic silica facilitated the fibrillation of LCP, because of preferential residence of the hydrophobic silica in the PP phase. They found that the hydrophilic-silica-filled ternary composite was more viscous than the hydrophobic-silica-filled one and they ascribed this phenomenon to the orientation of the LCP domains in the ternary composite; which was better in hydrophobic silica blend than that in the hydrophilic blend. It was also found that when LCP fibrils were developed, the fibrous LCP phase could readily lower the viscosity and could couple with the fillers to improve the shear-thinning response of the ternary composite. Silica was used as a viscosity thickening agent to improve the fibrillation of the LCP phase in PP/LCP blend system (Lee et al. 2002). It was shown that with the incorporation of 5–15 wt% of fillers, fibers of LCP were formed which improved the flow properties of the LCP/PP/SiO₂ composites. Addition of hydrophobic silica led to an increase of the aspect ratio of the LCP fibrils, which, in turn, improved their effectiveness as reinforcements and/or toughening agents. Zhang et al. (2003) also reported similar phenomenon for the PP/LCP/SiO₂ ternary blends. Zhang et al. (2005) studied the influence of nano-clay on the morphology of TLCP in nylon-6 matrix. They showed that clay platelets had dramatic influences on the dispersion and deformation of TLCP phase. With the addition of 3 wt% of nanoclay TLCP droplets got smaller as compared to the binary blend and deformed into fibrils at the clay loading up to 5 and 7 wt%. This enhanced fibrillation of TLCP droplets was attributed to the compatibilizing ability of the nanoclay particles which improve the interfacial adhesion and suppress the interfacial slip between TLCP and nylon phases in the melt, so that the shear stress was effectively transferred to the dispersed TLCP phase. Tang et al. (2010) reported the influences of blending sequence on viscosity reduction of high molecular mass polyethylene (HMMPE)/TLCP blend system filled with organoclay. They found that large amounts of organoclay formed partially intercalated structures in TLCP, when the organoclay was first blended with TLCP and then with HMMPE, with phase separation occurring at the temperature when TLCP was in the nematic phase, corresponding an antagonistic effect which weakens viscosity reduction ability of TLCP for HMMPE. However, with first blending of TLCP with HMMPE and then adding organoclay into the blend, most of the organoclay enriched on TLCP surfaces in the blend which prevents TLCP droplets from coalescing at high shear

stresses and enlarging the processing window. When the clay was added to the binary blend system, due to the polar nature of TLCP, the clay platelets showed preference for the TLCP phase. However, due to the high viscosity of HMMPE and short resident time all the clay platelets were not able to interact with TLCP as a result of which they were trapped in the PE matrix. Tan et al. (2006) demonstrated a phase diagram with PC/LCP blend system, for predicting the type and extent of fibrillation of the LCP phase in LCP-based polymer blends taking three factors into consideration namely, the shear rate, the LCP content in the blend, and interfacial adhesion between the LCP phase and the matrix polymer; which can be extended for other types of LCP containing blend systems. The effect of interfacial adhesion between the LCP and the PC matrix on fibrillation was considered by using a compatibilizer for the PC/LCP blend. They proposed a phase diagram with three regions (1) a lower region where no fibrillation occurred and the morphology of the LCP phase in the blend either existed in the form of spheroids or ellipsoids, (2) an intermediate region where the LCP existed predominately as short fibers with aspect ratios between 5 and 10, and (3) the upper region where the LCP phase developed into long continuous fibers. They have shown that the LCP content, in LCP containing blends, also plays a significant role for the development of fibers because below a critical domain size of LCP, the spheroid could not be deformed to form fibers. It was demonstrated that the fiber coalescence and fiber attrition processes occurred simultaneously during processing. Hence, the final morphology of the LCP in the blend depended on whether the fiber coalescence or attrition process was predominant at the specific combination of LCP content and processing shear rate. The use of a compatibilizer steps up the interfacial adhesion and also promotes more extensive fibrillation of the LCP phase. Wu et al. (2006) showed that in PC/TLCP blend system better compatibility and finer TLCP dispersion were reached in the unfilled blend, which made the fibrillation of TLCP difficult in capillary flow even at high shear rate. In contrast to this, well-developed TLCP fibrils were formed by capillary flow in nano-SiO₂ filled TLCP/PC blends. By increasing the nano-SiO₂ concentration and shear rate, the fibrillation of TLCP was significantly enhanced. They have ascribed this phenomenon to the selective distribution of nano-SiO₂ in PC and TLCP phases, driven by the interfacial tension thermodynamically and the viscosity discrepancy of components dynamically. During melt blending, the transesterification was reduced by the localization of nano-SiO₂ at the interface of TLCP/PC and subsequent increase in shear rate enlarged the viscosity disparity between TLCP and PC, thus made nano-SiO₂ particles migrate from the TLCP/PC interface to PC matrix. This migration of nano-SiO₂ and reduced transesterification enhanced the mobility of TLCP phase, promoted the coalescence and hence the fibrillation of TLCP droplets in capillary flow. Lee et al. (2003d) studied the effect of shear flow, extensional flow and addition of nanofillers on the fibrillar morphology of LCP in PP matrix. They showed that shear flow which predominates in injection molding is insufficient for the fibrillation of LCP, whereas under the extensional flow, the fibrillation could be improved but require an additional drawing process. However, incorporation of nanosilica promoted the LCP fibrillation under the shear flow due to the increased

viscous force of the matrix upon the LCP phase. In addition to that, presence of both nanosilica and LCP improved the properties of the ternary blend systems due to the dual reinforcement effect. Ding et al. (2004) studied the effect of glass beads (GB) on the properties of nylon/TLCP blend system. They showed that under strong extensional action of the micro-rollers of the GB, TLCP microfibrils with an average diameter of 30 nm are formed due to the thermodynamic and dynamic driving forces. In PA6/TLCP/GB ternary blends, a thermodynamically unsteady system is formed because of different interfacial tensions between PA6 and GB, and between TLCP and GB, respectively which drives the glass beads to migrate to the vicinity of the TLCP melt droplets resulting in the dispersion of TLCP coils during the melt flow. The extensional flow field formed by these micro-rollers of glass beads exerts strong extensional action on TLCP coils and formed the TLCP microfibrils with an average diameter of 30 nm. Elias et al. (2008) demonstrated the hydrophilic silica migrate from the PP matrix to the dispersed EVA domains in immiscible polypropylene/poly(ethylene-co-vinyl acetate) (PP/EVA) blend. It was also shown than silica can also able to migrate from a dispersed PP phase to an EVA matrix. However this migration was found to be slower than the migration from PP to the EVA phase. In case of hydrophobic silica, the nanofillers were found to be accumulated at the blend interface and in PP. The mechanism behind this migration was assigned to the shear induced movements and collisions with dispersed drops. Pisharath and Wong (2003) studied the effect of variation of LCP content in the rubber toughened nylon 6,6/LCP/short glass fiber blend system. They showed that maximum miscibility was achieved at 5 wt% of LCP, and decreased with increasing LCP content. They observed that LCP hybridization increased the interplanar spacing of hydrogen-bonded sheets of nylon crystals rather than the spacing between hydrogen-bonded chains. Garcia et al. (2004) studied the effect of glass fiber reinforced LCP content on the properties of PES/LCP blend system. They reported that despite of higher viscosity of glass fiber reinforced LCP, the viscosity of PSF/LCP blend decreases with the LCP content. The Young's modulus and notched impact strength of the composites increased while break properties decreased linearly with glass fiber reinforced LCP content. The composite with 10 % LCP showed an increase in stiffness of 18 %, 6.5-fold impact strength, and a tensile strength similar to that of PES. Tjong and Xu (2004) studied the PP/LCP blend system in presence of maleic anhydride (MA) grafted styrene ethylene butylene styrene (SEBS-g-MA) elastomers, with and without glass fibers. Addition of both LCP and glass fibers improved the tensile strength and stiffness of hybrid composites prepared at 265 and 285 °C due to the formation of long LCP fibrils at these temperatures, in presence of MA compatibilizer, which was not achieved at 220 °C leading to the poorer mechanical performance of the hybrid composites. The LCP fibrils act synergistically with short glass fibers as the load bearing agents and thereby improved the mechanical strength. However, composites prepared at higher temperatures of 310 °C exhibit poorer mechanical performance owing to the degradation of polymer matrices. He et al. (1997) studied the dual reinforcement of PES with TLCP and carbon fiber. They showed that in presence of TLCP the processibility of the ternary blends improved and the breakage of carbon fibers also

minimized during the blending process. The LCP fibers act as the reinforcing media although the major part of the reinforcement comes from the carbon fiber.

8.11 Effect of MWCNT and Modified MWCNT on LCP Based Polymer Blend Nanocomposites

We have studied the effect of MWCNT and its modification on various LCP based polymer blends to access its role in morphological growth of LCP during blending. Since dispersion of MWCNT in polymer matrix is a major challenge due to Van der Waals force between the nanotubes, the MWCNT surface was modified with SiC coating. This coating reduced the interaction between the nanotubes (which resulted in better dispersion in blend matrix) and also made the nanotube surface rough for physical anchoring of polymeric chains. Better dispersion of modified MWCNT exposed significant surface area of these nanotubes for interaction with the polymer matrix and rough surface increased the physical anchoring. Apart from dispersion of these nanofillers in the blend matrix, migration and localization of these nanofillers in the polymer blends can significantly alter the properties of the polymer blends (Nayak et al. 2012a, b). Dispersion of the nanofillers, in the polymer blends during mixing, has been controlled by two factors, kinetic and thermodynamic. During the initial stage of mixing the fillers distribution is controlled by the kinetic factor and fillers will be accommodated in the lower viscous phase. During mixing the thermodynamic effect comes into play and the migration of fillers occurs from the low viscous to the high viscous medium, if the affinity of the fillers towards the viscous polymer is higher than that with the low viscous medium. If the blending time is shorter than the complete migration time, nanotubes will be trapped at the interface and hence act as a bridge between the blend partners. On similar line, analysis of PEEK/LCP/MWCNTs and PEEK/LCP/SiC coated MWCNTs nanocomposites showed that incorporation of MWCNT to PEEK/LCP blend can enhance the droplet deformation and this effect was prominent in case of SiC coated MWCNT (Nayak et al. 2009). Dispersion of SiC coated MWCNTs was also found to be better than unmodified MWCNTs, in the blend matrix. Similar result was also observed in case of PEI/LCP, (Nayak et al. 2010) PPO/LCP (Nayak et al. 2011a) and PPS/LCP (Nayak et al. 2011b) blend systems. For all the systems, fibrillation of LCP increased with the incorporation of MWCNTs and the effect is more prominent for the SiC coated MWCNTs filled blend system. Nanocomposites with S-MWCNTs showed superior mechanical properties than the pure MWCNTs filled blend system. The better fibrillation of LCP, in presence of MWCNTs, was due to the bridging effect of nanotubes at the interface of blend partners which generated the drag force by the matrix phase upon the LCP domains as a result, the LCP domains were elongated in the flow direction. Owing to this fibrillation the base matrix was reinforced with both LCP fibers and MWCNTs. This synergetic reinforcement enhanced both thermal and mechanical properties of the LCP blend

nanocomposites. Due to high aspect ratio of MWCNTs, during mixing the nanotubes were trapped at the interface and hence bridged the two blend partners which prevented the phase separation. In addition to this the rough surface developed on MWCNT surface by SiC coating also triggered the physical anchoring of polymer chains which not only increased the drag force during blending, which facilitate LCP fibrillation but also decreased the LCP fiber pull out during tensile testing. Rheology of such systems, with MWCNT, greatly influenced by the nanotubes. Since most of the high performance polymers like PEI, PEEK, PPO and PPS are very difficult to process due to their high viscosity, LCP can enhance the processibility by acting as a lubricating agent. Once fibrillated, LCP can facilitate the flow during blending and due to its low viscosity can ease up mold filling. On comparison of compatibilizing ability of SiC coated MWCNT with organic compatibilizer polyphosphazene for the compatibilization of PEI/LCP blend, it was found that in presence of Polyphosphazene average particle size of LCP was reduced as compared to PEI/LCP binary blend. But fibrillation of LCP was observed for the PEI/LCP/SiC coated MWCNT system. This suggests that compared to organic compatibilizer; modified MWCNT can facilitate fibrillation of LCP to a greater extent.

8.12 Conclusion and Future Perspective

LCP based polymer blends can have a significant role for fabrication of high performance polymer blends. The incompatibility among the blend partners, which is a major road block for fibrillation LCP and hence the controlling factor for mechanical and thermal properties can be addressed with a suitable compatibilizer. However, for high performance polymers whose processing temperature exceeds 300 °C it is difficult to find a compatibilizer of such thermal stability. In this scenario, high aspect ratio carbon nanotube can be used as a compatibiliser for these systems which can enhance LCP fibrillation by acting as a bridging agent between the blend partners.

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